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Electrical and thermal properties of polyamide 12 composites with hybrid fillers systems of multiwalled carbon nanotubes and carbon black

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Abstract

Hybrid filler systems of multiwalled carbon nanotubes (MWCNTs) and carbon black (CB) were incorporated into two types of polyamide 12 (PA12) using small-scale melt mixing in order to identify potential synergistic effects on the interaction of these two electrical conductive fillers. Although no synergistic effects were observed regarding the electrical percolation threshold, at loadings well above the percolation threshold higher volume conductivities were obtained for samples containing both, MWCNT and CB, as compared to single fillers. This effect was more pronounced when using a higher viscous PA12 matrix. The formation of a co-supporting network can be assumed. The combined use of CB and MWCNTs improved the macrodispersion of MWCNT agglomerates, which can be assigned as a synergistic effect. DSC measurements indicated an effect of the nanofiller on crystallisation temperatures of PA12; however this was independent of the kind or amount of the carbon nanofiller.

Keywords: A. Carbon nanotubes, Nano composites, Polymer-matrix composites (PMCs); B. Electrical properties; D. Optical microscopy, Dispersion

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1. Introduction

Besides the excellent insulating properties of most polymers, some applications require electrostatic dissipative or conductive polymer behaviour. Enhanced conductivity can be achieved using two different approaches, either using inherently conductive polymers or adding electrical conductive fillers to the polymer matrix. Polyaniline, polypyrrole or polythiophene are, amongst others, inherently conductive polymers because of their conjugated π -electron system [1]. With these materials, transparent electrical conductive polymer films can be easily achieved, for example in organic solar cells, where they are widely used [2]. The main drawbacks of this class of materials are high prices, the difficulties in melt compounding due to nonmeltability combined with degradation, and poor long-term stability.

In the second approach, electrical conductive filler are incorporated in the polymer matrix. Above a certain amount of filler, the so-called electrical percolation threshold is achieved, at which the conductive filler particles form electrical pathways through the polymer matrix. Besides metal powder, carbon based additives are quite commonly used in industry [3]. Carbon based fillers, for example carbon blacks (CBs), carbon fibres (CFs) or carbon nanotubes (CNTs) are available on the market. These carbon filler can be distinguished mainly due to their different shapes. CBs are based on spherical primary particles in the nanometer range that form aggregates agglomerating in differently structured clusters. Usually, in polymer composites relatively high volume fractions of CB (around 10 wt.%) are needed to reach the electrical percolation level depending on the size, grade, and details of the morphology [4, 5]. In commodity applications like tyres price is a key parameter and due to the relatively low price as compared to CNTs, CB is still the most applied conductive filler. In thermoplastic

matrixes, these high CB contents needed for percolation result in increased composite viscosities and losses in mechanical properties. In this comparison, CNTs gained huge interest due to their high conductivity up to 10,000 S/cm [6] and their extraordinarily high aspect ratio (typically > 1000), which makes them a suitable candidate to obtain very low electrical percolation thresholds [7-9]. In addition, mechanical properties especially modulus and strength at break can be even enhanced. Most of the CNTs used in different applications are multiwalled carbon nanotubes (MWCNTs) produced by chemical vapour deposition. The tubes are commonly highly entangled and due to Van der Waals interactions between the single tubes they form agglomerates with high agglomerate strengths. Hence, MWCNT agglomerates are difficult to disperse in the polymer matrix. When using melt mixing as the dispersion method, representing a well-established technique in industry, the reported percolation thresholds [10-14] in most cases are much higher than the theoretical ones [4, 15]. In addition, shaping of CNT based composites using e.g. injection moulding results in changes in the network structure which influences electrical properties [16, 17]. These difficulties in processing, together with the still relatively high prices of MWCNT materials limits the use of CNTs to materials for high price applications.

Therefore, the use of hybrid filler systems that combine the outstanding properties of CNTs with the lower costs of other conductive fillers are of economic interest. In such composites synergistic effects are of interest, meaning that the effect originating from the use of the hybrid filler system is larger than the summarised effects of the single fillers. However, the occurrence of synergistic effects concerning certain composite properties is seldom explicitly regarded. Concerning the electrical percolation threshold

of mixed carbon filler systems, Sun et al. [18] developed an equation based on the percolation of the single fillers by adapting an excluded volume approach (see 3.1).

Most of the studies reported in the literature on the use of hybrid filler systems were performed in epoxy resins [19-24]. Concerning the electrical percolation threshold, only small effects were found when replacing parts of the nanotubes by other conductive fillers or when additionally adding them. Sumfleth et al. [24] reported that due to synergistic effects in network formation and in charge transport the inclusion of both MWCNT and CB in the epoxy matrix leads to an identical electrical behaviour of this ternary nanocomposite. Furthermore, the addition of CB increases the maximal achievable conductivity at higher loadings.

Hybrid filler systems have also been applied to rubber based composites [25, 26].

Bokobza et al. [25] found better CNT dispersion, lower resistivity values and also a reduction in percolation threshold when using CNTs and CB together in styrene-butadiene rubber.

In thermoplastic matrices, only a few results are reported in the literature regarding the use of two carbon fillers [18, 27-29]. The mixture of carbon fibres and carbon black in polyethylene was described by Calleja et al. [28] where the fibres provide charge transport over large distances and CB particles improved the interfibre contacts leading to a conductivity rise. Lee et al. [29] observed a decrease of resistivity when adding MWCNTs in CB composites. However, the authors did not specifically discuss potential synergistic effects between these two fillers. The effect of organoclay addition to a PA6-CB composite was investigated by Konishi et al. [30]. In this paper, a reduction of CB percolation threshold was observed in the presence of a certain amount

of organoclay, which was attributed to a nanoplatelet induced enhanced self-assembly of CB network.

In a former study [31] for polyamide 12 (PA12) composites the influences of the addition of CB and different MWCNTs as well as the use of different PA12 matrices varying in end group functionality and melt viscosity were investigated. Percolation thresholds for MWCNTs were found to be between 0.7 wt.% and 2.1 wt.%. For CB, a percolation threshold of 4.3 wt.% was identified. Based on these results, in this paper, composites of PA12 with hybrid filler systems consisting of MWCNTs and CB were prepared and investigated regarding the electrical percolation threshold, their conductivity values, the dispersion of primary CNT agglomerates, and their thermal behaviour.

2. Experimental

2.1 Materials

As PA12 matrix, Vestamid types supplied by Evonik Degussa GmbH (Marl, Germany) were used. The two polymers having an excess of acid end groups differed in molecular weight leading to different melt viscosities at the processing temperatures used as shown in [31]. As MWCNT materials Baytubes[®] C150P (Bayer MaterialScience AG, Leverkusen, Germany) and Nanocyl[™] NC7000 (Nanocyl S.A., Sambreville, Belgium) were employed. Baytubes[®] C150P have been characterized by a carbon purity of about 95 %, a bulk density of 120–170 kg/m³ [32], an outer nanotube diameter of 11±3 nm [33], a length of 1-10 µm [32], and agglomerate sizes between 10 and 600 µm [34]. For Nanocyl[™] NC7000 the carbon purity is given as 90 % [35] and the bulk density was measured to be 66 kg/m³, and the mean agglomerate size was larger than 675 µm

[34]. The outer diameter was determined to be 10 ± 3 nm [33]. 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 [36]. Both MWCNT materials were produced by chemical vapour deposition. For the investigation of hybrid filler systems, Carbon Black Printex[®] XE2 (Evonik Degussa GmbH, Marl, Germany) with a carbon purity of more than 99 %, a bulk density of 100-400 kg/m³, a primary particle size of 30–35 nm, and a BET value of 400 m²/g [37] was used.

PA12 and PA12 composites were dried at 80°C and MWCNTs and CB at 120°C under vacuum overnight before processing.

2.2 Processing

Melt mixing was performed using a DACA microcompounder (DACA Instruments, Santa Barbara, USA). This conical twin screw microcompounder has an inner volume of 4.5 cm³. When used together, MWCNTs and CB were premixed before processing by hand shaking in a glass flask. PA12 and the filler material (MWCNTs, CB, or both) were added alternately (at least three changes) into the running compounder. As mixing conditions 210°C and 250 revolutions per minutes (rpm) were applied for composites based on the low viscosity matrix and 260°C and 150 rpm for those based on high viscosity matrix. The selection of the rotation speed of 150 rpm for the high viscosity matrix was based on an optimization as reported in [31]. Considering residence times in industrial applications, a short mixing time of 5 min was chosen.

Compression moulding was performed at 220°C (low viscosity) or 260°C (high viscosity) using a Weber hot press (Model PW 40 EH, Paul Otto Weber GmbH, Remshalden, Germany) following the procedure given in [14]. The strands extruded

were cut into small pieces and circular discs with a diameter of 30 mm and a thickness of 0.5 mm were pressed. 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 Characterisation

In order to measure electrical volume resistivity values higher than 10^7 Ohm cm (unfilled symbols in the figures) a Keithley Electrometer 6517A (Keithley Instruments Inc., Cleveland, USA) combined with a Keithley 8009 Resistivity Test Fixture Electrical was applied. For values lower than 10^7 Ohm cm a 4-point test fixture (gold contact wires with a distance of 16 mm between the source electrodes and 10 mm between the measuring electrodes) together with a Keithley Multimeter DMM 2000 was used on strips ($30 \times 3 \times 0.5$ mm³) cut from the compression moulded plates. For discussion, resistivity values were transformed into conductivity values.

If possible, the electrical percolation thresholds (p_c) were fitted using the power law function for the composite conductivity near the electrical percolation threshold [38]:

$$\sigma(p) = B(p - p_c)^t \quad (1)$$

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 root mean square error minimisation.

For analysis of the macrodispersion of remaining primary MWCNT agglomerates, light transmission microscopy was performed. Thin sections of 5 μ m were cut from extruded strands using a Leica RM 2155 microtome (Leica Microsystems GmbH, Wetzlar, Germany) and analysed with a microscope BH2 in transmission mode connected to a

camera DP71 (both Olympus Deutschland GmbH, Hamburg, Germany). To quantify the macrodispersion, the area ratio A/A_0 of undispersed primary agglomerates was calculated using the area A of remaining agglomerates in each micrograph and the total area of the micrograph A_0 ($\sim 0.6 \text{ mm}^2$). Increasing area ratio A/A_0 thus indicates worse dispersion. At least 7 images from different sections of the samples were used for this quantification which was done using the software ImageJ Version 1.43g. Additionally, the size of the largest agglomerates was evaluated.

Differential Scanning Calorimetry (DSC) analysis was carried out with a DSC Q 1000 (TA Instruments, New Castle, USA) between -80°C and 230°C under a nitrogen atmosphere at a scan rate of 10 K/min. To evaluate the influence of mixed filler systems on the crystallisation behaviour of the composites, heating-cooling-heating cycles were performed. The second heating was used to determine the melting temperature (T_m), whereas second cooling was used for the determination of the maximum ($T_{c,m}$) and onset crystallisation temperatures ($T_{c,o}$). To allow a comparison between samples with different MWCNT contents, the crystallisation enthalpies (H_c) were normalised to the PA12 fraction for crystallisation during cooling.

3. Results and discussion

3.1. Effect of hybrid filler systems on electrical percolation

The influence of hybrid filler systems containing CB and MWCNTs on the electrical percolation threshold in PA12 was investigated by comparing samples containing 50/50 wt.% and 75/25 wt.% mixtures of MWCNTs (Nanocyl™ NC7000) and CB (Printex® XE2) and the pure fillers. From the dependence of volume conductivity versus

filler content, the electrical percolation thresholds were determined (Figure 1). Figure 1A shows the electrical volume conductivity vs. the total filler content. Figure 1B plots the conductivity versus the MWCNT content. For 50/50 wt.% mixtures, the electrical percolation threshold was achieved at 0.9 wt.% MWCNT (1.8 wt.% total filler) content. In the case of 75/25 wt.% mixtures, percolation occurs also at a MWCNT content of 0.9 wt.% (1.2 wt.% total filler). These percolation thresholds were not found to be lower than in Nanocyl™ NC7000-PA12 composites without CB (0.9 wt.%). It is clearly visible that the addition of CB to MWCNT composites does not reduce the MWCNT content needed for the electrical percolation. It has to be assumed, that the formation of the conductive networks is dominated by the MWCNTs with their high aspect ratio. However, the additional conductive CB filler can lead to a better charge transport in the conductive pathways if localized mainly at the contact points between neighbored nanotubes or bridging nanotubes (see schema in Figure 2). Interestingly, hybrid filler systems with 50 wt.% CB content show higher electrical conductivity values than those with pure MWCNTs starting at 2 wt.% loading. For example, in samples with 3 wt.% MWCNTs, the addition of 3 wt.% CB (50/50 wt.%) increased the electrical volume conductivity from 1.7 E-04 S/cm to 1.0 E-02 S/cm. Thus, at higher loadings the formation of a co-supporting network between MWCNTs and CB can be supposed. In order to calculate the expected percolation threshold of the mixed filler system the approach of Sun et al. [18] was adapted to our system. Equation (2) gives the condition for additive behaviour of the filler components. Only if the measured percolation threshold for the mixed filler system is lower than that calculated from the measured values of the components, synergism is given.

$$\frac{m_{CNT}}{\varphi_{c,CNT}} + \frac{m_{CB}}{\varphi_{c,CB}} = 1 \quad (2)$$

For our example, m_{CNT} is the content of Nanocyl™ NC7000 and c_{CNT} is the corresponding electrical percolation threshold (here: 0.9 wt.%); m_{CB} is the content of CB and c_{CB} is the electrical percolation threshold of CB (here: 4.3 wt.%). In the case of 50/50 wt.% mixtures, the calculated value to achieve percolation is 1.5 wt.% total filler. In the experiment, 1.8 wt.% filler in PA12 were needed. For the 75/25 wt.% mixtures 1.1 wt.% of total filler content was calculated and 1.2 wt.% was experimentally found. As a result, the experimentally found electrical percolation thresholds were higher than those calculated according to equation (2) clearly indicating that no synergistic effect of the hybrid filler system can be found on electrical percolation threshold for that system. As a second way to identify synergistic or additive effects of MWCNTs and CB in PA12 composites (low viscosity), the effect of adding CB to a fixed MWCNT content below the percolation threshold was studied. For this investigation, samples with 1 wt.% Baytubes® C150P (insulating, conductivity 1.1×10^{-14} S/cm) and different CB contents were prepared. In composites containing only Baytubes® C150P the percolation threshold was found at 2.1 wt.%. It can be seen in Figure 3 that the percolation level in these hybrid filler systems containing 1 wt.% MWCNTs is reached at a CB addition of 2 - 3 wt.%. With a percolation threshold for neat CB composites of 4.3 wt.%, the theoretical percolation threshold according to equation (2) for samples containing 1 wt.% Baytubes® C150P should be obtained with the addition of 2.3 wt.% CB which is within the experimental range. Thus, also for systems with a fixed CNT content below the percolation threshold addition of CB does not lead to synergistic effects between these two conductive fillers.

Both results indicate that no synergistic effects regarding the electrical percolation threshold were found in low viscous PA12 systems. This finding is in accordance with

Rahatekar et al. [39], who modelled the percolation in mixtures of fibers and spheres using a Dissipative Particle Dynamics (DPD) method. For both isotropic and uniaxially oriented fibre - sphere mixtures, they found that gradually replacing fibres with an equivalent volume of spheres increased the percolation threshold.

To identify a potential influence of matrix viscosity, mixtures of 50/50 wt.% Baytubes[®] C150P and Printex[®] XE2 were investigated in high viscous PA12 with acid excess and the corresponding volume conductivities are shown in Figure 4. In this matrix percolation occurs at approximately 2.75 wt.% for Baytubes[®] C150P, for Printex[®] XE2 this concentration was found at approximately 7.25 wt.%. In the 50/50 wt.% mixtures, the percolation threshold is estimated to be at 4.5 wt.% (see Figure 4A, curve fitting not possible). As seen in Fig. 4B where conductivity is plotted versus the MWCNT content, an increase in electrical volume conductivity was found for the mixed filler systems at MWCNT contents above 2 wt.%. For example, electrical volume conductivity of $1.2 \text{ E-}03 \text{ S/cm}$ was found for the 50/50 wt.% mixture with a content of 2.5 wt.% MWCNTs, compared to $7.1 \text{ E-}08 \text{ S/cm}$ for the compound containing only MWCNTs. In composites with 3 wt.% MWCNTs an increase in conductivity of 3 orders of magnitude was observed when comparing the hybrid filler system vs. MWCNTs alone. It has to be considered that in high viscous systems a much higher MWCNT content was needed to reach the electrical percolation than in the low viscous ones. Using equation (2), no real synergistic effect regarding the percolation threshold of the system could be found (calculation: expected percolation threshold 4 wt.% of total filler content). The filler content needed for percolation in the hybrid filler system was again higher than the

calculated one. The observed rise in conductivity is therefore an additional effect of two conductive fillers in the matrix.

3.2. Effect of hybrid filler systems on MWCNT dispersion

Additionally, the state of macrodispersion of the hybrid fillers was investigated in low viscous PA12 composites. For samples containing 2 wt.% Nanocyl™ NC7000 an area ratio of remaining CNT agglomerates A/A_0 of 1.3 % was found. Carbon Black is much easier to disperse and therefore only small remaining agglomerates with an A/A_0 ratio of 0.3 % were detected. Surprisingly, in samples containing 2 wt.% Nanocyl™ NC7000 and 2 wt.% Printex® XE2 a significantly reduced A/A_0 ratio of 0.7 % was observed. Whereas in composites containing 2 wt.% Nanocyl™ NC7000 (and no additionally filler) remaining agglomerates with sizes up to 82 μm were seen. In samples containing 2 wt.% Nanocyl™ NC7000 and 2 wt.% Printex® XE2 only agglomerates smaller than 57 μm were observed indicating a positive effect of the additional second filler on the nanotube dispersion. When melt mixing the hybrid filler system containing 4 wt.% filler, slightly higher torque values during mixing in the microcompounder were observed as compared to samples with only 2 wt.% Nanocyl™ NC7000. Therefore, higher shear forces during compounding acting on the nanotubes agglomerates have been applied. Higher shear forces contribute to the agglomerate dispersion and decrease the area of remaining agglomerates [12, 14]. This could be one reason for the better dispersion of MWCNTs in the hybrid filler systems. Additionally, it has to be considered that due to the addition of CB another non-melting component is added which could result in an increase of internal friction and therefore the erosion process of MWCNT agglomerates could be accelerated.

3.3 Effect of hybrid filler systems on thermal properties of the PA12 matrix

To identify effects of the two different carbon fillers on the melting and crystallisation behaviour of the PA12 matrix, DSC was performed. It is well known that MWCNTs and CB influence and induce polymer crystallization [40, 41] and even shish-kebab structures were observed [42, 43]. In the literature, it is still under discussion if the growing crystallites cover the nanofillers acting as nucleating sites or if the nanotubes are expelled into the amorphous parts between the crystallites. In both cases, an influence on the electrical conductivity can be expected. If nanotubes are covered by crystallites, as implied, e.g. in [44], the conductivity is expected to decrease depending on the thickness of the insulating interface layer. If nanotubes are expelled to the amorphous phase, due to an increase in the degree of crystallinity induced by the nanotubes, conductivity is expected to increase and the percolation threshold can be reduced as the local filler concentration in the amorphous part increases.

In our study, the neat PA12 composites (low viscous) with two different Nanocyl™ NC7000 contents (1 wt.% and 3 wt.%) and two mixed filler compounds with Printex® XE2 (50/50 mixtures with 2 wt.% and 6 wt.% total filler content) were investigated via DSC. The results are summarized in Table 1. The melting behaviour of similarly processed PA12 was characterized by a double-peak with maxima (T_m) at 172.4°C and 178.9°C, whereas all composites showed only one peak laying at around 188°C (± 0.6 K). The crystallisation behaviour shows differences between the PA12 and the composites, but no significant variations depending on amount or kind of nanofiller. The onset temperature of crystallization ($T_{c,o}$) increased by about 8-9 K with slightly higher increases when using 3 wt.% MWCNTs as compared to 1 wt.% MWCNTs. The

maximum crystallisation temperature ($T_{c,m}$) of PA12 increased by about 7-8 K nearly irrespective of the amount and kind of carbon nanofiller added. The crystallisation enthalpy (H_c) increased slightly with addition of MWCNTs. No additional effect was observed for hybrid filler systems with the addition of CB. Thus, the crystallisation behaviour of the PA12 matrix is not influenced when adding CB as second filler to MWCNTs and the electrical percolation thresholds of the mixed filler systems are not influenced by differences in the crystallinity of the matrix.

4. Summary and conclusion

In this study, hybrid filler systems consisting of MWCNTs and CB were incorporated by melt mixing in two different PA12 matrices having different melt viscosities. The aim was to investigate if synergistic effects can be achieved concerning electrical percolation threshold or dispersion of primary CNT agglomerates.

For composites of low viscous PA12 and Nanocyl™ NC7000 in combination with Printex® XE2, no reduction of the MWCNT content needed to achieve electrical percolation was found when CB was added. The percolation threshold in 50/50 wt.% mixtures was reached at 1.8 wt.% total filler, which is higher than the content predicted by an equation presented in the literature [18] for the percolation in mixed filler systems (1.5 wt.% total filler). However, with the addition of CB, the absolute values for volume conductivity were significantly increased at higher loadings, which is in agreement with findings in the literature on epoxy systems [21]. In the high viscous systems, a reduction of the MWCNT content for percolation was also not achieved, even if again an increase of the conductivity values at higher filler loadings were found. Regarding the dispersion of primary CNT agglomerates a synergistic effect of both fillers was found. Whereas

samples containing 2 wt.% Nanocyl™ NC7000 show an area ratio of undispersed MWCNT agglomerates of 1.3 %, this ratio decreased to 0.7 % when 2 wt.% CB was added (total filler content 4 wt.%). This clearly indicates that CB is helping to improve the MWCNT dispersion and to reduce especially the size of big primary nanotube agglomerates possibly due to viscosity effects and internal friction. Interestingly, the significant positive effect of CB in dispersing MWCNTs is not reflected in lower electrical percolation thresholds, as one would expect. The melting and crystallization behaviour was influenced by the nanofillers as reflected by increases in the crystallization temperatures; however this effect was nearly independent on kind and amount of the nanofiller. Combined use of CB to MWCNTs did not show additional effects. Therefore, influences of crystallinity on electrical properties can be excluded. In summary, the expectations of synergistic effects of hybrid filler systems of CB and MWCNTs on the electrical percolation threshold could not be complied with the used systems. However, such systems at high loadings did show higher conductivity values than what was achievable from systems containing filler of only one type.

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Table 1. DSC data for PA12 and PA12 composites containing MWCNT or MWCNT/CB mixtures

MWCNT	CB	T _m	T _{c,o}	T _{c,m}	H _c
[wt.%]	[wt.%]	[°C]	[°C]	[°C]	[J/g]
0	0	172.4/178.9	158.5	157.1	-77.0
1	0	177.9	166.9	163.9	-80.1
1	1	178.4	166.9	164.1	-80.2
3	0	177.5	167.6	164.7	-79.9
3	3	177.6	167.7	164.8	-79.2

ACCEPTED MANUSCRIPT

Figures and captions

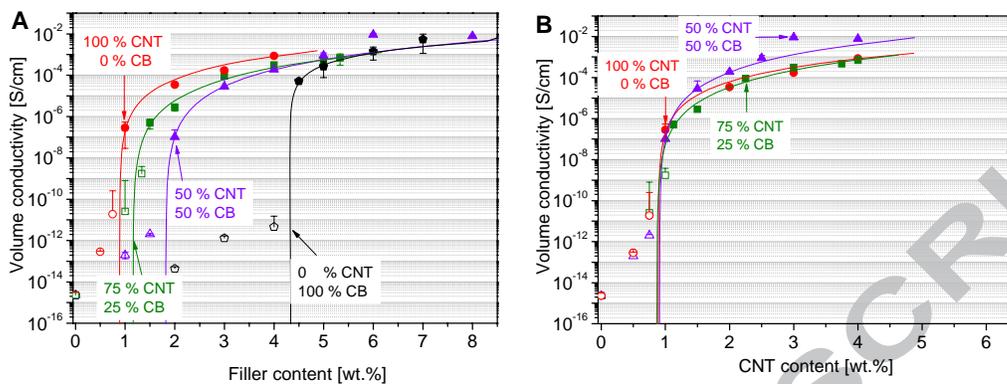


Figure 1. Electrical volume conductivity of composites based on low viscous PA 12 containing hybrid filler systems of Nanocyl™ NC7000 and Printex® XE2; (A) versus filler content, (B) versus MWCNT content

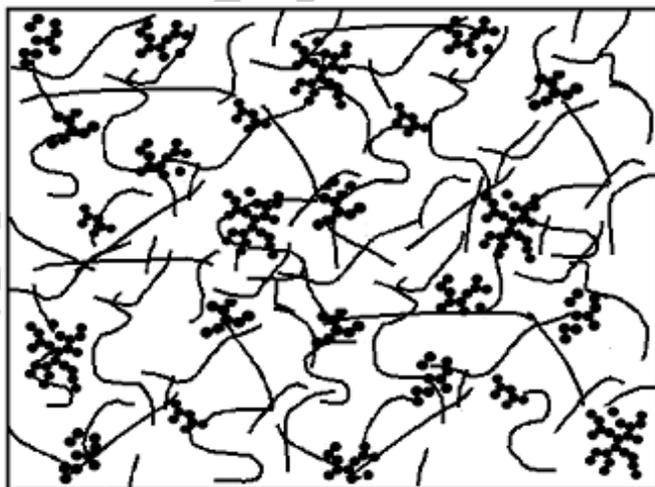


Figure 2. Schema of a co-supporting networked formed by MWCNTs and CB.

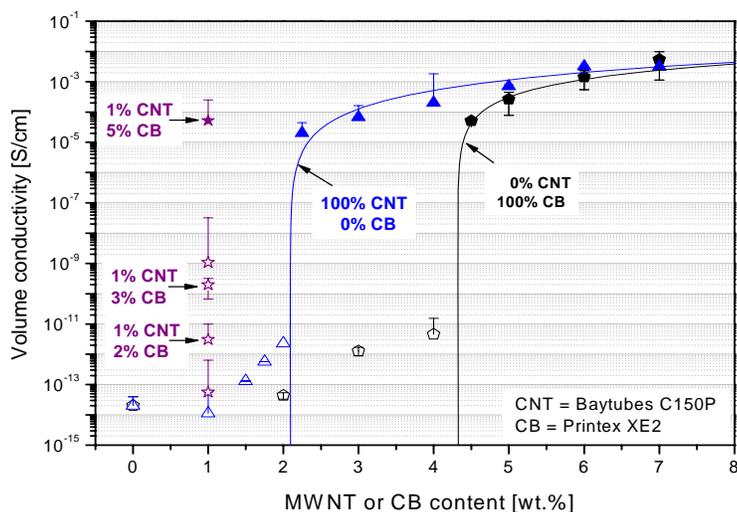


Figure 3. Electrical volume conductivity of composites based on low viscous PA12 when using hybrid filler systems with a fixed MWCNT content of 1 wt.% and different CB amounts in comparison to MWCNT and CB.

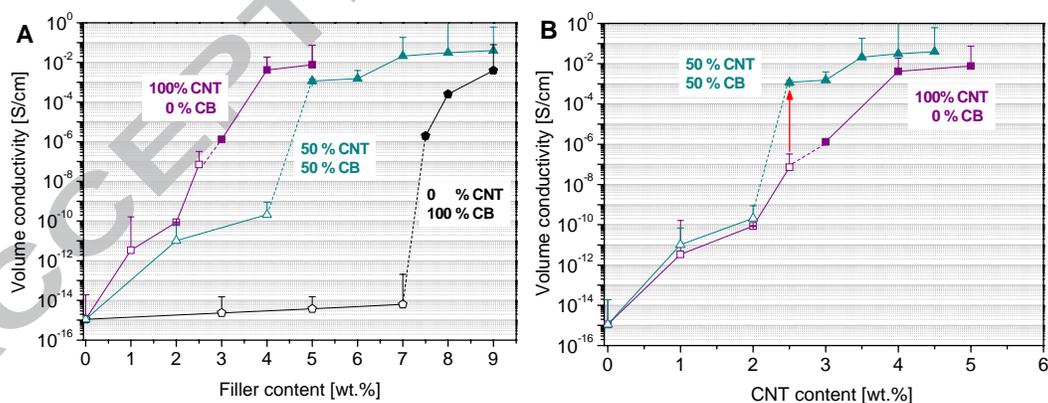


Figure 4. Electrical volume conductivity of composites based on high viscous PA 12 containing a hybrid filler system of Nanocyl™ NC7000 and Printex® XE2; (A) versus filler content, (B) versus MWCNT content

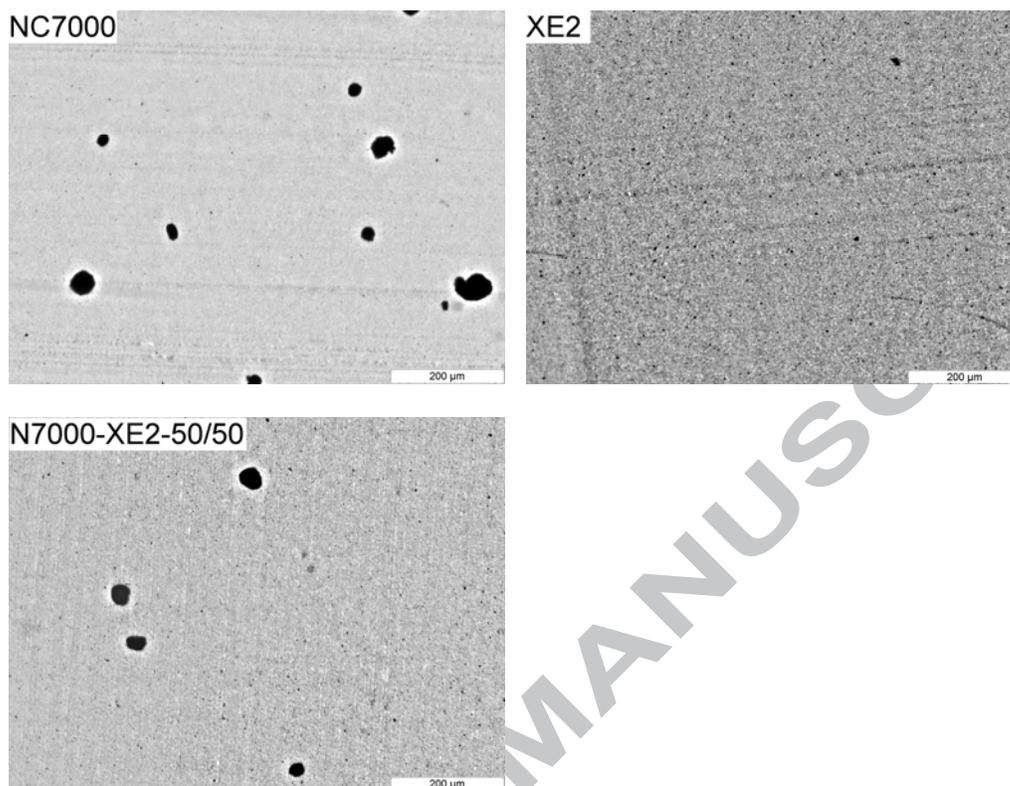


Figure 5. Light microscopy images of PA12 (low viscosity) with 2 wt.% Nanocyl™ NC7000, 2 wt.% Printex® XE2 and a 50/50 combination containing 4wt.% total filler.