

A successful approach to disperse MWCNTs in polyethylene by melt mixing using polyethylene glycol as additive

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Abstract

An additive-assisted one-step melt mixing approach was developed to produce nanocomposites based on linear low density polyethylene (LLDPE) with multiwalled carbon nanotube (MWCNT). The polymer granules, nanotube powder (2 wt% Nanocyl™ NC7000) and 1-10 wt% of the non-ionic additives consisting of poly(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO) with molar masses between 100 and 100,000 g/mol were simply fed together in the hopper of an small-scale DSM Xplore 15 twin-screw microcompounder. The so produced MWCNT/LLDPE composites showed excellent MWCNT dispersion and highly improved electrical properties as compared to samples without the additive, whereas the effects depend on the amount and molar mass of the additive. When 7 wt% PEG (2000 g/mol) were used, a reduction of the electrical percolation threshold from 2.5 wt% to 1.5 wt% was achieved.

Keywords: Carbon nanotubes; Additives, Dispersion; Polymer-matrix composites (PMCs); Electrical properties; Optical microscopy; Transmission electron microscopy

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1. Introduction

Polyethylene (PE) is one of the most common low cost thermoplastic. For electrostatic discharge applications, the addition of carbon nanotubes (CNTs) seems to be promising method of modification. The achievement of a good CNT dispersion needed for property enhancement is known to be very difficult in PE matrices. Therefore, to produce suitable PE composites with multiwalled carbon nanotubes (MWCNTs) by melt mixing it is necessary to develop knowledge about the factors influencing the dispersion of MWCNTs within the polymer matrix ^[1]. The properties of nanocomposites containing MWCNTs are strongly influenced by the structure of the used MWCNTs (e.g. aspect ratio, purity, functionalization and morphology), the preparation conditions in the melt mixing process (e.g. mixing speed, throughput, and temperature), and the properties of the polymer matrix (e.g. viscosity, surface tension, crystallinity) as well as the dispersability of the CNT material in the polymer matrix ^[2-8]. Summarizing the literature on PE based nanocomposites ^[9-12], within the spare results on varying the melt mixing conditions at moderate mixing times no report was found which reports composites which are free of remaining nanotube agglomerates.

Different other approaches to achieve good dispersion of MWCNTs during melt compounding in olefinic matrices are described in the literature, e.g. the enhancement of interfacial interaction due to a covalently bonded hydrophobic groups on the MWCNT surface, as e.g. described by Koval'chuk et al. for undecyl-modified MWCNTs in polypropylene (PP) ^[13]. Another way is the in-situ polymerization of polyolefins in presence of MWCNTs ^[14-16] or the use of maleic anhydride (MA) grafted polyolefine as a compatibilizer or coupling agent ^[17, 18]. Also the preparation of nanocomposites by masterbatch dilution ^[19] or especially the dilution of MA containing masterbatches ^[18] was reported to improve CNT dispersion, whereby the nanotubes experience twice the shear effects of the mixing equipment. Another strategy shown in literature is the use of

ultrasonic supported CNT-polymer solution mixing^[20-23] where the nanotubes are dispersed by using additives in organic solvents with long ultrasonic treatments. These nanotube dispersions are blended with polymer solutions by stirring followed by vacuum evaporation. In a second step the highly loaded CNT-polymer powder is diluted in the PE matrix using melt mixing like a masterbatch. Both, processing CNTs in two steps and ultrasonication of CNT dispersions, may lead to CNT shortening which increases the content necessary to get electrical percolation.

Poly(ethylene glycol) (PEG) is an additive mainly used as a compatibilizer to produce stable aqueous CNT dispersions. It can be applied as surfactants^[24, 25] or used covalently bonded at the CNT surface which is known as PEGylation^[26-28]. Kim et al.^[29] produced MWCNT/PVA composites via aqueous solution mixing with PEGylated MWCNTs. Lee et al.^[30] prepared polyurethane/PEG-modified MWCNT composite films by in-situ condensation polymerization and solution casting. Vaisman et al.^[31] use a poly(ethylene glycol) derivate as an additive in an ultrasonic supported CNT-PP solution mixing followed by film formation by spin coating. Even though in a recent paper Zou et al.^[32] used a PEG with low molecular weight to improve the dispersion and rheological percolation of functionalized MWCNTs melt mixed into poly(L-lactide), no studies are known on the effect of PEG on electrical percolation or electrical resistivity behavior. In the field of polyethylene as matrix material, no example can be found in the literature where PEG is used as an additive for direct melt mixing of polymers with MWCNTs.

In this study, an easy applicable additive supported one-step procedure to achieve well dispersed MWCNTs in an olefin polymer matrix was developed. Melt mixing technique was applied and PEGs of different molar masses were used as additives. The developed method resulted in significantly lower electrical percolation threshold of the MWCNTs with the LLDPE composites. The macrodispersion was quantified using light microscopy

on thin sections illustrating significant improvements in MWCNT dispersion. In this approach, no further pre-treatment of the non-functionalized CNT powder or the polymer is required, so that both materials, MWCNTs and polymer, can be used as received from the producers. The polymer granules, the nanotube powder and the additive are fed together in the hopper of the mixing device and after a certain mixing time a well dispersed nanotube-polymer composite with improved electrical properties is achieved.

2 Experimental

A LLDPE having a melting range of 105 - 130°C and a melt flow index of 2 g/10 min (ISO 1133) was used as the matrix. Non-functionalized commercially available MWCNT (Nanocyl™ NC7000; Nanocyl S.A., Belgium) was employed. According to investigations presented in [33], the Nanocyl™ NC7000 have a mean diameter of 10.0 nm and a mean length of 1341 nm. The additives PEG or PEO with low melting temperatures (T_m) having different number average molar masses (M_n) of about ~100 g/mol (PEG100, T_m -10°C), ~200 g/mol (PEG200, T_m 5-7°C), ~2000 g/mol (PEG2k (T_m 52-54°C), ~4600 g/mol (PEG4600, T_m -57-61°C), ~10.000 g/mol (PEG10k, T_m 63-65°C) and ~100.000 g/mol (PEO100k, T_m 65°C) were received from Sigma Aldrich. The term PEG is used for low molar mass polymer (up to M_n ~30.000 g/mol) when the nature of the hydroxyl end-group still matters, whereas the term PEO is used for the higher molar mass when the influence of the end groups can be disregarded. According to TEM (Figure 4) and DSC investigations LLDPE and PEG or PEO were not miscible.

The composites were produced using a twin-screw microcompounder (DSM Xplore, Netherland) with a chamber volume of 15 cm³. The LLDPE granules, MWCNT powder, and the additive were premixed by slightly shaking in a glass and were fed in the hopper of

the compounder. The mixing conditions were a melt temperature of 200°C, a speed of 200 rpm, and 5 min mixing time. The extruded strands were compression molded (180°C, 50 kN, 2 min) into circular plates (60 mm diameter, 0.3 mm thickness) using a hot press (Model-PW40EH, Paul-Otto Weber GmbH, Germany). The electrical volume resistivity of the compression molded plates was determined according to the standards ASTM-D4496 and ASTM-D257. At least three compression molded samples were measured to get the geometric mean value with the associated standard deviation of resistivity. The measurements on the pressed plates with resistances $>10^7$ Ohm were performed using a Keithley 8009 Resistivity Test Fixture (open symbols in the graphs). For resistances $<10^7$ Ohm the measurements were carried out on strips (5 mm x 55 mm x 0.3 mm, cut from the plates) 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 (Keithley Instruments Inc., USA). To determine the state of MWCNT macrodispersion light microscopy (LM) investigations were performed according to the standard ISO-18553 on thin sections (7 μ m thickness) taken from extruded strands. An Olympus-BH2 microscope combined with a camera DP71 (Olympus Deutschland GmbH, Germany) in transmission mode was applied. The agglomerate area ratio was determined from the LM images using the software ImageJ Version 1.43o by calculating the area ratio A_A (%) of the area of remaining MWCNT agglomerates A related to the total area of the image A_0 . According to the ISO-18553 standard only agglomerates with circle equivalent diameters $> 5 \mu$ m were regarded. For quantification 10 cuts were investigated for each sample and the mean value as well as statistical uncertainty within the 10 cuts are shown in the plots. To investigate the state of MWCNT nanodispersion a transmission electron microscope (TEM, LIBRA-120, Carl-Zeiss GmbH, Germany) was used. Ultra-thin sections with a thickness of ca. 80 nm were

cut from extruded strands (-160°C) using a Reichert Ultracut S ultramicrotome (Leica Microsystems GmbH, Germany).

3 Results and Discussion

The results of this investigation clearly indicate the influence of the application of the additive, namely poly(ethylene glycol) or (ethylene oxide), on the nanotube dispersion and the electrical percolation behavior of MWCNT/LLDPE composites prepared using small-scale melt mixing. To form an electrically conductive network for the semi-crystalline LLDPE usually relatively high nanotube contents are needed. The electrical percolation threshold using Nanocyl™ NC7000 as shown in Figure 1A was found at about 2.5 wt% and the plateau volume resistivity value of $10^2 \Omega \cdot \text{cm}$ was reached only if the filler content is higher than about 6 wt%. Through the use of PEG2k in the excess of 2.3 times in relation to the MWCNT content the electrical percolation threshold decreased to values of about 2.0 wt%. Using a constant PEG2k amount of 7 wt% at all MWCNT contents resulted in further decrease in the electrical percolation threshold toward values of about 1.5 wt%. When using PEG2k the volume resistivity of $10^2 \Omega \cdot \text{cm}$ can be reached at MWCNT contents of 3 wt%.

To study deeper the influence of PEG addition on the electrical properties of the MWCNT composite, a constant nanotube amount of 2 wt% was chosen. At this filler content, the LLDPE/MWCNT composite starts to get percolated but is still acting as an insulator with a volume resistivity of $2 \cdot 10^{14} \Omega \cdot \text{cm}$. When adding PEG with M_n values from 100 g/mol to 10.000 g/mol, a continuous decrease of the electrical volume resistivity with the PEG amount from $10^{14} \Omega \cdot \text{cm}$ to $10^5 - 10^2 \Omega \cdot \text{cm}$ was observed (Figure 1B). The lowest volume resistivity of $3.6 \cdot 10^2 \Omega \cdot \text{cm}$ was found using 9 wt% of PEG2k. On the other hand the addition of PEO100k did not result in a resistivity decrease.

The state of macrodispersion as assessed by light microscope for LLDPE/MWCNT composites with 2 wt% Nanocyl™ NC7000 clearly illustrates the positive effect of the addition of PEG. In Figure 2 the agglomerate area ratio A_A is plotted versus the PEG or PEO content, whereas Figure 3 shows light microscopy images of selected samples. For the composite without additive an area ratio of 3.4 % was found. The state of macrodispersion was significantly improved at the addition of 5 - 6 wt% PEG with M_n up to 2.000 g/mol and the area ratio decreased to values in the range of 0.1-0.4 %. In comparison to that, the addition of PEG with higher M_n up to 10.000 g/mol showed less decrease of the agglomerate area ratio in the composites. In contrast, the use of PEO with M_n of 100.000 g/mol did not result in such a decrease in the area ratio. Comparing the values in Figure 2 the most significant drop occurs between 4 wt% and 5 wt% for PEG100 and PEG200. Thus, 5 wt% PEG addition seems to be sufficient for the improvement in MWCNT macrodispersion to achieve materials nearly free of remaining agglomerates. The general decrease in the agglomerate area ratio with increasing additive content is also reflected in the volume resistivity which decreases in a similar manner. In case of PEO100k, where no significant changes in the agglomerate area ratio were found, also the resistivity is not changed significantly upon PEO addition.

The MWCNT nanodispersion was studied using TEM (Figure 4) on composites with 2 wt% MWCNT after 5 min mixing with and without 8 wt% PEG2k. At this content the sample without PEG2k is still electrically insulating whereas the addition of 8 wt% PEG2k resulted in a conductive sample. In the sample without additives also in the scale of TEM images agglomerates in the size of about 500 nm can be seen, which are located between the big remaining agglomerates as seen in Figure 3. Between these agglomerates also some dispersed tubes are visible. In contrast, after adding 8 wt% PEG2k, well dispersed and distributed MWCNTs were observed and no remaining agglomerates could be detected.

In order to explain the positive effects of the addition of PEG on the nanotube dispersion and electrical properties of the composites, several influences may be considered. Firstly, it may be expected, that the poly(ethylene glycol) wets and infiltrates the loosely packed primary MWCNT agglomerates in early state of the melt mixing process (Figure 4 middle) and thus reduces the agglomerate strength. Due to the low melting temperature of poly(ethylene glycol) in comparison to the melting temperature of the LLDPE matrix, the nanotube agglomerates are already wetted in the feeding zone of the mixing equipment before the LLDPE melts. Thus the compaction of the filler agglomerates, which is typical for feeding zones of melt mixing equipments^[34], can be prevented or reduced. Therefore, the shear stresses needed to disperse the nanotube agglomerates are lower as compared to dry agglomerates. Despite the reduction in melt viscosity when adding PEG, which results in reduced applied shear stresses of the matrix acting on the MWCNT agglomerates, the dispersion is better when using the additive as seen in Figures 2-4. This indicates, that obviously the processes of rupture and erosion are promoted followed by a thermodynamic driven process of the MWCNT phase transfer from the PEG into the PE phase. However, these mechanisms are still not completely understood and further investigations are needed to completely reveal the influencing factors. At the same time, the addition of poly(ethylene glycol) up to a molecular weight of 10.000 g/mol leads to continues decrease in the electrical volume resistivity at a constant 2 wt% Nancy™ NC7000 content. PEO100k with higher molecular weight did not show such an effect on the electrical volume resistivity. Reasons for this molecular weight-dependency in dispersion and electrical behavior could be the increase in viscosity of the polymer matrix which restricts the wetting and infiltration observed at low molar masses. Another aspect could be the considerable decrease of influence of the end groups at higher molar masses at constant additive content, indicating that also the amount of end groups could have an influence on

the extent of the effects. Also, these assumptions have to be studied in more details in further studies.

4 Summary and conclusion

In summary, this study shows an additive assisted method to produce olefinic MWCNT composites which are nearly free of MWCNT agglomerates. This can be realized by a simple one step melt-mixing extrusion process. PEGs with different molar masses (100 g/mol to 100.000 g/mol) were added in different amounts (1-10 wt%) during the mixing process of LLDPE with 2 wt% Nanocyl™ NC7000. In addition, the percolation behavior without and with PEG2k was studied. When adding poly(ethylene glycol) significant positive effects on the MWCNT macro- and nanodispersion and the electrical properties of LLDPE nanocomposites could be shown. Through the addition of 5 wt% poly(ethylene glycol) with low molar masses up to 200 g/mol during melt mixing, the particle size of remaining MWCNT agglomerates decreased under 5 µm and the MWCNT area ratio could be reduced from 3.4% to 0.1-0.4%. At the same time, a decrease of electrical volume resistivity from $10^{14} \Omega \cdot \text{cm}$ towards $10^4 \Omega \cdot \text{cm}$ could be found. The decreases in the agglomerate area ratio and the volume resistivity occurred in similar manner. The effects were generally more pronounced when adding PEGs with lower molar masses.

Even if the positive effects of PEG on dispersion and electrical resistivity are very clear, so far the mechanism behind them cannot be fully explained and needs further investigations. In addition, the use of low molar mass PEG up to 10 wt% is expected to affect the mechanical and thermal properties, which has to be studied in more detail. For industrial applications the migration of the PEG towards the surface might be a problem. However,

due to the two existing hydroxyl groups on each PEG chain a chemical crosslinking using maleic anhydride-grafted LLDPE is possible which fixes the PEG phase within the LLDPE matrix preventing migration.

5 Acknowledgments

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6 References

- [1] J. H. Du, J. Bai, H. M. Cheng, *Express Polymer Letters* **2007**, *1*, 253.
- [2] R. Andrews, D. Jacques, M. Minot, T. Rantell, *Macromolecular Materials and Engineering* **2002**, *287*, 395.
- [3] G. Kasaliwal, A. Gödel, P. Pötschke, *Journal of Applied Polymer Science* **2009**, *112*, 3494.
- [4] G. R. Kasaliwal, S. Pegel, A. Gödel, P. Pötschke, G. Heinrich, *Polymer* **2010**, *51*, 2708.
- [5] B. Krause, P. Pötschke, L. Häussler, *Composites Science and Technology* **2009**, *69*, 1505.
- [6] S. Pegel, P. Pötschke, G. Petzold, I. Alig, S. M. Dudkin, D. Lellinger, *Polymer* **2008**, *49*, 974.
- [7] P. Pötschke, S. M. Dudkin, I. Alig, *Polymer* **2003**, *44*, 5023.
- [8] R. Socher, B. Krause, R. Boldt, S. Hermasch, R. Wursche, P. Pötschke, *Composites Science and Technology* **2011**, *71*, 306.
- [9] O. Valentino, M. Sarno, N. G. Rainone, M. R. Nobile, P. Ciambelli, H. C. Neitzert, G. P. Simon, *Physica E: Low-dimensional Systems and Nanostructures* **2008**, *40*, 2440.
- [10] M. Morcom, K. Atkinson, G. P. Simon, *Polymer*, *51*, 3540.
- [11] S. Bocchini, A. Frache, G. Camino, M. I. Claes, *European Polymer Journal* **2007**, *43*, 3222.
- [12] N. T. Dintcheva, F. P. La Mantia, V. Malatesta, *Polymer Degradation and Stability* **2009**, *94*, 162.
- [13] A. A. Koval'chuk, V. G. Shevchenko, A. N. Shchegolikhin, P. M. Nedorezova, A. N. Klyamkina, A. M. Aladyshev, *Macromolecules* **2008**, *41*, 7536.
- [14] P. Pötschke, S. Pegel, M. Claes, D. Bonduel, *Macromolecular Rapid Communications* **2008**, *29*, 244.
- [15] S. Park, S. W. Yoon, H. Choi, J. S. Lee, W. K. Cho, J. Kitn, H. J. Park, W. S. Yun, C. H. Choi, Y. Do, I. S. Choi, *Chem. Mat.* **2008**, *20*, 4588.

- [16] M. Trujillo, M. L. Arnal, A. J. Müller, S. Bredeau, D. Bonduel, P. Dubois, I. W. Hamley, V. Castelletto, *Macromolecules* **2008**, *41*, 2087.
- [17] B. X. Yang, K. P. Pramoda, G. Q. Xu, S. H. Goh, *Advanced Functional Materials* **2007**, *17*, 2062.
- [18] M. Pöllänen, S. Pirinen, M. Suvanto, T. T. Pakkanen, *Composites Science and Technology* **2011**, *71*, 1353.
- [19] J. F. Vega, J. Martinez-Salazar, M. Trujillo, M. L. Arnal, A. J. Müller, S. Bredeau, P. Dubois, *Macromolecules* **2009**, *42*, 4719.
- [20] D. Zhao, Q. Lei, C. Qin, X. Bai, *Pigment & Resin Technology* **2006**, *35*, 341.
- [21] S. L. Ruan, P. Gao, X. G. Yang, T. X. Yu, *Polymer* **2003**, *44*, 5643.
- [22] X. J. He, J. H. Du, Z. Ying, H. M. Cheng, *Appl. Phys. Lett.* **2005**, *86*, 3.
- [23] Y. Bin, M. Kitanaka, D. Zhu, M. Matsuo, *Macromolecules* **2003**, *36*, 6213.
- [24] S. L. Chen, Y. G. Jiang, Z. Q. Wang, X. Zhang, L. M. Dai, M. Smet, *Langmuir* **2008**, *24*, 9233.
- [25] J. U. Lee, J. Huh, K. H. Kim, C. Park, W. H. Jo, *Carbon* **2007**, *45*, 1051.
- [26] P. Zhang, D. B. Henthorn, *Aiche J.* **2010**, *56*, 1610.
- [27] Y. Wang, H. Xiong, Y. Gao, H. Li, *Journal of Materials Science* **2008**, *43*, 5609.
- [28] Y. Xiao, T. Gong, S. Zhou, *Biomaterials* **2010**, *31*, 5182.
- [29] M. J. Kim, J. Lee, D. Jung, S. E. Shim, *Synthetic Metals*, *160*, 1410.
- [30] J. Lee, E. J. Park, J. Choi, J. Hong, S. E. Shim, *Synthetic Metals* **2010**, *160*, 566.
- [31] L. Vaisman, G. Marom, H. Wagner, *Advanced Functional Materials* **2006**, *16*, 357.
- [32] S. Zou, B. Na, R. Lv, H. Pan, *Journal of Applied Polymer Science* **2011**, *123*, 1843.
- [33] F. Y. Castillo, R. Socher, B. Krause, R. Headrick, B. P. Grady, R. Prada-Silvy, P. Pötschke, *Polymer* **2011**, *52*, 3835.
- [34] M. Gale, *Advances in Polymer Technology* **1997**, *16*, 251.

Figure captions

Figure 1 [A] The effect on the electrical percolation of Nanocyl™ NC7000 using PEG2k in LLDPE [B] Influence of the poly(ethylene glycol) or poly(ethylene oxide) content on the volume resistivity in LLDPE composites at a 2 wt% Nanocyl™ NC7000 loading

Figure 2 Nanotube agglomerate area ratio in LLDPE filled with 2 wt% Nanocyl™ NC7000 plotted [A] versus the contents of PEG or PEO and [B] related to the volume resistivity (the small percentage figures represent the PEG or PEO content)

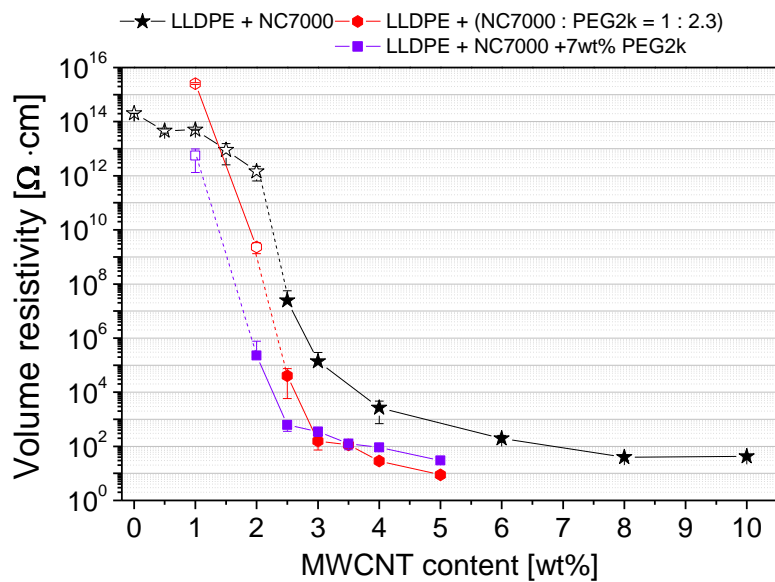
Figure 3 Characteristic light microscopy images (section thickness 7 μm) illustrating the drop of remaining primary agglomerates in 2 wt% Nanocyl™ NC7000/LLDPE composites between the addition of 4 wt% and 5 wt% PEG200 including the agglomerate area ratio A/A_0

Figure 4 Transmission electron microscopy images of 2 wt% Nanocyl™ NC7000/LLDPE composites without additive after 5min mixing (left), with 8 wt% PEG2k at 10sec mixing (middle) and with 8 wt% PEG2k after 5min mixing (right); the light phase represents the PEG phase and the cloudy grey phase represents the LLDPE phase

Figures

Figure 1

A



B

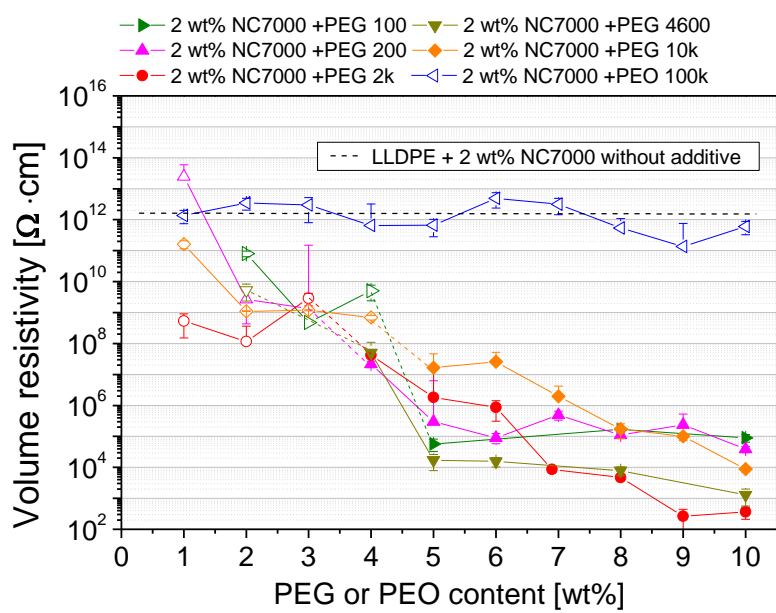


Figure 2

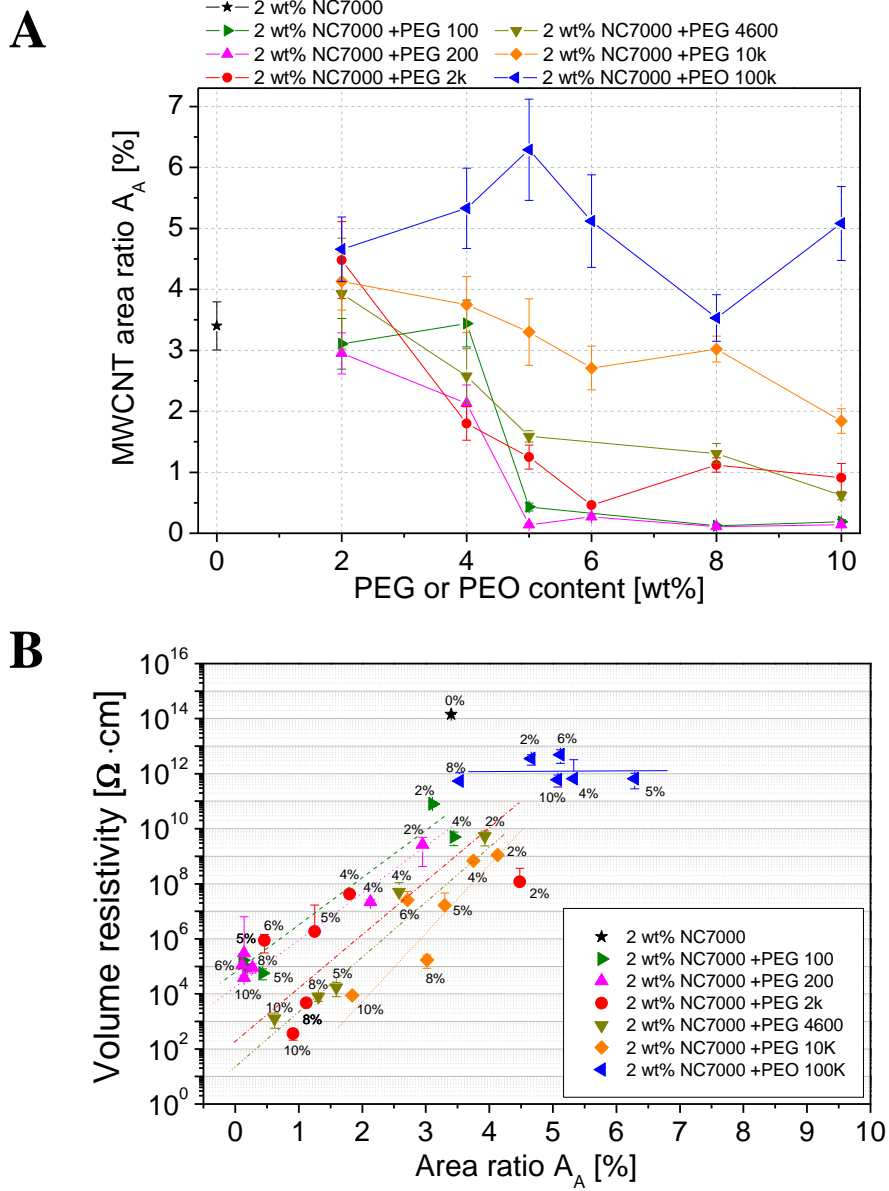


Figure 3

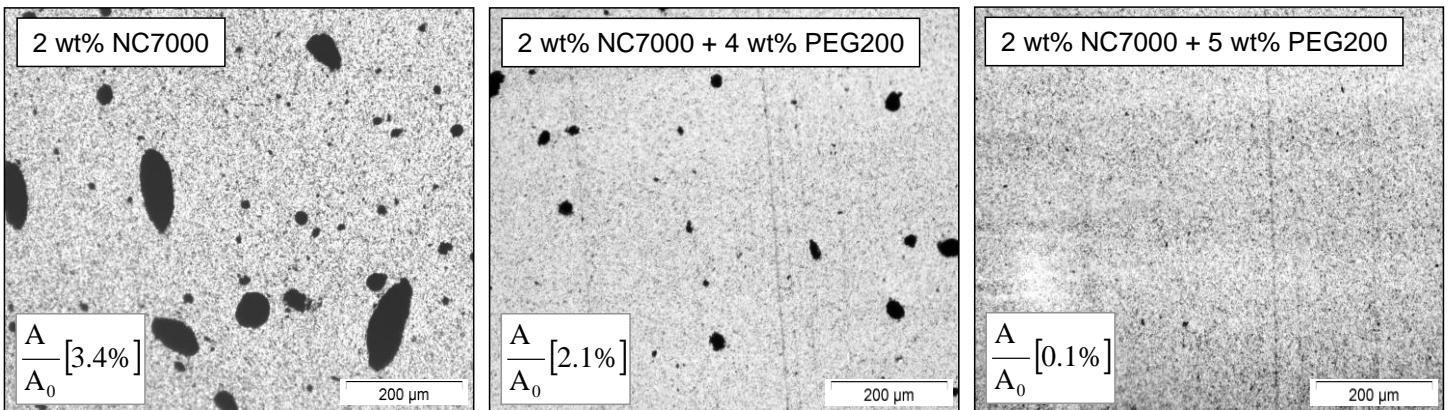
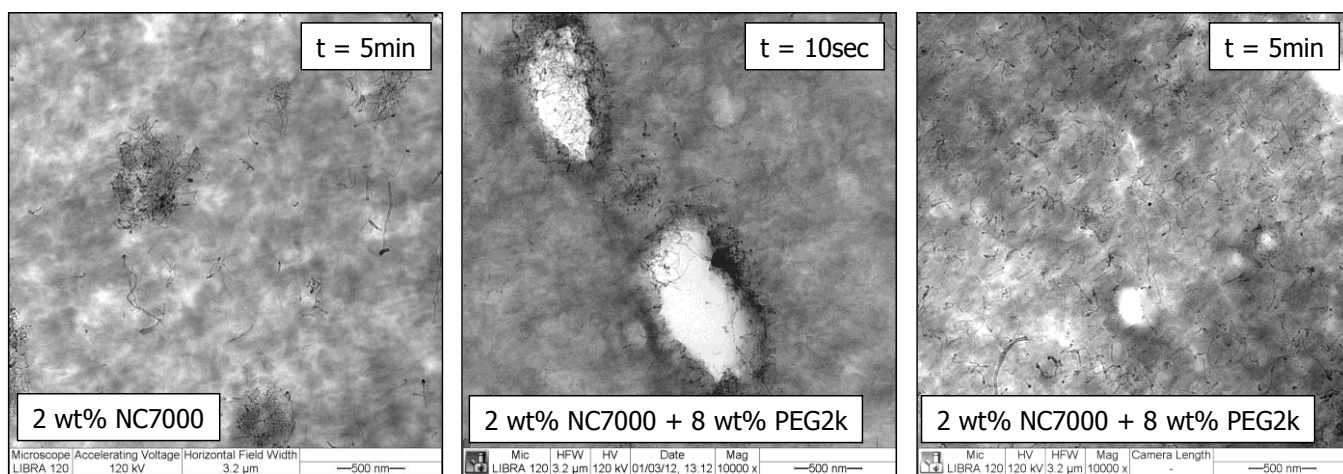
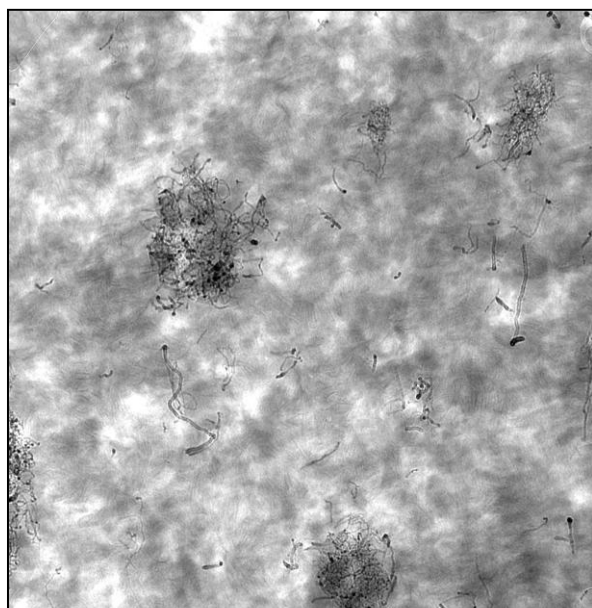


Figure 4



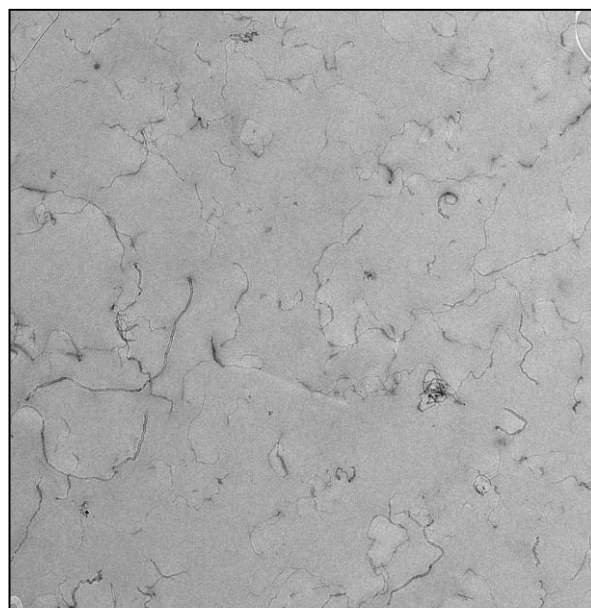
LLDPE + 2wt% MWCNT



Microscope	Accelerating Voltage	Horizontal Field Width	Magnification
LIBRA 120	120 kV	3.2 μm	10000 x

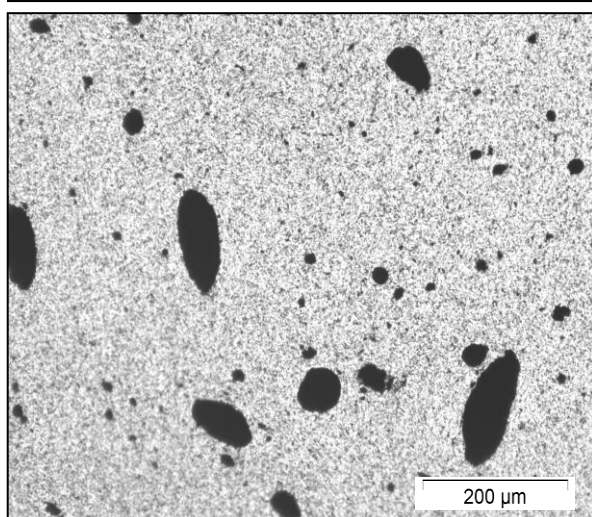
—500 nm—

LLDPE + 2wt% MWCNT + additive

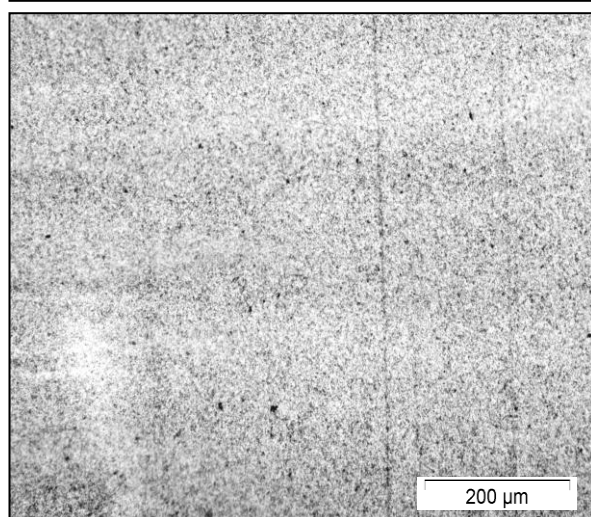


Microscope	Accelerating Voltage	Horizontal Field Width	Magnification
LIBRA 120	120 kV	3.2 μm	10000 x

—500 nm—



200 μm



200 μm