



Influence of twin-screw extrusion conditions on the dispersion of multi-walled carbon nanotubes in a poly(lactic acid) matrix

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ABSTRACT

Twin-screw extrusion using a co-rotating Berstorff ZE25 extruder was applied to disperse multi-walled carbon nanotubes (MWNT) in poly(lactic acid) (PLA). The masterbatch dilution technique was used whereas four different masterbatches were produced under variation of MWNT content, screw profile, temperature profile, and rotation speed which then were diluted to composites with 0.75 wt% MWNT under varied process conditions. The state of dispersion was investigated by light microscopy from which a dispersion index was quantified. Transmission electron microscopy was performed to observe the MWNT dispersion and network formation in the sub-micron scale.

The state of MWNT dispersion within the diluted composites was predominated by the state of filler dispersion in the masterbatches. High rotation speed (500 rpm) that still ensures a certain residence time of the melt combined with a screw profile containing mainly mixing elements were found to be highly convenient to disperse and distribute the MWNT in the PLA matrix as well during masterbatch production as the dilution step. The temperature profile showed less influence, however, an increasing profile resulted in slightly better nanotube dispersions. By means of these processing conditions a percolation set was performed indicating an electrical percolation threshold below 0.5 wt% MWNT content as measured on compression molded samples.

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1. Introduction

The outstanding performance of carbon nanotubes (CNT) [1–3], which combines unique electrical [4–9] and thermal properties [10–13] with high mechanical strength [14–18] predestines them as filler for polymer matrices. These new composite materials can be used in a wide range of industrial applications in the fields of electrostatic dissipation [19,20], electromagnetic interference-shielding [21–23], and electrically conductive materials achieving at the same time enhanced stiffness, strength, impact properties, thermal stability, tribological properties, and reduced thermal expansion [24].

To pave the way for these applications of polymer/CNT composites, it is important to develop processing technologies, which are compatible to already available industrial technologies. For this reason it is essential to reveal the relations between processing conditions and properties of melt mixed composites, wherefore this work contributes. Most of the previous studies on melt mixing of CNT into polymers were done using small-scale mixing devices in the gram scale and results obtained may not be transferable directly towards large-scale processes [25,26]. Even if large-scale melt mixing of nanotubes into thermoplastic polymers is reported

in literature [27–29] no systematic investigations on the influence of melt mixing conditions on nanotube dispersion could be found. Therefore, the influence of extrusion conditions using a twin-screw extruder on the dispersion of multi-walled carbon nanotubes (MWNT) in a poly(lactic acid) (PLA) matrix is investigated in this study with the aim to develop a guideline for plastic fabricators.

The key challenge for the successful implementation of applications based on polymer/CNT composites is a suitable distribution and dispersion of the filler inside the polymer matrix to ensure low percolation thresholds combined with high mechanical performance. Remaining primary agglomerates of the nanotubes not only reduce the nanotube amount available for electrical percolation, but also act as imperfections in mechanical tests. Therefore, the CNT material has to be individualised during the melt mixing process and for electrical conductivity they finally have to form a network, where the distance of neighbouring tubes is smaller than the maximum tunnelling distance of electrons, which is reported to be about 1.8 nm [30]. This objective is hindered by the intrinsic properties of the raw MWNT materials, which are characterised by the presence of compact primary agglomerates (up to diameters of several millimetres) often combined with physical entanglements of the spaghetti like flexible MWNT, which result from the synthesis process as well as the high van-der-Waals forces between the tubes.

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High shear forces during the melt mixing process and relatively long processing times are found to be suitable for the successful individualisation of MWNT, as reported for different systems [25–29,31–36]. Pötschke et al. [36] discussed for small-scale mixing the influence of rotation speed on the state of MWNT dispersion and electrical and dielectric properties for concentrations below and above the percolation threshold. At MWNT contents below the percolation threshold, increased screw speed resulted in better dispersion, whereas above the percolation threshold a decrease of DC conductivity was observed, which could be explained only with an enhanced breakage of the MWNT. Furthermore it is reported that an increase of mixing time improved the state of MWNT dispersion significantly for all MWNT concentrations. Similar results were reported by Takase [37] who showed that increase in rotation speed of a twin-screw extruder decreased the agglomerate size.

These practical results are comparable to findings on the dispersion kinetics of carbon black (CB) in non-Newtonian fluids. It is reported that dependent on the shear stress level either CB agglomerates are ruptured into smaller agglomerates or erosion from their surfaces takes place. The erosion process is more gradual and takes place at lower shear stresses [38,39], however, both the processes occur simultaneously. The work of Li et al. [40] showed that the dispersibility of CB agglomerates decreases with increasing aggregate structuring, which may be assumed also for CNT agglomerates, even if CNT and CB are quite different filler materials and may not be directly comparable.

In case of CNT a certain decrease of the aspect ratio during melt mixing may improve the dispersibility due to the decreasing number of physical entanglements as indicated by investigations of Andrews et al. [35]. The authors reported that during melt mixing of MWNT with polystyrene in a laboratory mixer a shortening of MWNT occurred with mixing time down to a third of the origin length, despite the high elasticity and flexibility of the nanotubes. At the same time a better MWNT dispersion was generated with increasing mixing energy input.

For industrial applications of melt mixing extrusion technique the two-step masterbatch dilution seems to be favourable as compared to the direct nanotube incorporation. Here, in the first step a concentrate of polymer containing high CNT contents is produced which is diluted in the second step with the same polymer in order to get well dispersed low amounts of nanotubes within the matrix. Besides the fact that high nanotube contents in the masterbatches resulting in high melt viscosity lead to high shear stresses during melt mixing, the handling of polymer bonded CNT is much easier for fabricators. In addition, the accurate dosage of small CNT amounts is easily achievable. Such masterbatch dilution processes are described in literature to be an appropriate technique to disperse and distribute CNT in polymer melts [20,31–33,41,42] whereas in these examples industrially available masterbatches were used. Therefore, the masterbatch dilution technique was applied in our work. In contrast to microcompounders that have a fixed assembly, a twin-screw extruder has a modular assembly, which can be varied in the diameter/length ratio of the screw, the screw profile itself, and the feeding positions. In this contribution, especially the screw profile, the temperature profile, and the rotation speed were varied systematically as well during masterbatch production as during the dilution process to determine their impact on the MWNT dispersion and distribution within the matrix.

PLA was selected as matrix polymer exemplarily. This type of polymer has generated great interest as one of the most innovative materials being developed for a wide range of applications. This polymer is thermoplastic and biodegradable, which makes it highly attractive for biological and medical applications. Especially in the field of tissue engineering PLA was found to be one of the most favourable matrix materials to create high performance fibres. Some reports were found on PLA/CNT composites. Moon et al. [43]

reported about mechanical, thermal, and electrical properties of composites containing MWNT, which were processed using solution technique. Besides an increase of Young's modulus an improvement in electromagnetic wave shielding effectiveness was observed by adding CNT. Wu and Liao [44] presented a study on PLA with MWNT where melt mixing was applied on acrylic-grafted PLA and chemically modified MWNT. In this paper, thermal and mechanical characterisation of the composites was in focus next to the proof of the expected chemical reaction whereas the state of nanotube dispersion and electrical conductivity were not regarded. Furthermore, McCullen et al. [45] reported about PLA/MWNT fibres, which were produced by electro spinning from a PLA solution to develop a scaffold for tissue engineering. Electrical percolation of fibre mats was reached at about 0.3 wt% CNT. For good spinning ability in electro spinning or melt spinning a good dispersion and distribution of the MWNT are needed to ensure a high mechanical level of the fibres and a certain melt strength required for the formation of the fibres.

2. Materials and experimental methods

2.1. Materials

PLA Biomer[®] L9000 (Biomer, Germany) is based on poly-L-lactic acid produced by polymerisation of naturally occurring L-lactate and represents a semi-crystalline and biodegradable polymer. Chemically, PLA is an alpha hydroxyl ester, which tends to hydrolyse (degrade). This hydrolysis process is fast in humid conditions at temperatures above the glass transition temperature ($T_g \sim 55^\circ\text{C}$). Due to this fact, the material was dried at least for 8 h at 40°C in a vacuum oven before each processing step.

PLA having a density of 1.25 g/cm^3 was melt mixed with Nanocyl[®] 7000 (Nanocyl S.A., Belgium), which are thin multi-walled carbon nanotubes (MWNT) with a purity of 90% produced via the catalytic carbon vapour deposition process. The nanotubes have a typical diameter of 9.5 nm and an average length of $1.5\ \mu\text{m}$. The density of MWNT after incorporation into a polymer is approximately 1.75 g/cm^3 [46].

2.2. Composite preparation

The compounding processes of masterbatch production and dilution were performed using a co-rotating twin-screw extruder ZE25 (Berstorff, Germany) having a screw diameter of 25 mm and a barrel length of 900 mm ($L/D = 36$). For the masterbatch production PLA pellets and the powdery MWNT material were fed simultaneously into the hopper by gravimetric dosing. For the masterbatch dilution, pellets of the masterbatch and the diluting PLA were premixed.

Two different screw configurations with different numbers of conveying, kneading, and mixing elements were applied to vary the flow and shear conditions. Screw profile SP1 (Fig. 1) included a melting zone of five left-handed conveying elements and three left-handed blocks of five kneading discs with positive (45°) and neutral (90°) staggering angles. Different right and left-handed conveying elements and different mixing and kneading blocks followed this zone. In screw profile SP2 (Fig. 2), melting was assured by a kneading element followed by a right-handed (backward conveying) conveying element. In comparison to SP1 now six different mixing elements of two and three discs each having 10 cogs were added. Moreover, the number of right-handed conveying elements was three times higher (6:2).

Besides different screw profiles two different temperature profiles were chosen. The processing limits of PLA were investigated on melt-processed samples using a DACA microcompounder to treat PLA under varied mixing times (5 min and 15 min at 180°C) and

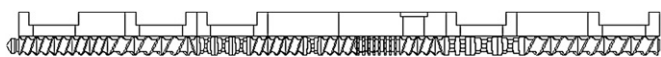


Fig. 1. Screw profile SP1 designed as standard compounding screw with mixing and kneading elements.

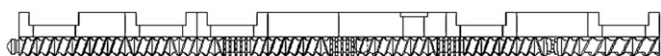


Fig. 2. Screw profile SP2 designed as a screw with mainly mixing elements for a good MWNT distribution within the PLA matrix.

temperatures (180 °C, 215 °C, and 250 °C for 5 min) with a constant rotation speed of 200 rpm. Afterwards, the inherent solution viscosity was measured by means of an Ubbelohde viscometer. PLA did not show significant decrease in inherent viscosity in the investigated range of mixing time at 180 °C. The inherent viscosity after 15 min processing in the DACA was the same as that of the untreated PLA, whereas the mixing temperature apparently had an influence on PLA degradation resulting in a significant drop of inherent viscosity at a processing temperature of 250 °C. Wang et al. [47] investigated the degradation behaviour of PLA processed with a HAAKE PolyLab by means of UV–vis spectroscopy and reported about increasing degradation with increasing processing temperature and rotation speed. Due to these results, the maximum processing temperature was set to 200 °C.

Temperature profile TP1 was designed with a low temperature level to achieve relatively high shear stresses applied from the polymer melt towards the primary MWNT agglomerates resulting from higher melt viscosity. Temperature profile TP2 was conceived having rising temperature devolution to promote a certain formation of secondary MWNT agglomerates at the end of the extrusion process (Table 1). A certain secondary agglomeration of individualised MWNT and MWNT clusters was described in literature as a suitable step to achieve highly conductive composites at low loadings [48].

Four different masterbatches were produced under varied processing conditions to evaluate the influence of extrusion conditions on the MWNT dispersion within the PLA matrix. A variation of MWNT content, temperature profile, screw profile, and rotation speed was executed (Table 2). The throughput was kept constant at 5 kg/h.

In a second step, three of these masterbatches (MB1, MB2, and MB4) were diluted to composites with a MWNT content of 0.75 wt% under variation of the processing conditions. The experiments were performed according to Table 3 with variation of rotation speed, temperature profile, and screw profile. The

Table 1
Temperature profiles TP1 and TP2 designed to perform different mixing tasks

	Heating zone (°C)					
	1	2	3	4	5	6
TP1	200	190	190	190	180	180
TP2	200	190	180	180	200	220
Extrusion direction	→					

Table 2
Processing conditions for the masterbatches

	MWNT content (wt%)	Temperature profile	Screw profile	Rotation speed (rpm)	Throughput (kg/h)
MB1	15.0	TP1	SP1	200	5
MB2	7.5	TP1	SP1	200	5
MB3	7.5	TP2	SP2	100	5
MB4	7.5	TP2	SP2	500	5

Table 3
Experiment matrix for masterbatch dilution experiments

	MWNT content (wt%)	Temperature profile	Screw profile	Rotation speed (rpm)	Throughput (kg/h)
<i>Diluted from MB1</i>					
PLA01	0.75	TP1	SP1	100	10
PLA02	0.75	TP1	SP1	500	10
PLA03	0.75	TP2	SP1	100	10
PLA04	0.75	TP2	SP1	500	10
<i>Diluted from MB2</i>					
PLA05	0.75	TP1	SP1	100	10
PLA06	0.75	TP1	SP1	500	10
PLA07	0.75	TP2	SP1	100	10
PLA08	0.75	TP2	SP1	500	10
<i>Diluted from MB4</i>					
PLA09	0.75	TP1	SP2	100	10
PLA10	0.75	TP1	SP2	500	10
PLA11	0.75	TP2	SP2	100	10
PLA12	0.75	TP2	SP2	500	10

throughput was kept constant at 10 kg/h. In addition to these experiments, a percolation series with MWNT contents between 0.5 wt% and 2.0 wt% was diluted from MB4 using the evaluated best extrusion conditions (SP2, TP2, 500 rpm, 10 kg/h). All masterbatches and composite materials were cooled down in a water bath and pelletised after the extrusion process.

2.3. Composite characterisation

2.3.1. Morphology investigations

The state of macro dispersion of remaining primary MWNT agglomerates within the PLA matrix was investigated by light transmission microscopy on thin sections of extruded pellets, which were prepared following the standard ISO 18553. The thin sections of the composites with 0.75 wt% MWNT had a thickness of 20 µm. In case of the masterbatches having MWNT contents of 7.5 wt% and 15.0 wt% the section thickness was reduced to 5 µm and 2 µm, respectively, in order to achieve visibility of remaining agglomerates. For each experiment 10 sections were prepared from 10 different pellets. The sections were cut with a JUNG RM 2055 microtome (Leica, Germany) at room temperature using a histodiamond knife with a cut angle of 45° (Diatome, Switzerland). The micrographs were imaged with a BH2 microscope (Olympus, Germany) using an objective with a magnification of 4× to obtain pictures of complete full cross-sections leading to an investigated area of about 2.5 mm² per section. In order to quantify the quality of dispersion a dispersion index D was used which reflects the normalised agglomerate area. For this, a particle analysis was performed using the software ANALYSIS (Olympus, Japan), neglecting those agglomerates with diameters smaller than 5 µm. The dispersion index D was calculated using Eq. (1):

$$D = \left(1 - f \frac{A_{\text{CNT}}/A_0}{\Phi_{\text{vol}}}\right) \times 100\% \quad (1)$$

The area occupied by MWNT agglomerates A_{CNT} and the total investigated area A_0 were obtained from the image analysis. The parameter Φ_{vol} is the CNT volume fraction and f is a factor related to the density of CNT agglomerates and was estimated to be 0.25. According to Eq. (1), a D value of 100% corresponds to a perfect macro dispersion of the CNT containing no agglomerates with sizes above 5 µm in the sample. A decreasing dispersion quality is reflected in a decreasing D value. Besides the dispersion index, the agglomerate size distribution, the mean agglomerate size, as well as the number of detected MWNT agglomerates were recorded for each sample. In the following, dependency of only the dispersion index D and the agglomerate number N related to counts per square millimetre on the processing conditions will be discussed.

Due to the high MWNT content in the masterbatches the cut thickness was decreased to 5 μm (7.5 wt% MWNT content) and 2 μm (15.0 wt% MWNT content). To make the calculated D values of the masterbatches comparable the D value of MB1 containing 15.0 wt% MWNT was normalised to a thickness of 5 μm . This normalised D value was calculated by analysing a regression equation between sample thickness and area ratio A_{CNT}/A_0 , for which a sample of PLA02 was cut with different section thicknesses (2 μm , 5 μm , 10 μm , and 20 μm) and analysed. A linear relationship between sample thickness t and the area ratio A_{CNT}/A_0 was found in which the slope was calculated to be $1.27 \mu\text{m}^{-1}$.

The state of micro dispersion and network formation of MWNT within the PLA matrix was investigated with transmission electron microscopy (TEM). Ultra thin sections having a thickness of 150 nm were cut with a Reichert Ultracut S (Leica, Germany) from the extruded pellets. An ultra-sonic diamond knife with a cutting angle of 35° (Diatome, Switzerland) was used to prepare sections with a minimised degree of sample compression. The TEM investigations were performed on an EM 912 (Zeiss, Germany) microscope, which was adjusted with an acceleration voltage of 120 kV.

2.3.2. Thermal behaviour

Dynamic scanning calorimetry (DSC) investigations were performed by means of a DSC Q 1000 (TA Instruments) in a nitrogen atmosphere between -60°C and 220°C at a scan rate of $\pm 10 \text{ K/min}$. Heating–cooling–heating cycles were performed to evaluate the influence of processing conditions and MWNT content on the crystallisation behaviour of the composites. The glass transition temperature T_g and the step height Δc_p were calculated from the 2nd heating run using the half step method. To allow a comparison between samples with different MWNT contents, the heat flow and the enthalpies in all DSC figures were normalised to the PLA fraction for crystallisation ΔH_c during cooling and cold crystallisation ΔH_{cc} during 2nd heating. The crystallinity α was determined from the melting enthalpy in relation to $\Delta H_m = 93.6 \text{ J/g}$ reported for 100% crystalline PLA [49].

2.3.3. Electrical resistivity

The volume resistivity of the masterbatches and composite materials was determined according to the standards ASTM D 4496 and ASTM D 257 on compression molded plates. Plates having diameters of 65 mm and thickness of 0.5 mm were prepared from the pelletised materials received from the extruder. The materials were hot pressed by means of a PW 40 EH press (Paul-Otto Weber GmbH, Germany) under optimised pressing conditions to obtain plates with very smooth surfaces to ensure good contact between the sample and the electrodes of the resistivity measurement equipment. The pellets were first melted within pressing frames

containing PTFE foils as release material at 220°C for 5 min. The pressing step was performed with a pressing speed of 6 mm/min till a force of 20 kN was reached which was then held for 3 min. Before reaching the final force the press was released at 10 kN twice in order to allow potential gasses to deflate. Then pressed samples were cooled down to temperatures of about 175°C before taking the pressing frames out of the press and cooling them for 5 min in a minichiller set to a temperature of -7.5°C .

The resistivity measurements were performed at room temperature on strips ($30 \times 3 \text{ mm}^2$) cut from the plates using a self-made four-point Test Fixture (gold contacts with a distance of 20 mm between the source electrodes and 7.1 mm between the measuring electrodes) in combination with a Keithley multimeter Model 2000. The value for the pure PLA was obtained using a Keithley 8009 Resistivity test fixture combined with a Keithley 6517A electrometer on the pressed plate with 65 mm diameter. Prior to resistivity measurements the sample surfaces were cleaned with ethanol. All measured volume resistances R_v were converted to volume resistivity ρ_v using the equation $\rho_v = R_v \times A/t$, where A is the effective area of the sample involved in the measurement and t is the specimen thickness.

3. Results and discussion

3.1. Influence of extrusion conditions on the dispersion of MWNT in PLA based masterbatches

As MWNT contents in the masterbatches 15.0 wt% and 7.5 wt% were selected. The content of 15.0 wt% follows the amount, which is typically incorporated in industrial available masterbatches, i.e. by Hyperion Catalysis International Inc. (Cambridge, USA). The amount was then reduced to 7.5 wt% since the torque during extrusion was near the limit using the 15.0 wt% and a further increase in temperature was not possible due to expected PLA degradation. After comparing both masterbatches under otherwise comparable conditions, the other experiments were carried out with 7.5 wt% under variation of the rotation speed and the selection of other temperature and screw profiles.

Comparing the four masterbatches, the investigation of MWNT dispersion via light microscopy revealed enormous differences in the remaining agglomerate size and number, as is illustrated in Figs. 3 and 4.

These differences are clearly reflected in the dispersion indices D and in the number of visible MWNT agglomerates as shown in Fig. 5. Depending on the processing conditions, dispersion indices between 13.3% and 94.3% were calculated and the number of agglomerates varied between 4.1 counts/ mm^2 and 264.5 counts/ mm^2 .

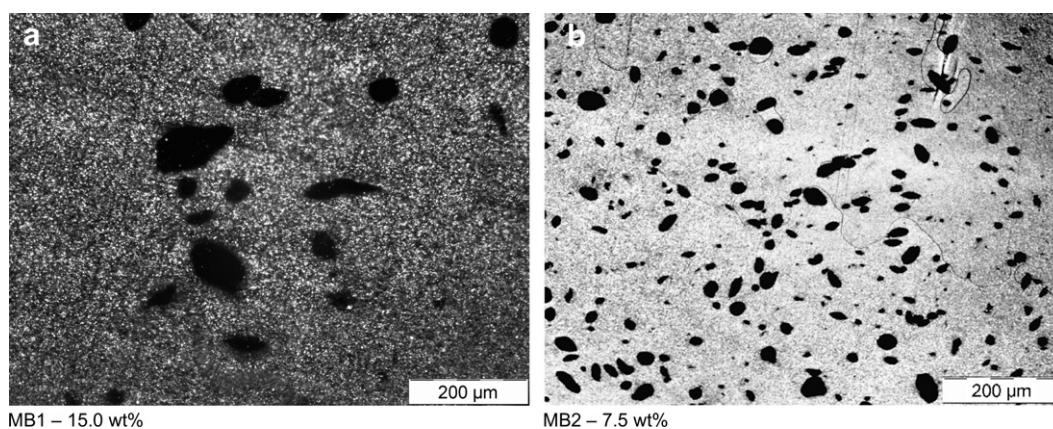


Fig. 3. Light microscopic images of masterbatches illustrating the influence of the MWNT content on the macro dispersion of MWNT in PLA: (a) MB1/15.0 wt%; (b) MB2/7.5 wt%.

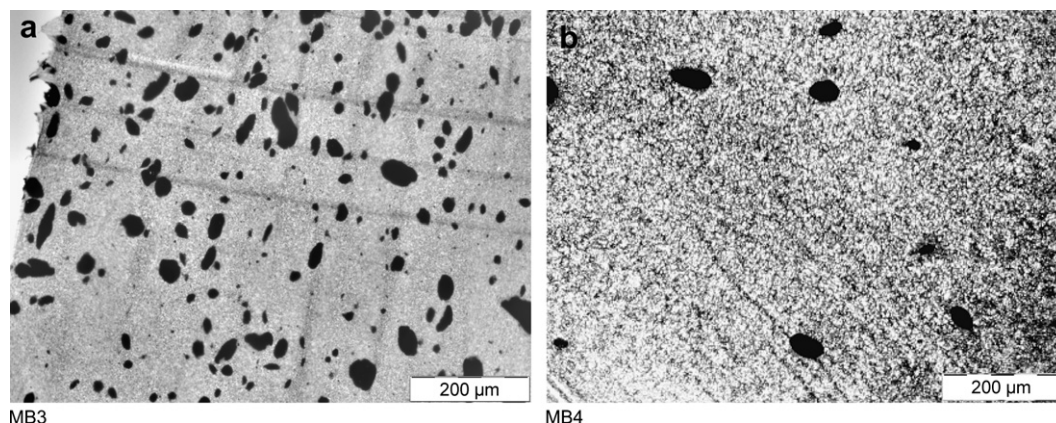


Fig. 4. Light microscopic images of masterbatches illustrating the influence of rotation speed on the macro dispersion of MWNT in PLA: (a) MB3/100 rpm; (b) MB4/500 rpm.

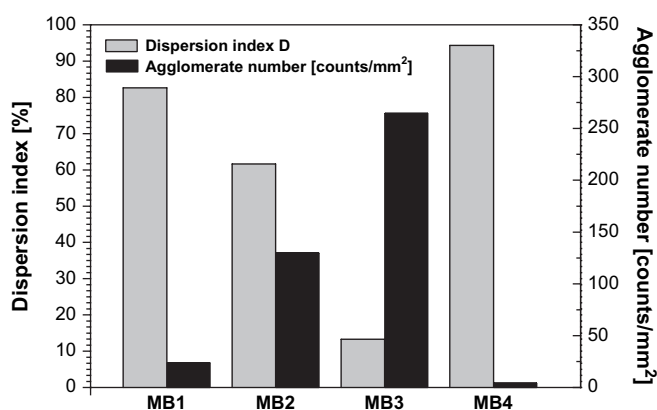


Fig. 5. Dispersion index D and agglomerate number for masterbatches based on PLA with MWNT.

The two masterbatches containing 15.0 wt% MWNT (MB1) and 7.5 wt% (MB2) processed with the same screw profile, temperature profile, and rotation speed (SP1, TP1, and 200 rpm) indicated a significantly higher dispersion index of 82.6% for MB1 as compared to that of 63.4% for MB2. The number of agglomerates counted in the masterbatch having the better dispersion index was 23.7 counts/mm², whereas the masterbatch showing a worse dispersion had 129.6 counts/mm², which is five times higher. However, the mean size of agglomerates is about 2.3 times higher in the masterbatch with the higher MWNT content. This means that in the masterbatch with 15.0 wt% MWNT content more CNT material was dispersed by remaining less but bigger agglomerates as compared to the masterbatch with 7.5 wt%.

As it was shown before on CB [37,38] shear stresses play an important role in dispersing agglomerated nanofillers. Thus, the observed differences in the dispersion level were assigned to differences in the flow properties of the melts. The viscosity increase resulting from already dispersed MWNT within the PLA matrix is much larger in case of MB1 having the higher MWNT amount which leads to higher maximum shear stresses applied to remaining MWNT agglomerates. Measurements of the melt flow rate (MVR, 190 °C, 21.6 kg) revealed a decrease from 100 g/10 min (pure PLA) to 10 g/min for MB2, whereas the MVR of MB1 containing 15.0 wt% MWNT could not be determined due to too high viscosity values. Similar tendencies were found concerning the influence of the rotation speed as investigated on MB3 and MB4, which were processed with the high-level temperature profile (TP2), the distributive screw profile (SP2), but different rotation speeds of 100 rpm and 500 rpm. Disregarding shear thinning of the

melt, the applied shear stress increases with the rotation speed. MB3 extruded at 100 rpm showed the worst dispersion index of all masterbatches with a D value of 13.3%. This low value results from a very high number of MWNT agglomerates, which was 265 counts/mm². Both parameters describing the macro morphology changed dramatically when increasing the rotation speed to 500 rpm. The number of agglomerates decreased and the interrelated dispersion index D increased significantly. This masterbatch showed the best dispersion index of 95.8% and showed also the lowest number of remaining MWNT agglomerates with a value of 4.1 counts/mm². However, it has to be noticed that these remaining primary agglomerates still had diameters up to approximately 100 µm.

Besides the increase in shear stress, another effect explaining the high impact of the rotation speed on nanotube dispersion could be a certain nanotube shortening reducing the number of physical entanglements and thereby increasing the dispersibility of the filler. Unfortunately, we could not succeed to quantify the CNT lengths in the extruded composites. Using the method named by Andrews et al. [35] no individualised nanotubes accessible for length measurements were obtained. A method described by Lin et al. [32] is accompanied by an additional sonication step which possibly leads to nanotube shortening during preparation. SEM investigations on pyrolysed composites as described by Krause et al. [50] led to different visual impressions about the length but no quantification was possible. Further efforts will be done to access this parameter.

Besides the light microscopy investigations to reveal the morphology in the micrometer-scale, investigations of the composites morphology in the nanometer-scale were performed by means of TEM. The images show the arrangement of individualised MWNT and clusters between the primary agglomerates observable via light microscopy. In all cases no large unfilled areas were observed. The TEM investigations revealed a good MWNT distribution with very dense MWNT arrangement in all four masterbatches as is illustrated in Fig. 6 for the masterbatch MB4. The degree of MWNT dispersion as observed by TEM was different for the four masterbatches. The highest degree of MWNT nanometer-scale dispersion was observed for MB4 (Fig. 6), which already showed the smallest number of primary agglomerates in the light microscopy investigations and the highest dispersion index D .

DSC measurements were performed in order to evaluate the influence of processing conditions on the crystallinity of the PLA nanocomposites, which is expected to influence electrical percolation and resistivity. In general, nanofillers and, thus, also carbon nanotubes are reported to act nucleating in nanocomposites [51] and crystalline layers may cover nanotubes [52] reducing or hindering electrical contacts between the tubes. The DSC

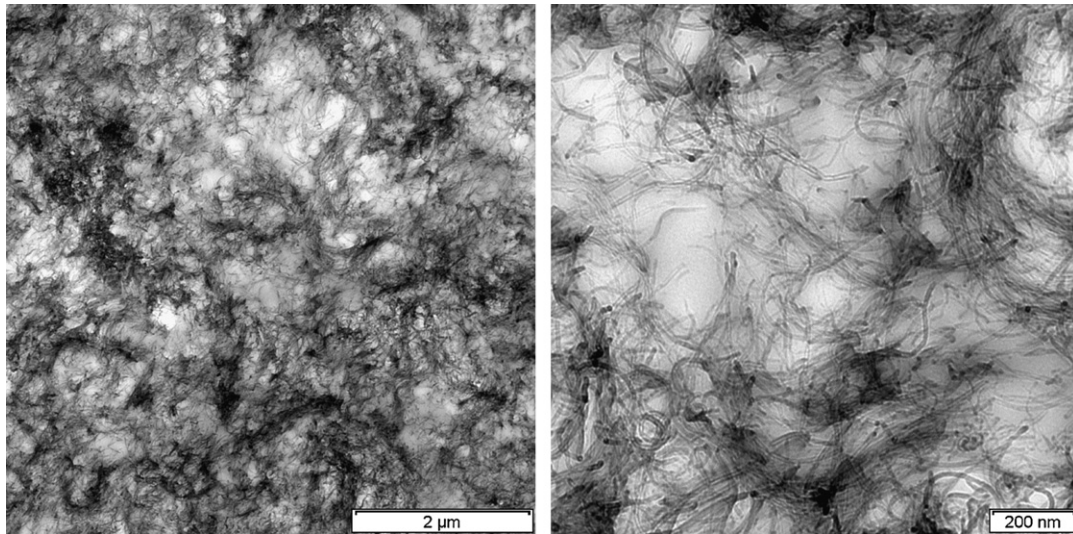


Fig. 6. TEM images of MB4 showing a high degree of distribution and dispersion of MWNT in the PLA matrix.

measurements of the masterbatch pellets reflected indirectly the results concerning the state of MWNT dispersion within PLA that were obtained by light microscopy. After producing a uniform thermal history in the DSC the crystallisation and melting behaviour of MB1, MB2, and MB4 was examined (Table 4, Figs. 7 and 8). It was observed that the higher MWNT content in MB1 led to an enhanced ability of PLA crystallisation due to the nucleating effect of the filler as compared to MB2. In general, the crystallisation

Table 4

DSC data of the masterbatches measured on compression molded sheets and pellets

		T_g (°C)	Δc_p (J/gK)	ΔH_c (J/gPLA)	α_{RT} (%)	ΔH_{cc} (J/gPLA)	α_{max} (%)
MB1	Pellet	59.4	0.42	-2.5	3	-33.7	39
	Plate	58.5	0.41	-4.7	5	-35.1	42
MB2	Pellet	60.0	0.48	-0.5	<1	-35.4	38
	Plate	59.6	0.47	-1.1	1	-35.8	39
MB4	Pellet	59.1	0.38	-9.6	10	-29.7	42
	Plate	57.5	0.29	-17.6	19	-24.6	45

α_{RT} = crystallinity after cooling from the melt at room temperature; α_{max} = the maximum achievable crystallinity of the samples after realisation of the cold crystallisation in the 2nd heating run.

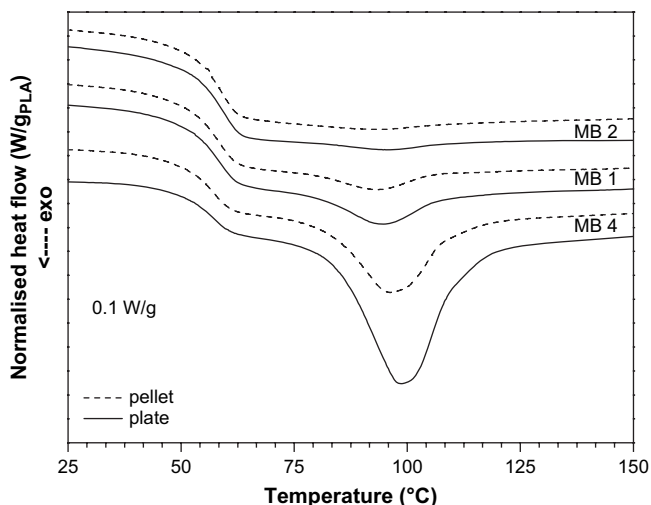


Fig. 7. Cooling run of the masterbatches showing different crystallisation behaviour dependent on MWNT content and processing conditions.

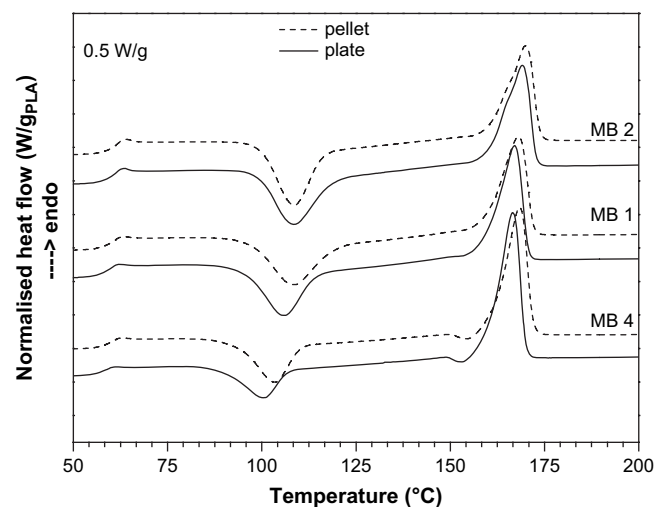


Fig. 8. The 2nd heating run of the masterbatches showing different crystallisation behaviour dependent on MWNT content and processing conditions.

intensity is more pronounced in case of pressed plates compared to the pellets.

A comparison of MB2 and MB4 having the same MWNT content led to the conclusion that a correlation between state of dispersion and crystallisation behaviour exists. The sample processed with a rotation speed of 500 rpm exhibiting the better MWNT dispersion with a reduced number of MWNT agglomerates is associated with a larger available nanotube surface area for nucleation and therefore crystallisation intensity increased. However, the main fraction of PLA is kept amorphous under the cooling conditions and crystallises above glass transition in the 2nd heating run (Fig. 8). It was observed in the 2nd heating run that an increasing dispersion leads to a decrease in cold crystallisation temperature. Furthermore, the maximum achievable crystallinity of PLA after realisation of the cold crystallisation increases with increasing MWNT dispersion.

3.2. Influence of extrusion conditions on the masterbatch dilution process and the resulting MWNT dispersion in PLA based composites

After the production and characterisation of the masterbatches three of them were diluted to composites with a MWNT content of 0.75 wt% by melt mixing with neat PLA. In the first instance this

process has the aim to adjust the desired MWNT content and to distribute the MWNT masterbatch in the polymer matrix. The influence of the dispersion process during the dilution step on the degree of MWNT dispersion within the matrix is expected to be smaller compared to the masterbatch production step, due to the fact that melt viscosities during this second compounding process are significantly lower. However, literature reports indicated that even during the masterbatch dilution step processing conditions play a big role on the nanotube arrangement and, thus, on the percolation state of the nanotubes within the matrix [36,48].

In order to study the influence of processing conditions on the state of MWNT dispersion and electrical resistivity of the composites, the masterbatches MB1, MB2, and MB4 were diluted under variation of temperature profile and rotation speed, both on two levels according to the experiment matrix given in Table 3.

3.2.1. Dilution of masterbatch MB1

The composites PLA01 to PLA04, which were produced by dilution of MB1 containing 15.0 wt% nanotubes were analysed by light microscopy to determine the amount of agglomerated MWNT within the PLA matrix. This masterbatch already had a relatively high dispersion index D . The calculation of the macro dispersion indices D of the diluted composites varying between 63.6% and 77.0% indicated a big influence of processing conditions on composite morphology even during the dilution step. Thereby, the rotation speed appeared to be again a crucial parameter. An increase of rotation speed from 100 rpm to 500 rpm led to an increase of dispersion index for both temperature profiles (Fig. 9). In case of temperature profile TP1 the dispersion index increased from 63.6% to 71.0%, whereas the increase in case of TP2 was a slightly lower from 72.4% to 77.0%. Correspondingly, the agglomerate counts were reduced to a third when increasing the rotation speed from 100 rpm to 500 rpm. The use of temperature profile TP2 with higher mean temperatures resulted in slightly higher values of the dispersion indices as compared to TP1. The slightly higher number of agglomerates originated from smaller agglomerates. This indicates that higher temperatures during dilution promote the rupture of the remaining agglomerates.

Comparing the quantitative values of the dispersion index D between the masterbatch with 15.0 wt% and the diluted composites slightly higher values were calculated for this masterbatch. We do assign this difference not to any agglomeration during the dilution but to the procedure of calculation of the D index. Especially the value set for the factor f related to the density of CNT

agglomerates may be different in the masterbatches where mostly primary nanotube agglomerates are expected, whereas in the dilutions a partial infiltration of polymer inside agglomerates is more probable and can lead to a lower density of CNT agglomerates. In addition, the normalisation of the D value for this masterbatch, necessary due to lower cut thickness used for evaluation in order to visualize agglomerates in this less transparent masterbatch, may be insufficient.

TEM investigations of all four composites indicated a homogeneous MWNT distribution with a large number of individualised MWNT and a certain number of loose associates with typical dimensions up to 250 nm (Fig. 10). The investigations have shown that the influence of processing conditions like rotation speed and temperature profile seem to be small on the sub-micron morphology compared to their big influence on the macro dispersion.

3.2.2. Dilution of masterbatch MB2

The masterbatch MB2 containing 7.5 wt% MWNT, which had a lower dispersion index than MB1, was diluted using the same conditions. This led to a significant broader range of macro dispersion indices D between 51.2% and 72.4% (Fig. 11) as compared to dilutions of MB1 which indicates that in this masterbatch dilution the influence of processing conditions is more pronounced as compared to the higher filled masterbatch. Again a very strong relation between rotation speed and MWNT dispersion was observed. An increase of rotation speed from 100 rpm to 500 rpm led to an increase of dispersion index and a decrease in the number of agglomerates for both temperature profiles whereas the raise in dispersion index was slightly smaller in case of TP2.

Interestingly, in contrast to the dilution of the masterbatch with 15.0 wt% (MB1) during this dilution process lower processing temperatures led to slightly higher dispersion indices of the composites. This result underlines that in masterbatches with bad dispersion and remaining big agglomerates shear induced rupture of agglomerates during dilution may be of higher dominance than the erosion process facilitated by lower melt viscosity.

3.2.3. Dilution of masterbatch MB4

This masterbatch had the best MWNT dispersion of the four investigated masterbatches. Its dilution to composites with 0.75 wt% MWNT content was done using the screw profile SP2 which was already used for the masterbatch production. The dilution resulted in samples with the highest dispersion indices of all diluted samples, which varied between 93.3% and 99.5%. Besides the fact, that all composites had nearly perfect MWNT dispersion, the tendencies concerning the influence of processing conditions were in accordance to the dilution series of masterbatch MB1. Again the macro dispersion was enhanced and the number of agglomerates decreased with increasing rotation speed (Fig. 12). Also, a small impact of the processing temperature was observed where higher temperatures (TP2) resulted in the higher macro dispersion indices and smaller agglomerates.

3.3. Influence of processing conditions on the electrical resistivity

The PLA/MWNT composites diluted from the three masterbatches were hot pressed to plates in order to measure the electrical volume resistivity. All composites with 0.75 wt% MWNT were well above the electrical percolation threshold and showed quite low mean resistivity values between 60 Ω cm and 300 Ω cm (Fig. 13). Thus, these materials can be regarded to be electrically conductive. These results indicate that at this MWNT concentration differences in the dispersion indices and numbers and sizes of agglomerates do not influence significantly the electrical resistivity. Nevertheless, a ranking can be done in which the best dispersion indices of the composites diluted from MB4 resulted also in the lowest electrical resistivities with values of about 60 Ω cm. In case of the composites

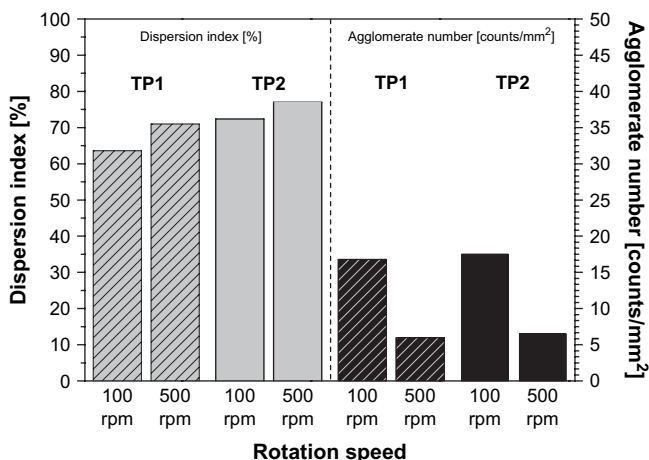


Fig. 9. Influence of rotation speed (100 rpm, 500 rpm) and temperature profile (TP1, TP2) on the dispersion index and agglomerate number of composites with 0.75 wt% MWNT content in PLA diluted by masterbatch MB1 using screw profile SP1.

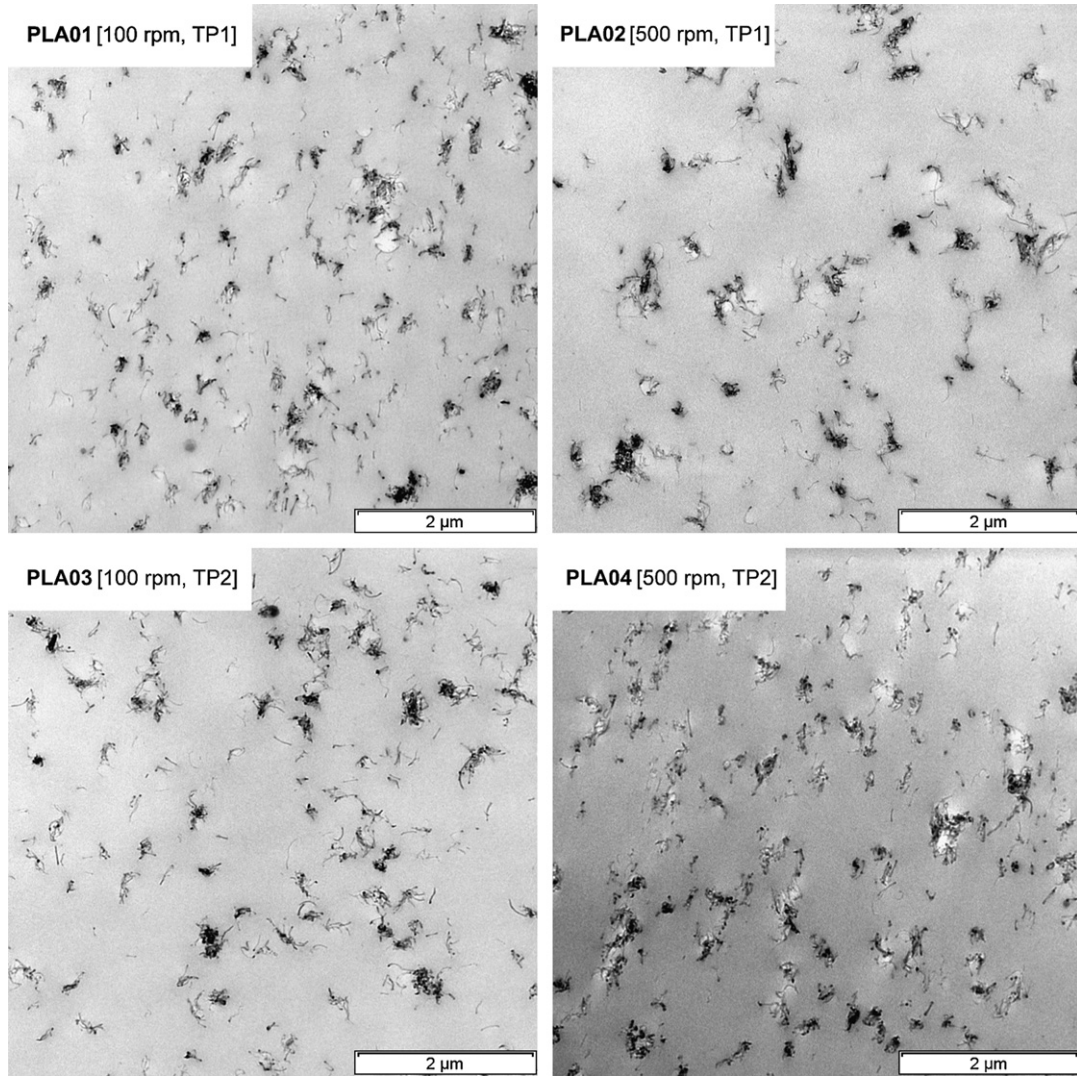


Fig. 10. TEM images of four composites with 0.75 wt% MWNT content in PLA diluted by masterbatch MB1 under variation of rotation speed and temperature profile.

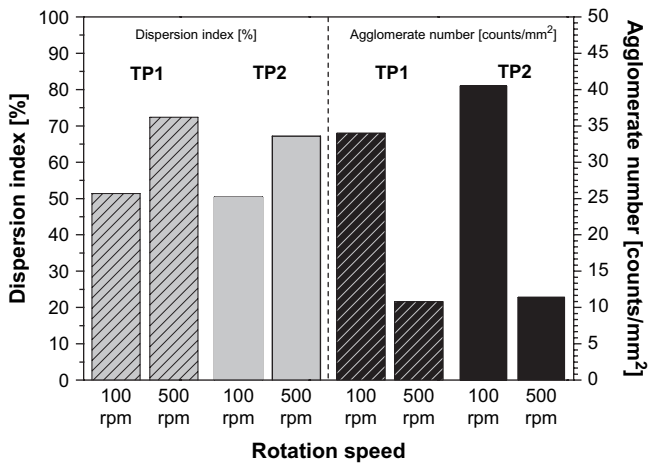


Fig. 11. Influence of rotation speed (100 rpm, 500 rpm) and temperature profile (TP1, TP2) on the dispersion index and agglomerate number of composites with 0.75 wt% MWNT content in PLA diluted by masterbatch MB2 using screw profile SP1.

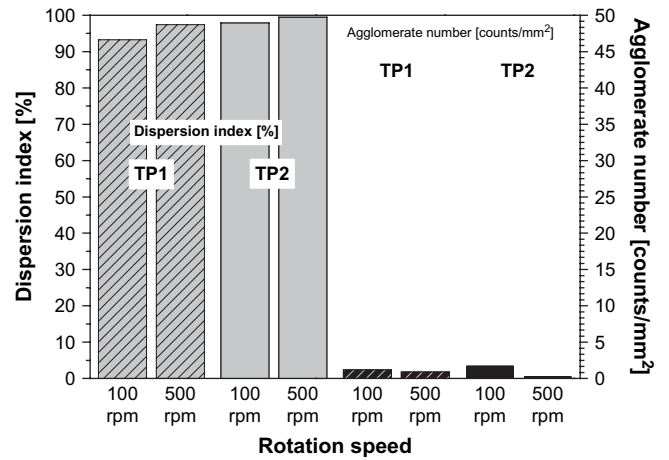


Fig. 12. Influence of rotation speed (100 rpm, 500 rpm) and temperature profile (TP1, TP2) on the dispersion index and agglomerate number of composites with 0.75 wt% MWNT content in PLA diluted by masterbatch MB4 using screw profile SP2.

diluted from the masterbatch having the higher MWNT content (MB1 with 15.0 wt%) slightly higher electrical resistivity values in the range between 140 Ω cm and 280 Ω cm were observed.

However, for mechanical testing the differences in the dispersion indices may be of higher importance since agglomerates are expected to act as imperfections and reduce the mechanical performance.

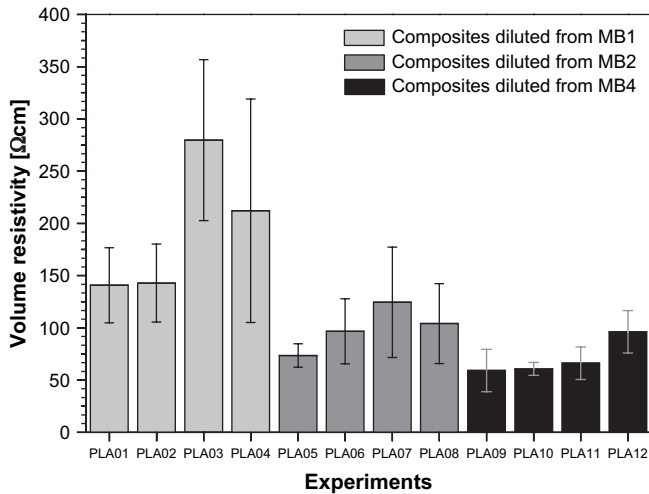


Fig. 13. Electrical resistivity of PLA with a MWNT content of 0.75 wt%, diluted from three masterbatches under different extrusion conditions (see Table 3).

3.4. Variation of the MWNT content under optimised extrusion conditions

The investigations indicated that the use of a distributive screw combined with high rotation speed during the masterbatch production and dilution processes led to composites with a high degree of MWNT dispersion and distribution. Using these optimised conditions (SP2, TP2, 500 rpm, 10 kg/h) a set of composites with different MWNT contents between 0.5 wt% and 2.0 wt% was produced from the masterbatch MB4. Light microscopy investigations revealed nearly agglomerate free composites with dispersion indices between 99.5% and 100.0% indicating no agglomerates with sizes > 5 μm. The electrical volume resistivity of pressed plates from these extrudates as shown in Fig. 14 indicated that already the composite with 0.5 wt% MWNT is percolated. This percolation threshold is much lower compared with that of 3.0 wt% reported by Moon [43]. The resistivity values are lower than 400 Ω cm. DSC investigations revealed a relationship between the MWNT content and the degree of crystallisation. The cooling traces of composites diluted from masterbatch MB4 and neat PLA indicated that the crystallinity of PLA increased with rising MWNT content from <0.5% up to a value of 1.8% for the composite containing 2.0 wt% MWNT (Fig. 15).

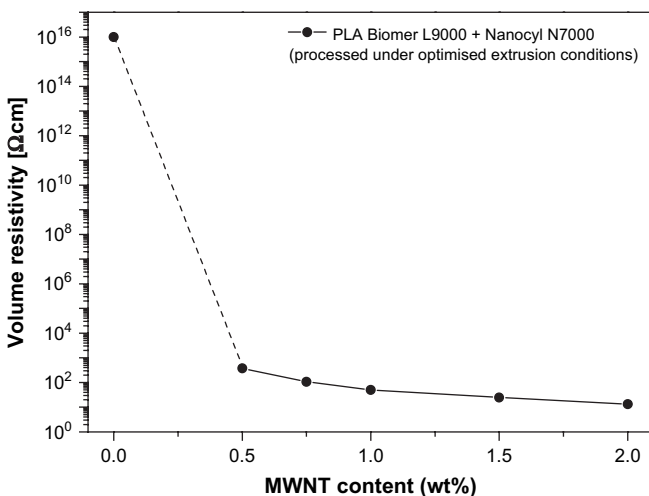


Fig. 14. Electrical resistivity of PLA/MWNT composites with filler contents between 0.5 wt% and 2.0 wt% indicating a percolation threshold below 0.5 wt%.

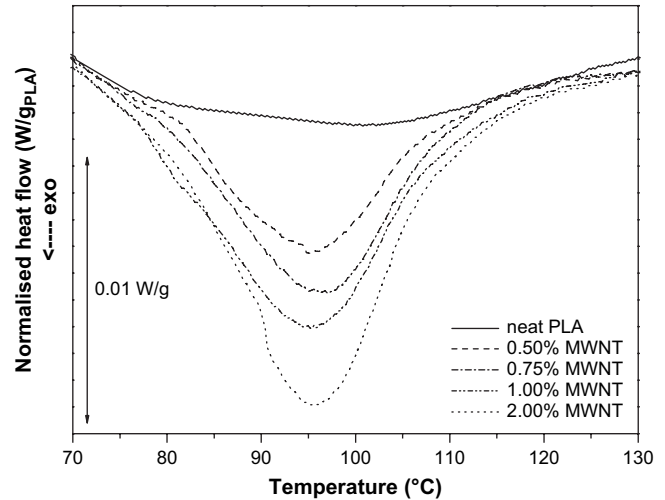


Fig. 15. Cooling run of the composite pellets diluted from masterbatch MB4 and neat PLA, revealing a relation between MWNT content and crystallisation intensity.

4. Summary and conclusions

The work demonstrates how processing conditions during the twin-screw extrusion process as an industrially relevant melt mixing process influence the distribution and dispersion of multi-walled carbon nanotubes in a poly(lactic acid) matrix. A masterbatch dilution technique was applied.

For the four masterbatches produced under variation of MWNT loading, temperature profile, screw profile, and rotation speed dispersion indices ranging between 13.3% and 94.3% and agglomerate numbers between 4.1 counts/mm² and 264.5 counts/mm² were obtained. Thereby, the highest impact was determined for the rotation speed, for which an increase from 100 rpm to 500 rpm led to significantly better MWNT dispersions with a lower number of agglomerates within the PLA matrix. This result is in accordance with former findings on polycarbonate/CNT composites using small-scale mixing [36] and results by Takase [37] who reported about a decreasing agglomerate size with increasing rotation speed using a twin-screw extruder. The applied shear stress increases with rotation speed, which leads to the conclusion, that the level of shear stress acting on the primary agglomerates is an important factor regarding the individualisation of MWNT during melt mixing.

Additionally, a high impact of the MWNT loading in the masterbatch was found. The processing of the highly filled (15.0 wt%) masterbatch led to a morphology with a low number of big agglomerates, whereas the masterbatch with 7.5 wt% MWNT showed a larger number of smaller agglomerates resulting in lower *D* values. In this comparison, the masterbatch with the highest dispersion index of 95.8% was obtained using 7.5 wt% MWNT content, a screw profile with mainly mixing elements (SP2), a temperature profile with rising temperature towards the extruder die (TP2), and a rotation speed of 500 rpm, whereas the throughput was set to 5 kg/h.

In addition to light microscopic investigations, TEM was used to analyse the state of nanotube dispersion and distribution between the primary agglomerates. In all cases, the density of the MWNT was very high. No big unfilled areas within PLA were found indicating that the filler is well distributed within the polymer matrix on the nanoscale.

During the diluting steps to composites containing 0.75 wt% the obtained state of MWNT dispersion was predominated by the state of filler dispersion in the masterbatches. Our experiments have shown that the potential of further MWNT dispersion during the masterbatch dilution process is limited. That means that primary MWNT agglomerates from the masterbatches will remain in the

final composites, if the number and dimension of the primary agglomerates in the masterbatches exceed certain values. Such agglomerates were found in all composites, which were diluted from the masterbatches containing 7.5 wt% and 15.0 wt% processed with 200 rpm using screw profile SP1 containing mixing and shearing elements (diluted from MB1 and MB2). Even though not all MWNT agglomerates of the masterbatch could be dispersed in the dilution step, a clearly high impact of rotation speed was observed also in the dilution step. The dispersion index D increased with increasing rotation speed from 100 rpm to 500 rpm, whereas this effect was higher in the masterbatch with the lower nanotube content having also the lower starting dispersion index D .

When using a masterbatch with a high dispersion index for dilution also the diluted composites are of high quality and showed dispersion indices higher than 96%. On such composites the influence of processing conditions is less pronounced, however, again high rotation speed (500 rpm), rising temperature profile (TP2), and a screw profile with mainly mixing elements (SP2) resulted in the best dispersion values as high as 99.8% (diluted from MB4). Using these optimised processing conditions, a percolation set was produced indicating electrical percolation already at contents as low as 0.5 wt% MWNT Nanocyl 7000.

TEM investigations on selected composites containing 0.75 wt% have shown that despite the big differences in the morphologies as observed in light microscopy a variation of processing conditions like rotation speed and temperature profile does not influence much the morphology in the sub-micron scale. In the areas between the primary agglomerates the nanotubes seem to be distributed and dispersed in a similar manner with individualised tubes and very small associates of up to about 10 tubes nicely distributed in the matrix. This result emphasizes the need to investigate composite morphologies on different length scales. Whereas light microscopy is useful to investigate large sample volumes to calculate the dispersion index, TEM is a supplementary investigation to observe the MWNT dispersion and distribution between primary agglomerates. As the results show, morphology investigations by TEM as the exclusive method can be misleading in the interpretation of the influence of processing conditions on the morphology of polymer/CNT composites.

DSC investigations indicated that the amount of added nanotubes as well as the state of nanotube dispersion is reflected in the degree of crystallinity. The nucleating effect of a given nanotube amount on the PLA matrix is as higher as better the nanotube dispersion.

As it was the aim of this work, we were able to establish a guideline for the processing of MWNT/PLA composites using the masterbatch dilution technique. Recently we found that these processing recommendations can be also adapted to other polymer matrices like polycaprolactone and polyethylenterephthalate.

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