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

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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.

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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 used in the manufacturing of PA6 [12] and PA12-SWCNT composites [13]. While the maleic anhydride-sites of the copolymer react with the end groups 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 Zhou 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 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 can not 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.

BCA
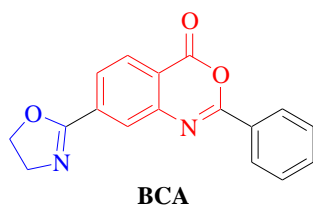
Fig. 1. Structure of the applied bifunctional coupling agent (**BCA**) with one benzoxazinone group (red) and one oxazoline group (blue).

A possible advantage of this approach as compared to adding a second polymeric component as 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 end groups 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 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 end groups 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 end groups (for details see [22]), low density polyethylene (BPD2000, INEOS Olefins & Polymers Europe, United Kingdom) and polycarbonate (Makrolon® 2600, Bayer Material Science AG, Germany). Amine 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 represent the as-synthesized product with a carbon purity of <90%, NC3152 was obtained after purification (C purity >95% a) and functionalization (NH_2 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 ^{1}H NMR spectra were recorded at 500.13 MHz, the ^{13}C NMR spectra at 125,74 MHz. Dimethyl sulfoxide-d_6 (δ(^{1}H) = 2.50 ppm, δ(^{13}C) = 39.6 ppm) was used for solvent, lock, and internal standard. Signal assignments were verified by [1]H–[1]H and [1]H–[13]C correlated two-dimensional NMR spectra. The atom numbering within the aromatic rings corresponds to those given here for the compound **6** (see Fig. 2).
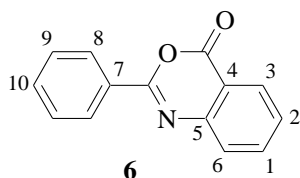
Fig. 2. Atom numbering within the aromatic rings for NMR signal assignments

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.

TGA measurements were performed with a TGA Q5000 (TA Instruments, USA) in the temperature range of 30 to 800°C under a nitrogen atmosphere at a heating rate of 10 K/min.

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 analyzer having pass energy of 160 eV or 20 eV was used.

The macrodispersion of the as-synthesized (primary) MWCNT agglomerates in PA12-CNT composites was studied by transmission light microscopy. For this purpose, 5 µm thin sections of the extruded strands (perpendicular to the extrusion direction) were cut using a Leica RM 2155 microtome (Leica Microsystems GmbH, Germany). These were analyzed with a BH2 microscope combined with a DP71 camera (both Olympus Germany GmbH, Germany). From these images, the area ratio of the undispersed MWCNT agglomerates $A_A = A/A_0$ was determined from the summarized area of the black appearing remaining agglomerates (A) and the entire area of the picture (A_0, ~ 0.6 mm^2) using the software ImageJ version 1.44n. Only agglomerates with a circle equivalent diameter > 5 µm and at least seven images were used for the quantification.

Scanning electron microscopy (SEM) was performed on selected composites using an Ultra Plus Field Emission Gun Scanning Electron Microscope (FEG-SEM, Carl-Zeiss AG, Germany). Surfaces of pressed plates of the composites were analysed using the charge contrast imaging (CCI) mode using an InLens-detector which shows the electrical conductive filler network of the sample.

For discussion in this paper, electrical volume conductivity values have been used. Therefore, volume resistivity was measured on the compression moulded plates using a Keithley electrometer 6517A (Keithley Instruments Inc., U.S.A.) in combination with a plate measuring device Keithley 8009 for resistivities > 10^7 Ohm cm (unfilled symbols in the figures). For electrical volume resistivities < 10^7 Ohm cm, a 4-point test fixture consisting of a Keithley DMM2000 was used with a strip measuring (distance between the inner electrodes 10 mm, outer electrode spacing 16 mm, filled symbols). Therefore strips in geometry of 30x3x0.5 mm^3 were cut from the compression moulded plates. In the plots, the geometric mean values and the standard deviations of 4-8 measurements are shown. The electrical percolation thresholds (p_c) were fitted using the power law function for the composite conductivity above the electrical percolation threshold [23]:

$$\sigma(p) = B(p - p_c)^t$$

with the experimental conductivity value $\sigma(p)$ for concentrations $p > p_c$, the proportionality

constant B, the electrical percolation threshold p_c and the critical exponent t, using the method

of mean square error minimisation.

2.3. Synthesis

7-Oxazolinyl-2-phenyl-4*H*-3,1-benzoxazin-4-one (BCA)

Compound **BCA** was synthesized according to published procedures [19] (compound 12a in

[19]).

NC3152-BCA (1)

0.47 g of Nanocyl^{TM} NC3152 and 0.18 g (0.62 mmol) of **BCA** were stirred in 50 ml of *N,N*-

dimethylacetamide (DMAc) at 130°C for 3 h. The product was washed with hot DMAc and

tetrahydrofuran in a water jet vacuum equipped with a frit and filter paper. Further purification

was performed by Soxhlet extraction with tetrahydrofuran as solvent at 65°C for 6 h with

several changes of solvent. Yield: 0.50 g

3-Benzoylamino-4-*n*-butylcarbamoyl-phenyloxazoline (2)

2.92 g (0.01 mol) of **BCA** was stirred for 2 h at 120°C with 3.65 g (0.05 mol) of *n*-butylamine

in 20 ml of DMAc. After cooling to room temperature the reaction mixture was added to

150 ml of ice water and the resulting precipitate was filtered and washed with water until

neutral pH was achieved. The recrystallization was carried out in ethanol. Yield: 2.10 g

(57.5%). Melting point Mp: 155–56°C. ^{1}H-NMR (DMSO-d_6, δ): 12.55 (s, 1H, NHPh), 9.18

(s, 1H, H^6), 8.96 (t, 1H, NHAlk), 7.94 (d, 2H, H^8), 7.91 (d, 1H, H^3), 7.67 (d, 1H, H^2), 7.65 (t,

1H, H^{10}), 7.60 (t, 2H, H^9), 4.46 (t, 2H, CH$_2$O), 4.01 (t, 2H, CH$_2$N), 3.32 (q, 2H, C$\underline{H}_2$NH), 1.54

(m, 2H, C$\underline{H}_2$CH$_2$NH), 1.35 (m, 2H, C$\underline{H}_2$CH$_3$), 0.70 ppm (t, 3H, CH$_3$). ^{13}C-NMR (DMSO-d_6,

δ): 167.92 ($\underline{C}$ONHCH$_2$), 164.49 (CONH), 162.43 (C=N, Oxazoline), 139.43 (C^5), 134.39

(C^7), 132.18 (C^{10}), 130.59 (C^1), 129.01 (C^9), 128.46 (C^3), 126.98 (C^8), 122.55 (C^4), 121.91

(C^2), 119.58 (C^6), 67.65 (CH$_2$O), 54.62 (CH$_2$N), 39.11 (CH$_2$NH), 30.86 ($\underline{C}$H$_2$CH$_2$NH), 19.69

($\underline{C}$H$_2$CH$_3$), 13.68 ppm (CH$_3$).

7-(2-hydroxyethyl)carbamoyl- 2-phenyl-4*H*-3,1-benzoxazin-4-one (3)

The preparation was carried out according to the procedure of Jakisch et al. (compound 11a in [19]).

3-Benzoylamino-4-*n*-butylcarbamoyl-*N*-(2-hydroxyethyl)benzamide (4)

3.10 g (0.01 mol) of **3** was stirred with 3.65 g (0.05 mol) of *n*-butylamine in 20 ml of DMAc at 120°C for 2 h. After cooling to room temperature the reaction mixture was added to 150 ml ice water, the resulting precipitate was filtered and washed with water until neutral. Yield: 2.10 g (54.8%). Mp: 155–156°C. ^{1}H-NMR (DMSO-d_6, δ): 12.50 (s, 1H, PhNHCOPh), 9.04 (s, 1H, H^6), 8.92 (t, 1H, NH*n*Bu), 8.53 (t, 1H, N$\underline{H}$CH$_2$CH$_2$OH), 7.95 (d, 2H, H^8), 7.88 (d, 1H, H^3), 7.65 (d, 1H, H^2), 7.63 (t, 1H, H^{10}), 7.60 (t, 2H, H^9), 4.72 (b, 1H, OH), 3.54 (t, 2H, CH$_2$OH), 3.36 (t, 2H, C$\underline{H}_2$CH$_2$OH), 3.32 (q, 2H, CH$_2$NH), 1.55 (m, 2H, C$\underline{H}_2$CH$_2$NH), 1.35 (m, 2H, C$\underline{H}_2$CH$_3$), 0.90 ppm (t, 3H, CH$_3$). ^{13}C-NMR (DMSO-d_6, δ): 167.94 ($\underline{C}$ONH*n*Bu), 165.70 ($\underline{C}$ONHCH$_2$CH$_2$OH), 164.44 (PhNH$\underline{C}$OPh), 139.23 (C^1), 137.88 (C^5), 134.43 (C^7), 132.18 (C^{10}), 129.04 (C^9), 128.08 (C^3), 126.97 (C^8), 122.70 (C^4), 121.27 (C^2), 119.77 (C^6), 59.71 (CH$_2$OH), 42.36 ($\underline{C}$H$_2$CH$_2$OH), 39.05 (CH$_2$NH), 30.89 ($\underline{C}$H$_2$CH$_2$NH), 19.68 ($\underline{C}$H$_2$CH$_3$), 13.70 ppm (CH$_3$).

2-(4-Methoxycarbonyl)phenyloxazoline (5)

To prepare the first intermediate (terephthalic acid monomethyl ester chloride) 18.00 g (0.10 mol) of terephthalic acid monomethyl ester was stirred with 100 ml of thionyl chloride at 80°C. The resulting sulfur dioxide and hydrogen chloride gas was conducted through a reflux condenser into a saturated aqueous sodium hydroxide solution. After completion of gas evolution (ca. 2 h), the excess of thionyl chloride was distilled under a water pump vacuum and the remaining liquid residue was cooled with stirring to 0-5°C with 150 ml of n-hexane (external cooling with ice-sodium chloride mixture). After 2 h the formed precipitate (terephthalic acid monomethyl ester chloride) was filtered, washed with n-hexane and vacuum dried at room temperature (Yield: 14.75 g). Next, 9.925 g (0.05 mol) of terephthalic acid

monomethyl ester chloride were dissolved in 100 ml dry, ethanol-free chloroform at 0°C and a mixture of 3.05 g (0,05 mol) of ethanolamine, 5.05 g (0.05 mol) of triethylamine in 25 ml of chloroform was drop wise added. The mixture was stirred for 1 h at room temperature and the resulting precipitate (terephthalic acid monomethyl ester-*N*-(2-hydroxyethyl) amide) was washed with chloroform (Yield: 8.3 g). 4.46 g (0.02 mol) of the resulting amide was dissolved in 75 ml of dry THF at 0°C and 11.90 g (0.1 mol) of thionyl chloride in THF (small amount) was added dropwise. The reaction mixture was stirred for 6 h at -5 to 0°C (external cooling with ice-sodium chloride mixture). Then the resulting precipitate was filtered, washed with THF and dried. This compound was added slowly to a solution of 5.04 g (0.08 mol) sodium bicarbonate in 200 ml of water (note: evolution of carbon dioxide gas). The resulting precipitate was filtered and washed with water until neutral pH. Yield: 3.05 g (41.2%).Mp: 133°C. ^{1}H-NMR (DMSO-d_6, δ): 8.04 (d, 2H, H^3), 7.99 (d, 2H, H^2), 4.44 (t, 2H, CH$_2$O), 4.00 (t, 2H, CH$_2$N), 3.88 ppm (s, 3H, CH$_3$). ^{13}C-NMR (DMSO-d_6, δ): 165.67 (COO), 162.28 (C=N), 131.91 (C^4), 131.64 (C^1), 129.41 (C^3), 128.05 (C^2), 67.70 (CH$_2$O), 54.65 (CH$_2$N), 52.38 ppm (CH$_3$).

2-Phenyl-4*H*-3,1-benzoxazin-4-one (6)

2.81 g (0.02 mol) of benzoyl chloride was dissolved in 50 ml of DMAc and 2.74 g (0.02 mol) of 2-aminobenzoic acid (as a powder) was added while stirring. Subsequently, a mixture of 2.02 g (0.02 mol) of triethylamine in 5 ml of DMAc was added drop wise at room temperature. After 1 h of stirring at room temperature, 200 ml of water was added; the resulting precipitate was filtered, washed with water and vacuum dried at 80°C. Thereafter, the product was heated in 50 ml of acetic anhydride for 2 h at reflux. After cooling, the resulting precipitate was filtered, washed with acetic acid and then water. Yield: 3.65 g (81.1%). Mp: 123°C. ^{1}H-NMR (DMSO-d_6, δ): 8.20 (d, 2H, H^8), 8.16 (d, 1H, H^3), 7.95 (t, 1H, H^1), 7.72 (d, 1H, H^6), 7.67 (t, 1H, H^{10}), 7.63 (t, 1H, H^2), 7.60 ppm (t, 2H, H^9). ^{13}C-NMR

(DMSO-d_6, δ): 158.89 (COO), 156.46 (C=N), 146.31 (C^5), 136.70 (C^1), 132.76 (C^{10}), 130.09 (C^7), 129.04 (C^9), 128.64 (C^2), 128.10 (C^3), 127.85 (C^8), 126.96 (C^6), 116.98 (C^4).

2.4. Processing

The composite preparation was performed via melt mixing in a DACA microcompounder (DACA Instruments, U.S.A.). This conical twin-screw extruder has an inner volume of 4.5 cm^3. The melt mixing was performed at 210°C with a mixing speed of 250 rpm for 5 min. Polymer and CNTs (PA12 0.25-5 wt.%, PE 4 wt.% and PC 0.5 wt.%) were alternatively added into the running microcompounder (at least three portions). The contents of MWCNT Nanocyl^{TM} NC 3152 used in PE and PC were selected to be in the percolation range [24]. If the addition of additives (coupling agent or model substances) to the CNTs was required, these were dry-mixed with the CNTs. Additives were used 1:1 to the CNT content for CNT contents > 1 wt.%. For CNT contents < 1 wt.% a constant additive-content of 1 wt.% was used. The extruded strands were compression molded into plates (diameter: 30 mm, thickness: 0.5 mm) with a Weber hot press (Model PW 40 EH, Paul Otto Weber GmbH, Germany). Compression molding was performed according to Kasaliwal et al. [3] with a preheating time of 2.5 min, a pressing time of 1 min, and a pressure of 100 kN at 220°C.

3. Results and discussion

Using a PA12 type polymer with an excess of carboxylic acid end groups and an amino functionalized MWCNT type the addition of the **BCA** allows a rapid chemical attachment under the applied melt mixing conditions. In Fig. 3, the reactions to connect the MWCNTs to the polymer are demonstrated. The attack of the carboxylic end group of PA12 on **BCA** leads to an opening of the oxazoline ring. The benzoxazinone group also undergoes a ring opening reaction with the corresponding amino functionality of the carbon nanotube. As MWCNTs

and **BCA** were pre-mixed before adding to PA12-COOH, both reactions occur simultaneously.
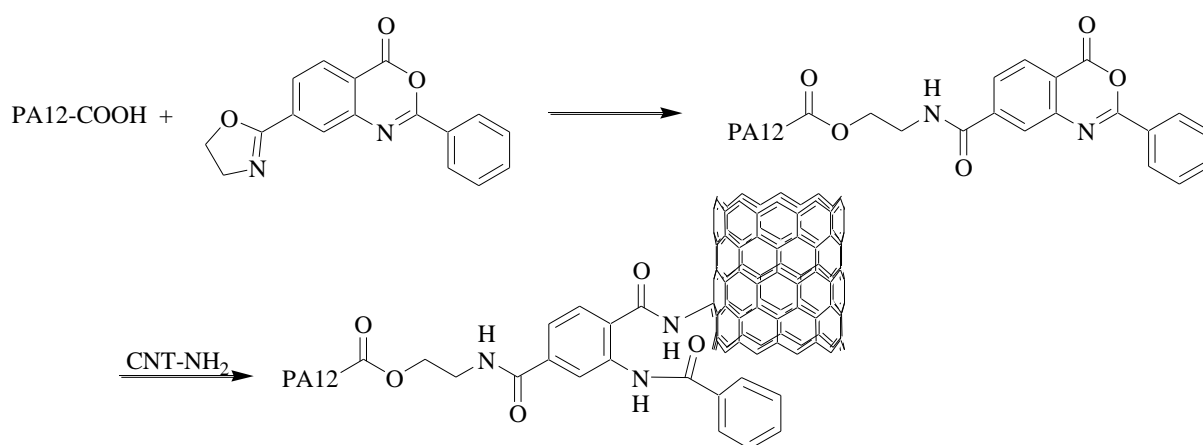

Fig. 3. Attachment of the PA12 to the surface of the amino functionalized MWCNTs mediated by the bifunctional coupling agent.

Direct detection of the reaction shown in Fig. 3 is difficult. Standard methods such as NMR spectroscopy fail for several reasons including the magnetic spin of the MWCNTs (or the metal catalyst) and their insolubility in all solvents. In addition, the number of detectable groups originating from the addition reaction is low compared to those of the macromolecules. Therefore, they are below the detection limit of many analysis methods. However, the reaction shown can be detected in model reactions.

For this, the coupling agent was reacted in an equimolar ratio to the carboxylic acid end groups of the polymer in the melt with PA12, corresponding to the first reaction equation in Fig. 3. Such reactions have been described for carboxylic acid terminated polyamide 12 [19], poly(propylene oxide) [20], and poly(butylene terephthalate) [21]. The reaction with the terminal carboxylic acid group of the polymer at 210°C for 5 min in the microcompounder results in a ring opening of the oxazoline group and was detected by means of ^{1}H NMR spectroscopy (results not shown). By integrating the signal intensities, a degree of conversion

of about 50% was determined. The NMR results are consistent with corresponding results from the literature [17, 19-21].
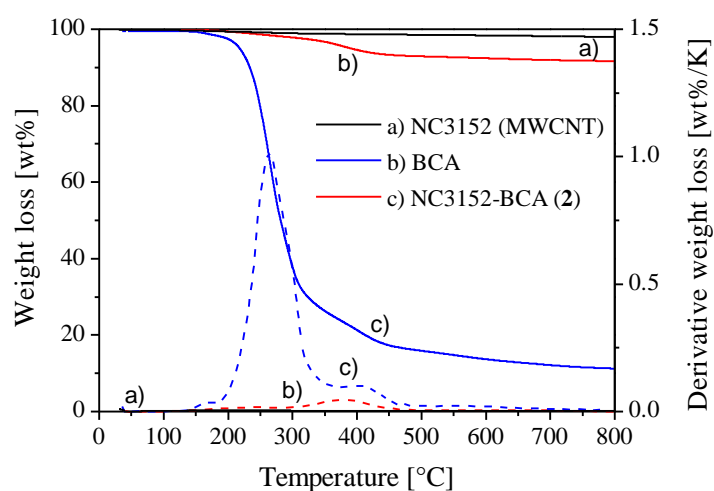
The reaction of the coupling agent with the amino functionalized MWCNTs was carried out in solution and can be seen in Fig. 4. The purification of **1** was performed by Soxhlet extraction in THF with multiple exchanges of the solvent. This was repeated until no more **BCA** could be detected in the concentrated solution by IR spectroscopy.
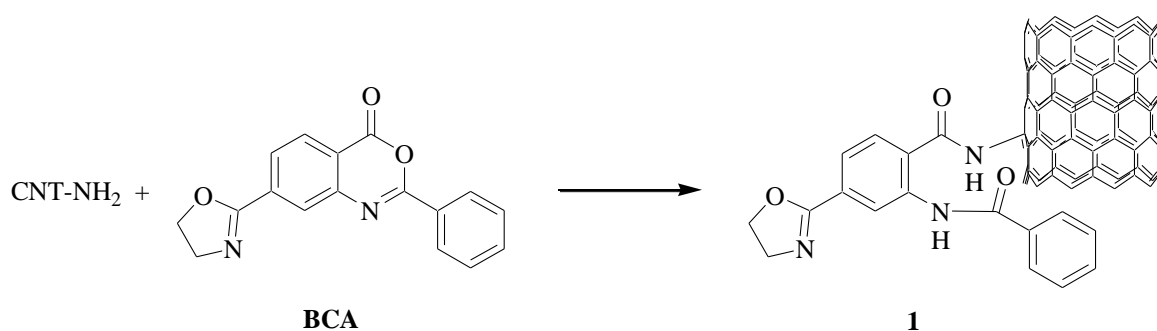
Fig. 4. Reaction of the amino functionalized MWCNTs with the benzoxazinone group of the bifunctional coupling agent.

After the complete removal of unreacted starting material from the surface of the MWCNTs, the product was characterized by TGA studies. For pristine amino functionalized nanotubes, a residue of 98% (at 800°C) was obtained (see Fig. 5). The degradation rates of the amino functionalized MWCNTs are small and throughout the temperature range relatively constant. Thus, up to 209°C the weight loss of only 0.6% was negligible and up to 500°C only a small weight loss of 1.4% was found. In contrast, the bifunctional coupling agent leaves a residue of 11.2% at 800°C. Between 200°C and 350°C, a weight loss of 75% in one step appears, most likely due to sublimation, as sublimation could be observed as main event under the light microscope upon heating of **BCA** above 200°C. In a further step with a maximum at about 400°C, an additional weight loss of 8% assigned to the decomposition of so far not sublimated **BCA** was observed. For compound **1**, a residue of 93.3% was obtained in the TGA study. The residue is accordingly significantly smaller than that of the pristine amino functionalized

MWCNTs. It is noteworthy that for **1** almost no weight loss was found between 200 and 350°C, where **BCA** undergoes the maximum weight loss. This may be an indication that sublimation of the bifunctional coupling agent is suppressed as it can be expected by covalent attachment to the MWCNTs. The degradation maximum of **1** (5.4%) is located between 350°C and 450°C at slightly lower temperature than for pure **BCA**, which is due to the change in the chemical structure after coupling. Above this temperature only a slight degradation is observed until 800°C, similar to that of the pristine MWCNTs. Therefore, strong evidence for covalent attachment of about 5 wt.% coupling agent to the MWCNT surface are found by the TGA investigation. This indicates a conversion of about every second NH_2 group on the MWCNT surface (assuming a NH_2 content of 0.5 wt.%).


Fig. 5. TGA curves of the thermal decomposition behavior of the bifunctional coupling agent (**BCA**), the amino functionalized nanotubes (NC3152) and the reaction product (**1**).

The covalent attachment can also be concluded from XPS measurements, showing enhanced ratios of $[N]:[C]_{spec} = 0.011$ and $[O]:[C]_{spec} = 0.022$ of NC3152-BCA(**1**) as compared to NC3152 (0.004 and 0.007, respectively).

In addition to the investigation of a covalent bonding through TGA and XPS, fluorescence spectroscopy was employed. It is known from the literature that structures containing an open benzoxazinone ring show a second fluorescence band in comparison to closed ring structures

as well as a strong Stokes shift to a longer wavelength [25]. As the closed benzoxazinone ring does not show this second emission band [26], the application of fluorescence spectroscopy for the detection of the reaction product **1** seems promising. Three model compounds were synthesized in order to explore this method (shown in Fig. 6): with an opened oxazoline group (**2**), with an opened benzoxazinone group (**3**) or containing both opened groups (**4**).
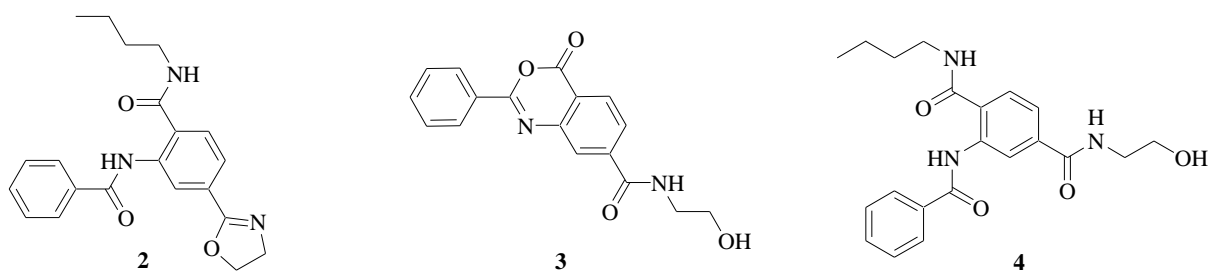
Fig. 6. Structures of the model compounds with opened benzoxazinone (**2**), opened oxazoline (**3**) or opened benzoxazinone and oxazoline groups (**4**).

The fluorescence emission was measured for the three model compounds, the bifunctional coupling agent (**BCA)**, as well as the reaction product (**1**) of the bifunctional coupling agent and the amino functionalized MWCNTs. All compounds show strong emission in the 390 nm range (see Fig. 7). In addition, compounds **1**, **2** and **4** show a long-wavelength emission band at 460 nm, most likely caused by an opened benzoxazinone structure. Accordingly, the fluorescence spectroscopy implies that **1** also contains an opened benzoxazinone group. This additional emission band could not be found in either the starting compound **BCA**, or in the model compound **3**, which in addition to the closed benzoxazinone group contain an opened oxazoline group. The fluorescence spectroscopy therefore supports the formation of **1** by the reaction shown in Fig. 4, in which a covalent attachment of the bifunctional coupling agent to the carbon nanotubes is proposed.
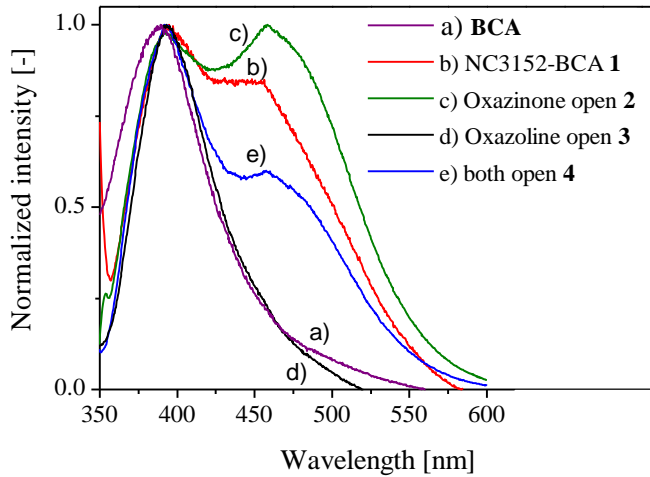
Fig. 7. Fluorescence emission spectra of the structures **BCA**, **1**, **2**, **3** and **4**.

After showing the occurrence of the expected chemical reactions, the bifunctional coupling agent **BCA** is now used in melt mixing PA12 and MWCNTs. For this purpose, samples with amino functionalized MWCNT content up to 5 wt.% were prepared in the microcompounder and characterized in terms of electrical conductivity (Fig. 8). Without the use of **BCA,** an electrical percolation threshold of 1.0 wt.% was obtained. Addition of the coupling agent during melt mixing reduced the percolation threshold significantly to 0.37 wt.%. For PA12-MWCNT composites without **BCA**, a MWCNT addition of at least 2 wt.% was required to achieve electrical conductivities in the range of 10^{-5} S/cm. In contrast, this conductivity range was reached below 0.5 wt.% MWCNT content with the addition of **BCA**. In addition, for a MWCNT content well above the percolation threshold the composites with the bifunctional coupling agent show much higher electrical conductivities.
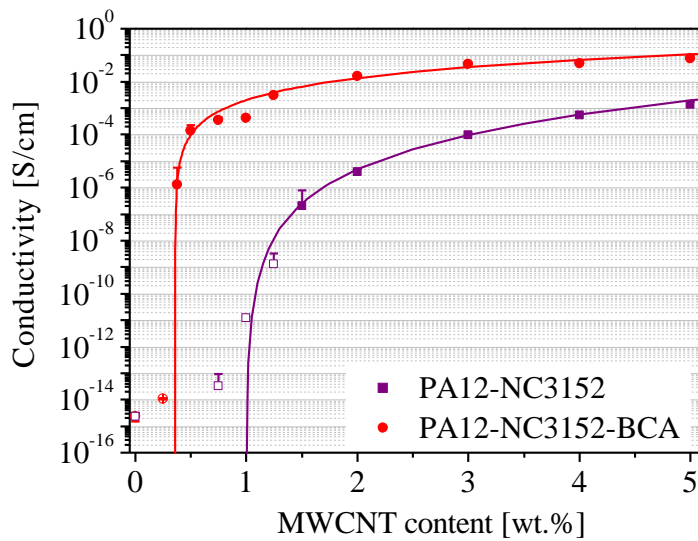
Fig. 8. Electrical volume conductivity of PA12 composites with amino functionalized MWCNTs without (NC3152) and with (NC3152-BCA) the bifunctional coupling agent (**BCA**).

To investigate whether the bifunctional coupling agent has an influence on the macrodispersion of the primary MWCNT agglomerates, light microscopy images of PA12-samples containing 2 wt.% amino-functionalized MWCNTs were taken (Fig. 9). These composites showed area ratios of undispersed agglomerates of 1.3%±0.5% (without **BCA**) and 1.5%±0.5% (with **BCA**) indicating that the macrodispersion does not differ in a statistically manner and was unexpectedly not increased using **BCA**.
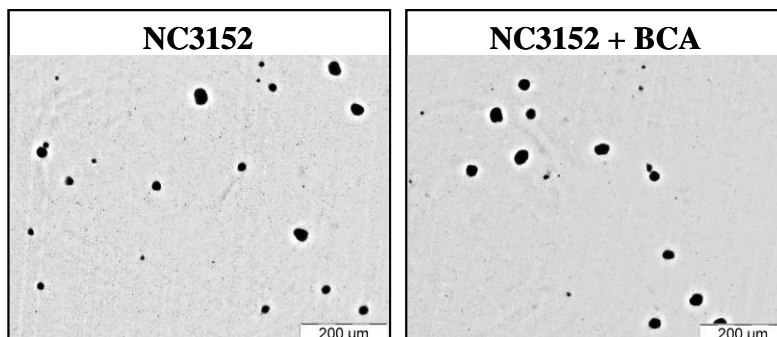
Fig. 9. Light microscopy images of PA12 composites with 2 wt.% Nanocyl[TM] NC3152 (left) and additional 2 wt.% **BCA** (right).

SEM images were taken in the charge contrast imaging (CCI) mode on composites having 1 wt.% NC3152 without and with **BCA** looking at higher magnification in areas between the remaining primary agglomerates. In this mode only those CNTs near to the surface can be seen, which contribute to the conductive network. Whereas for the conductive composite with **BCA** an image showing well dispersed nanotubes creating such a network can be seen (Fig. 10), no image could be obtained for the nonconductive sample without **BCA**. This indicates sufficient nanodispersion for forming an electrical network in case of **BCA** addition, but insufficient dispersion for network formation without **BCA**.


Fig. 10. SEM-CCI images of the PA12 composite with 1 wt.% Nanocyl[TM] NC3152 and 1 wt.% **BCA**.

Thus, the much higher electrical conductivity in PA12-MWCNT composites with **BCA** may be attributed to the generation of a state of MWCNT nanodispersion more suitable for the network formation on the nanoscale.

Furthermore, was hypothesized that both functional groups in the **BCA** are necessary to achieve enhancements in nanodispersion and conductivity. In order to investigate that, two

model compounds containing either only an oxazoline (**5**) or a benzoxazinone group (**6**) were used as shown in Fig. 11.
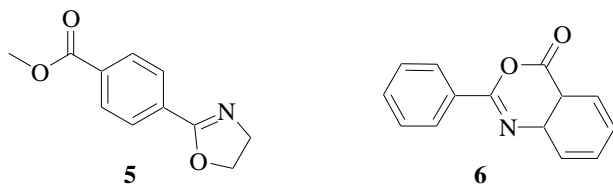

Fig. 11. Structure of model compounds containing only the oxazoline (**5**) or benzoxazinone (**6**) group.

The influence on the electrical conductivity by using **5** and **6** was examined in PA12-MWCNT composites with 0.75 wt.% and 1 wt.% MWCNT content (see Table 1). With **5**, an unaltered electrical behavior in comparison to the samples containing no additive was obtained. The reaction of the oxazoline group with the PA12 alone is therefore not responsible for the enhanced conductivities. A slight improvement was obtained with the addition of **6**. In a previous publication, a clear effect of the PA12 endgroups on the electrical properties was found [22]. A much higher MWCNT contents had to be applied to achieve electrical percolation in PA12-MWCNT composites with an excess of polymer amino endgroups as compared to those with carboxy endgroups. As the PA12 used here also contain some amino groups, the use of **6** is expected to result in a reduction of amino endgroup concentration and therefore perhaps also enhances the conductivity. In addition, the reaction between CNTs and compound **6** may help to disperse the nanotubes which can result in improved conductivity values. However, the electrical conductivities when using **6** are by decades lower than those of composites containing the bifunctional coupling agent (**BCA**).

Table 1 Electrical conductivity of PA12-MWCNT composites with the additives **1**, **5** and **6**.

PA12-samples	Conductivity 0.75 wt.% MWCNT [S/cm]	Conductivity 1 wt.% MWCNT [S/cm]	Conductivity Improvement
without additive	$3.2*10^{-14}$	$1.2*10^{-11}$	-
with **BCA** (1 wt.%)	$1.4*10^{-5}$	$4.2*10^{-4}$	Yes
with **5** (1 wt.%)	$5.1*10^{-15}$	$2.0*10^{-11}$	No
with **6** (1 wt.%)	$4.9*10^{-10}$	$2.0*10^{-6}$	Slightly

In order to provide a negative control of the reaction, CNTs without functional groups on the surface are needed. This is possible by using specially prepared single-walled CNTs. Fig. 12 shows the Raman spectrum of the SWCNTs used (SWeNT$^®$ CG100). The strong G-band is clearly visible at 1550 cm^{-1}, due to the presence of sp^2-hybridized carbon. The D-band typically in the range around 1340 cm^{-1} is only weekly developed. Therefore, sp^3-hybridized carbons on the surface of the SWCNT are not detected in a significant amount and thus, the existence of functional groups on the CNT surface, such as hydroxy groups, can be nearly excluded.
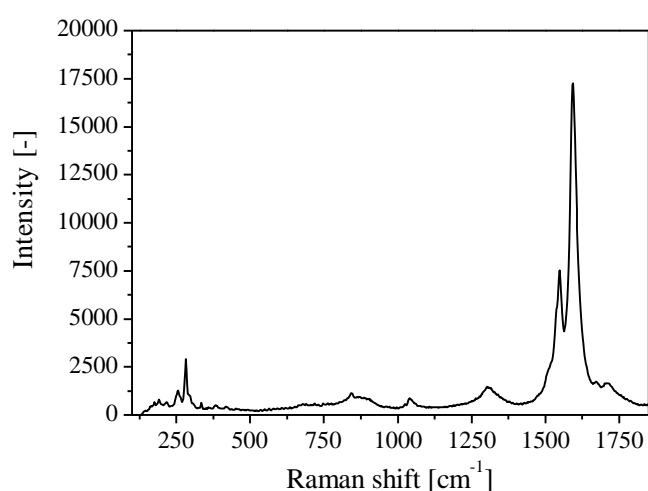
Fig. 12. Raman spectrum of the SWCNTs SWeNT$^®$ CG100

PA12 composites with 1 wt.% of SWCNTs, representing a content in the electrical

percolation range, were melt mixed. Without the presence of the bifunctional coupling agent,

the electric conductivity of the sample is $5.0*10^{-6}$ S/cm. The sample showed nearly the same

conductivity of $3.3*10^{-6}$ S/cm when **BCA** was added. Therefore, no improvement in the

electrical properties is determined in the SWCNT composite by using the bifunctional

coupling agent. Due to the relatively low surface functionalisation of the SWCNTs, nearly no

covalent bonding of the polymer to the nanotube surface by adding **BCA** is possible.

In order to demonstrate the necessity of a linkage between the polymer and the carbon

nanotubes enabled by the coupling agent to improve the electrical conductivity, in the next

step the use of non-reactive polymers is described. For these polymers, higher electrical

conductivities with the use of the bifunctional coupling agent were not expected. Polyethylene

(PE) and polycarbonate (PC) were employed as polymer materials. The end groups of these

polymers show no reactivity with the benzoxazinone or oxazoline groups of the coupling

agent. In the case of PC, these end groups are, for example, phenyl or alkylphenyl carboxylic

acid esters [27]. For these materials, samples with MWCNT Nanocyl^{TM} NC3152

concentrations in the range of the electrical percolation thresholds (4 wt.% for PE and

0.5 wt.% for PC) were prepared. As expected, the bifunctional coupling agent did not improve

the electrical conductivity in these composites (see Table 2).

**Table 2** Electrical conductivity of PE and PC-MWCNT composites with the additive **BCA**.

Sample	MWCNT content [wt.%]	Conductivity [S/cm]	Conductivity Improvement
PE without additive	4	$3.0*10^{-10}$	-
PE with **BCA**	4	$1.9*10^{-15}$	No
PC without additive	0.5	$2.5*10^{-8}$	-
PC with **BCA**	0.5	$1.9*10^{-8}$	No

These investigations also showed that the principal effect of the bifunctional coupling agent is probably due to attachment of the CNTs to the polymer. If such an attachment is not possible, a higher electrical conductivity by the use of **BCA** cannot be achieved.

Surprising results were obtained when **BCA** and nominally unfunctionalized MWCNTs (Nanocyl^{TM} NC7000) were melt mixed with PA12. As shown in Fig. 13, similar to the amino functionalized MWCNTs, a significantly lower electrical percolation threshold and higher conductivities at high MWCNT contents were achieved when applying **BCA**. It is known that on the surface of multiwalled CNTs produced by chemical vapour deposition (CVD), usually significant amounts of oxygen functionalities such as hydroxy groups are present [28, 29]. These hydroxy groups are also able to react with the benzoxazinone group under ring opening giving a carboxylic ester bond [30]. In our example, the percolation threshold of PA12-NC7000 composites was significantly reduced from 0.75 wt.% to only 0.2 wt.%. It can therefore be concluded that the additive **BCA** will have a significant impact on the electrical properties of PA12 composites with most of the commercially available MWCNTs.

In addition, DSC investigations (not shown here) indicated that crystallization enthalpy did not change at all upon addition of BCA to composites with 1 wt.% nonfunctionalized MWCNT, whereas the temperatures of melting and begin of crystallization decreased only very little [31]. Thus, a significant influence of **BCA** on the matrix crystallinity can be excluded.
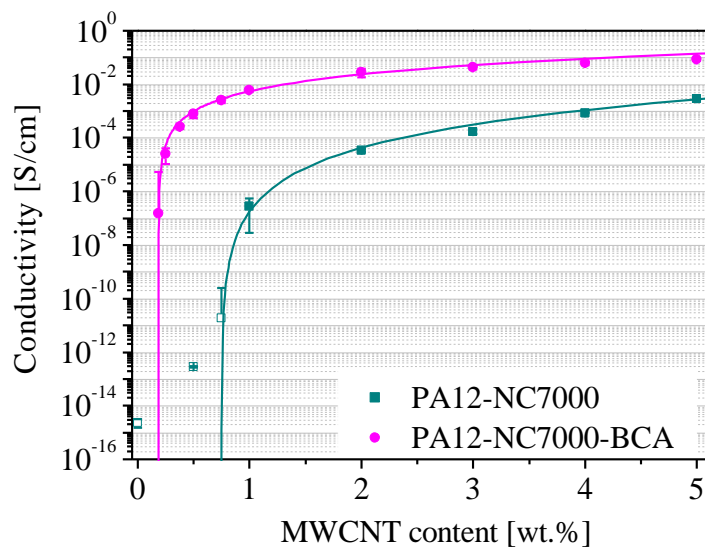
Fig. 13. Electrical volume conductivity of PA12 composites with nominally nonfunctionalized MWCNTs without (NC7000) and with (NC7000-BCA) the bifunctional coupling agent (**BCA**).

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4.   Summary and conclusion

In this study, we have demonstrated that it is feasible to apply a bifunctional coupling agent containing a benzoxazinone and an oxazoline group to selectively link the amino groups of MWCNTs and the carboxylic acid end groups of the PA12 polymer. The covalent attachment of the coupling agent **BCA** to the MWCNTs could be shown by TGA and XPS. In addition, a fluorescence spectroscopy study further supported the results. In melt mixed composites of PA12 with MWCNTs the state of macrodispersion of MWCNT agglomerates was not changed significantly when adding BCA, however, a conductive network could be detected by SEM on the nanoscale. A significantly lower electrical percolation threshold was achieved with **BCA** addition (i.e. reduction from 1.0 wt.% to 0.37 wt.%) as well as significantly higher electrical conductivities above the electrical percolation threshold. Similar positive results

were found when nominally unfunctionalized MWCNTs were mixed with PA12 and **BCA** due to existing hydroxy groups on the CNT surface which are also able to react with the benzoxazinone group. To identify which functional groups of the additive are essential for improved electrical properties, several model compounds were studied, containing either only the oxazoline or the benzoxazinone group. It could be shown that the presence of the benzoxazinone group in addition to the oxazoline group is necessary. Control reactions with non-reactive polymers or SWCNTs with low functionality showed no reduction in the percolation threshold or conductivity improvement by the addition of **BCA**. The results indicate that the effect of the bifunctional coupling agent on the electrical conductivity is caused by the chemical bonding of the CNTs to the polymer.

In summary, the results show the applicability of the concept of adding **BCA**s as an easy route to prepare CNT containing composites with low electrical percolation threshold, if the polymers and the CNTs contain the corresponding functional groups. Simple melt-mixing of all components at appropriate conditions without the need of modifying the polymer or nanotubes is suitable to get such improved electrical properties [32]. Due to the coupling between CNTs and the polymer matrix also enhancements in mechanical and other properties may be expected, however, this has to be proven in future investigations.

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Graphical Abstract:
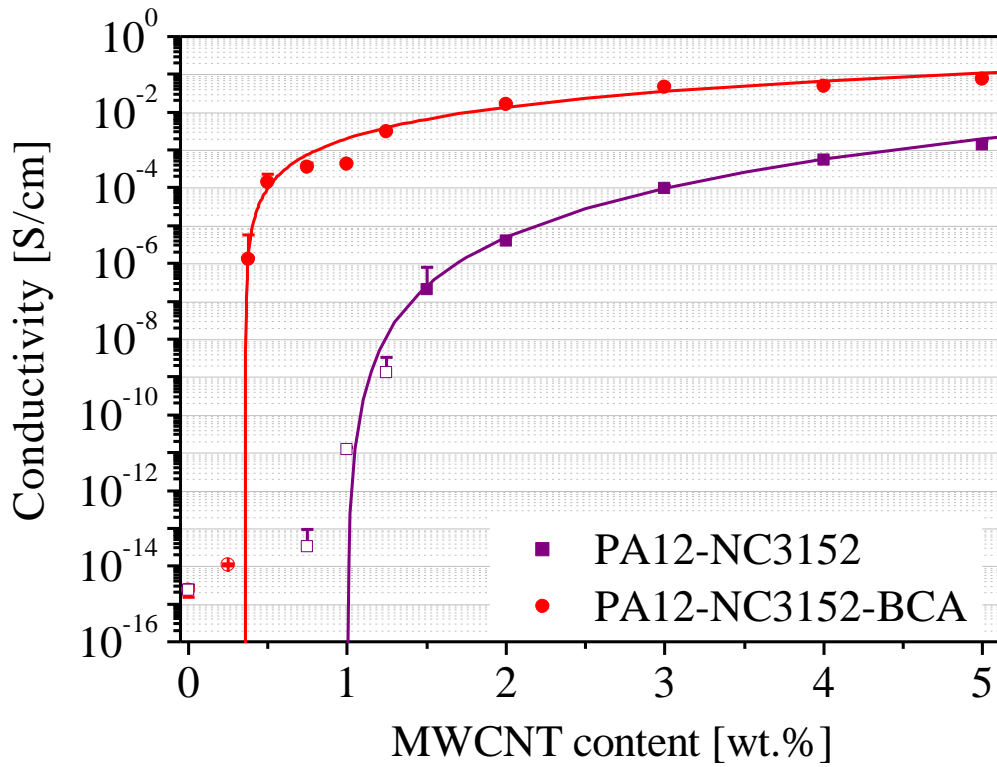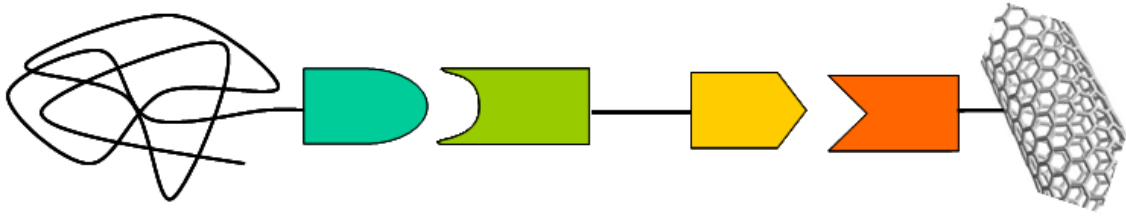
A bifunctional coupling agent (**BCA**) containing one oxazoline and one benzoxazinone group was applied to promote a reaction between polyamide 12 (PA12) and multiwalled carbon nanotubes (MWCNTs) during melt mixing. With this modification, the MWCNT content needed for the electrical percolation was significantly reduced by a factor of about three.