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Dispersion, agglomeration, and network formation of multiwalled carbon nanotubes in polycarbonate melts

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Abstract

Three different industrially available multiwalled carbon nanotube (MWNT) materials were directly incorporated into polycarbonate by melt mixing using a small-scale compounder. Despite of similar aspect ratios the electrical percolation behaviour was different. TEM investigations reveal significant differences in the nanotube dispersion which can be attributed to different dispersability of the raw MWNT materials. It is shown that the investigation of the sedimentation behaviour of aqueous MWNT dispersions is a simple method to estimate the nanotube dispersability.

The relationships between melt processing conditions and MWNT dispersion and distribution were studied on polycarbonate samples containing 0.875 wt% MWNT prepared by masterbatch dilution. During melt mixing only high shear forces can provide suitable MWNT dispersion because firstly the MWNT disentanglement is facilitated and secondly secondary agglomeration is prevented. At low shear agglomeration of formerly well dispersed MWNT could be observed. During hot pressing the network or MWNT arrangement and the resulting electrical conductivity can be manipulated by the processing conditions like melt temperature and pressing speed. A certain nanotube agglomeration can enhance the development of an electrical percolated network as shown by dielectric spectroscopy.

Keywords: Multiwalled carbon nanotubes; Polymer composites; Melt mixing

1. Introduction

Due to the versatile physical properties of carbon nanotubes (CNT) [1–4] and, thus, the promising application as filler for nanocomposites the industry attempts great efforts on the upscale of CNT production and the market has grown rapidly during the last years. Nowadays, multiwalled carbon nanotubes (MWNT) can be obtained for prices that make them reasonable for applications as fillers for thermoplastic materials in commercial products. Especially for electrically dissipative or conductive composite materials there is great potential for a high market share. Conventional melt processed polymer composites with carbon blacks or other conductive fillers have to be highly loaded to obtain sufficient conductivity and in turn loose their mechanical performance (e.g. [5]). Due to the theoretically extreme low percolation threshold (the critical filler volume fraction at which the sample resistivity drops down dramatically) caused by the very high aspect ratio only small amounts of MWNT have to be added to the polymer matrix host in order to get electrical percolation [6] and the mechanical properties are supposed to remain intact. To realise this, the MWNT have to be dispersed and distributed in a way that an extended network over the whole matrix host can be achieved. Ideally, all introduced nanotubes are connected to the network with low contact resistances among them.

For large-scale preparation of thermoplastics filled with MWNT, melt processing is the preferred method because it enables the use of existing techniques. However, for successful

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application of such materials for consumer durables the fabricators need guidelines to set up the processing parameters. Thus, the aim of this article is to gain more insight in the procedures of dispersion and distribution as well as network formation during simple melt processing of MWNT filled polycarbonate (PC) composites. Additionally, the here presented results can support the understanding and interpretation of scientific studies.

The first path on the route to MWNT composites is the dispersion and distribution of the powdery MWNT materials in a polymer matrix. This is naturally hindered due to strong attractive forces between the nanotubes. MWNT materials produced by large-scale chemical vapour deposition (CVD) processes tend to form strong agglomerates due to high van der Waals forces and physical entanglements. Additionally, in polymer melts the individualization of MWNT from primary agglomerates of the base MWNT material can be complicated due to high interfacial tensions and depletion forces. In principle, the emerging high shear forces during the melt compounding processes are suitable to individualise MWNT and have been successfully applied for many systems [7−13].

However, the individualization can become very difficult if the agglomerate strength of the base MWNT powder is too high. Then the desired composite properties, e.g. low electrical percolation threshold or resistivity, cannot be obtained. The knowledge about the correlation between the MWNT dispersability and the physical properties of the composite materials is of significant importance for researchers as well as manufacturers. In the first part of this article the relationship between the dispersability of MWNT base materials and electrical percolation will be discussed. In this context a simple and fast method to characterize the dispersability of MWNT in terms of primary agglomerate strength will be introduced.

The MWNT incorporation by means of masterbatch dilution will be discussed subsequently. The producers of durable goods naturally prefer this processing route because the fluffy MWNT material is bounded in the polymer and, thus, easier to handle. Furthermore, the viscosity and, with that, the applied stress to the primary agglomerates during masterbatch production is quite high due to the high loadings, whereby the dispersion process is enhanced [14]. Although the MWNT agglomerates in masterbatches should be almost disintegrated, the dilution process has to be carried out under appropriate processing conditions to distribute the filler and avoid remaining primary masterbatch agglomerates. In the literature some publications can be found which examine the dilution of MWNT containing masterbatches [7−9,13,15−17]. However, only a few examine the correlation between processing and MWNT dispersion or electrical percolation behaviour. In Ref. [8] the efficiency of different miniature mixers is discussed. It turned out that a DACA microcompounder as used for this study is suitable to dilute PC/MWNT masterbatches. Furthermore, it was assumed that the existence of some small agglomerates can enhance electrical percolation. In Ref. [17] the influence of mixing time and speed on the electrical and dielectric properties of PC/MWNT composites is discussed for concentrations below and above the percolation threshold. For this study, more comprehensive investigations on the influence of processing (extrusion) and post-processing (pressing) conditions were carried out. By means of transmission electron microscopy (TEM) and light microscopy the dispersion and agglomeration after mixing at different temperatures and speeds were investigated and discussed extensively.

After the preparation of MWNT/polymer composites shaping usually is the next step to obtain consumer durables or to analyse sample properties. For scientific studies hot pressing is a commonly used method to prepare plate like geometries. However, it has to be considered that the composites morphology can change during this procedure with dramatic impact on the materials properties. Very recently [18], we reported on the influence of thermal annealing of pressed plates of polypropylene/MWNT composites with 2 wt% MWNT on the electrical conductivity. An increase of the conductivity by about four orders of magnitude was found during annealing at 200 °C, well above the melting temperature. In the last part of the investigations introduced in this article the influence of the pressing speed and temperature on the MWNT network and the resulting conductivity will be discussed by means of TEM and dielectric spectroscopy.

2. Materials and methods

2.1. Materials and their characterization

2.1.1. Filler and matrix materials

Three different MWNT materials have been directly incorporated into PC Iupilon E2000 (Mitsubishi Engineering-Plastics Corporation, Japan) by melt mixing. The nanotubes were produced in a large-scale CVD process and, therefore, they are interesting for industrial applications. Nanocyl 7000 nanotubes obtained from Nanocyl S.A. (Sambreville, Belgium) have diameters in the range of 10 nm and length of around 1.5 μm [19]. The purity was reported with 90%. Furthermore, two different charges of TsNa-Cnt1 (Tsinghua-Nafine Nano-Powder Commercialization Engineering Center, Beijing, China), delivered at different dates, have been processed. In the data sheet the diameters are reported to be smaller than 10 nm and the carbon purity is larger than 80% [20].

Beside the crude nanotube materials a masterbatch with 15 wt% of multiwalled carbon nanotubes obtained from Hyperion Catalysis International, Inc. (Cambridge, MA, USA) was processed to composites. As dilution polymer PC Lexan 121 (GE Plastics, Europe) was used. The nanotubes of the masterbatch were also produced by a CVD process. They have a curved structure with outer diameters of 10−15 nm and length up to 10 μm ([21,9], www.fibrils.com).

2.1.2. Preparation and characterization of aqueous MWNT dispersions

The MWNT were dispersed in the following way: 0.0025 g of MWNT were given into 35 ml of an aqueous solution of sodium dodecylbenzene sulfonate (SDDBS, 0.7 g/l) and dispersed for different times by means of a sonicator (G. Heinemann Branson Sonifier 250, frequency 20 kHz) at room temperature.

Low power (20 W) sonication for 2 h was compared with high power (160 W) for short time (5 min). The stability was characterized by means of a LUMiFuge (L.U.M GmbH, Germany), a microprocessor controlled analytical centrifuge that detects a large variety of demixing phenomena of disperse systems. The centrifugation at 3000 rpm results in an accelerated migration of the dispersed particles. The evaluation of the transmission profiles allows the quantification of the dispersion stability.

2.1.3. Rheological investigations

To obtain information about the flow properties of the polymer materials an ARES rheometer (TA Instruments, New Castle, Delaware, USA) was employed. Frequency sweeps in the range between 0.03 and 100 rad/s were done at temperatures of 250, 265, 280, and 300 °C using a plate–plate tool with a diameter of 25 mm and a gap of around 1.6 mm.

A master curve with a reference temperature (T_0) of 250 °C was constructed. The Arrhenius function (Eq. (1)) was fitted to the shift factors (a_T) since the temperatures were more than 100 K above the T_g. In this equation η_0 is the zero shear viscosity obtained by extrapolation ($f \to 0$), E_0 is the activation energy, R the gas constant, and T the absolute temperature.

$$\ln(a_T) = \ln\left(\frac{\eta_0(T)}{\eta_0(T_0)}\right) = \frac{E_0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \qquad (1)$$

2.2. Composite preparation

2.2.1. Melt mixing

All materials i.e. the nanotubes, masterbatch, and polymers were properly dried in a vacuum oven for at least 4 h at 120 °C before each processing step and the rheological investigation. The mixing was done in a Daca Microcompounder (Daca Instruments, Goleta, CA, USA). The total amount of processed material was 4.2 g. Temperature, rotation speed, and mixing time were set as mentioned in Section 3. After mixing the materials were taken out as extruded strands using the mixing speed without additional cooling.

2.2.2. Hot pressing

The extruded strands were placed in a mould consisting of two sheet metals and a spacer with a thickness of 0.5 mm and a hole of 65 mm in diameter. As release agent a polyimide foil was used. To have controlled processing conditions a PW 40 EH hot press (Paul-Otto Weber GmbH, Germany) was employed. The filled mould was placed into the press at the desired temperature and closed until the cover plate got slight contact with the upper heating. After 2 min the composite material was softened and ready for the pressing cycle with the adjusted speed. The press was closed until a force of 100 kN was reached. By this, a low pressing speed resulted in a longer residence time of the melt in the press. All samples were pressed for 30 s followed by quenching with a mini chiller.

2.3. Composite characterization

2.3.1. Microscopical methods

A light microscope (Olympus BH2) together with CSS 450 shearing system (Linkam Scientific Instruments Ltd, UK) was used to observe agglomeration behaviour in the upper micron scale. The experiments were carried out exemplarily on a composite with 0.875 wt% MWNT prepared by masterbatch dilution. A piece of extruded strand was placed between the glass plates of the preheated stage (300 °C). The gap was set to 50 μm. After the thermal equilibrium was reached a harmonic oscillating shear strain γ of five was applied to the melt for 120 s at different frequencies. In this case the deformation is far above the linear viscoelastic region. The maximum shear deformation rate $\dot{\gamma}$ is simply correlated to the frequency f by: $\dot{\gamma} = 2\pi f \gamma$. The first frequency of the test series was set to 10 Hz. Then the frequency was reduced successively to 0.05 Hz. After each shear experiment with frequencies smaller than 10 Hz the sample was homogenized by shearing at 10 Hz for 120 s.

TEM was carried out to get information about the MWNT dispersion and distribution on the submicron level. For this an analytical TEM (Zeiss EM 912, Zeiss, Germany) was employed. The microscope was adjusted with an acceleration voltage of 120 kV. The best contrast between filler and matrix was obtained by defocusing and use of a zero loss filter. The thin sections with a thickness of approximately 120 nm were prepared using a Reichert Ultracut S ultramicrotome (Leica, Austria). In case of extruded strands they were taken perpendicular to the extrusion direction from the middle part of the sample. In case of pressed plates they were obtained perpendicular to plate surface. A diamond knife having a cutting angle of 35° with a tub (Diatome, Switzerland) was used as cutting tool. The cutting was carried out at room temperature with water to float away the sections.

2.3.2. Characterization of electrical and dielectrical properties

In order to measure the frequency dependent (AC) conductivity (σ') and the real (ε') and imaginary part (ε'') of the complex permittivity dielectric spectroscopy in the range of 10^{-2}–10^{7} Hz was employed to pressed samples at room temperature. These measurements allow to obtain information on the state of conductive filler percolation (see Ref. [17] and references therein). For this, a frequency response analyser SI 1260 (Solartron) in combination with a broad band dielectric converter (Novocontrol, Germany) was used. The measurements were carried out on discs with 22 mm in diameter which were punched out from the hot pressed plates. For good contact gold electrodes with 20 mm in diameter were sputtered on both sides of the discs. The measured data were analysed by means of the software WinDeta (Novocontrol, Germany).

Beside the dielectrical measurements also DC measurements were performed on the hot pressed plates at room temperature. The characterization of high resistivity samples was done on the pressed plates (65 mm diameter) by means of a high resistance meter (Keithley 6517A) in combination with the resistivity test fixture Model 8009 (Keithley). The data points measured in this way are represented in Fig. 1 (see below) as open symbols. Low resistivity samples were investigated using a four-point test fixture for strips (construction by IPF) connected to a Keithley DMM 2000 electrometer. The strips (length 30 mm, width 3 mm) were cut from the hot pressed plates. These data points are represented (Fig. 1) as closed symbols.

3. Results and discussion

3.1. Dispersion and agglomeration during melt mixing

3.1.1. Dispersability and percolation behaviour of MWNT

To obtain low electrical percolation thresholds the MWNT have to be efficiently arranged in an electrically conductive network within the matrix host. To achieve this, the MWNT have to be released from the primary agglomerates of the MWNT base materials. However, if the MWNT are strongly bounded to primary agglomerates, this can be almost impossible or a strong damage of the filler particles has to be accepted. In both cases, i.e. the high spatial concentration in agglomerates or the reduction of aspect ratio, the electrical percolation is negatively effected.

In Fig. 1 the percolation curves of composites with MWNT directly incorporated into polycarbonate are compared. The materials were mixed at 280 °C and 50 rpm for 15 min. The two MWNT types Nanocyl 7000 and TsNa-Cnt1 (1st charge) exhibit a quite similar percolation behaviour as expected because of similar geometry i.e. aspect ratio. The percolation thresholds are 0.5 and 1 wt%, respectively. The slightly higher percolation concentration of the TsNa-Cnt1 (1st charge) might be caused by its lower purity. In contrast to that the electrical percolation threshold of the TsNa-Cnt1 (2nd charge) is observed at much higher filler contents (5 wt%).

TEM investigations of the extruded strands indicate a strong difference in the filler dispersion in the composites with 1 wt% (see Fig. 2). Despite of the comparatively high shear forces during the mixing at 280 °C the TsNa-Cnt1 (2nd charge) could not be dispersed at all. The main fraction is concentrated in agglomerates and, thus, gives no contribution to the percolation network. Only some separated MWNT could be observed. This is assumed to be caused by strong attractive forces originating from entanglements, and high van der Waals forces (strongly dependent on interparticle distance) of compact primary MWNT agglomerates which almost eliminate the possibility of individualization. The percolation at 5 wt% occurs due to the percolation of agglomerates. The sample containing 1 wt% of the first charge of TsNa-Cnt1 exhibits a significant better dispersion. The MWNT form a wide meshed network with a much lower electrical sample resistivity (Fig. 1). In comparison to the composite with 1 wt% Nanocyl 7000 the filler concentration appears to be slightly lower (see Fig. 2) which could be related to the lower carbon purity. The network structure of Nanocyl 7000 is denser, resulting in a lower electrical resistivity of this sample.

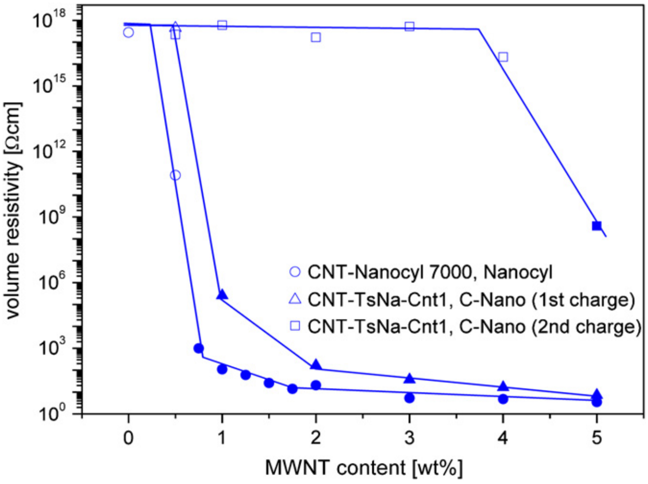

Fig. 1. Volume resistivity versus nanotube content illustrating the different percolation behaviour of various MWNT directly incorporated in PC (the lines are guides for the eyes).

These results point out that different nanotube materials can exhibit different dispersion behaviour in the same matrix material. Even the products from the same supplier can have strong variations in their dispersability. However, for a broad industrial application of MWNT certain quality standards are crucial. The existing information of the suppliers concerning purity, diameters, and in some cases length is not sufficient to rate the materials. For composite or masterbatch preparation the strength of primary agglomerates is an important material property, especially for MWNT with an entangled structure, that has to be considered independently of the used matrix material and processing route. Without doubt the use of MWNT materials with low agglomerate strength is preferred. For ceramic powder some methods were developed to characterize the agglomerate strength e.g. [22]. However, until now no standard method is available to access this material property of carbon nanotubes. Gàbor et al. investigated the dispersability of different single and multiwalled carbon nanotubes in different solvents [23]. The stability of the dispersions was rated qualitatively directly after sonication and after two month storage. The MWNT could be well dispersed in solvents with a relative permittivity between 7.58 and 24.55 as well as aqueous solutions of sodium octylbenzene sulfonate, gum arabic, and ENVIRO-PHARM oil cleaner. An influence of MWNT shape and structure was not found and the agglomerate strength was not discussed at all. In the following a simple approach to gain fast information about this material characteristic will be introduced. For this, the segregation behaviour of aqueous MWNT dispersions in a water/surfactant solution was characterized utilizing an analytical centrifuge (LUMiFuge, L.U.M. GmbH, Germany).

In Fig. 3 the integrated optical transmission of aqueous MWNT dispersions at 3000 rpm over the time is presented. The integrated transmission indicates the particle segregation under the influence of the force field caused by rotation. The higher the stability of the dispersion the lower is the overall light transmission. It can be seen that the Nanocyl 7000 and TsNa-Cnt1 (1st charge) dispersions are very stable. Both materials can be dispersed very well and the surfactant acts at the

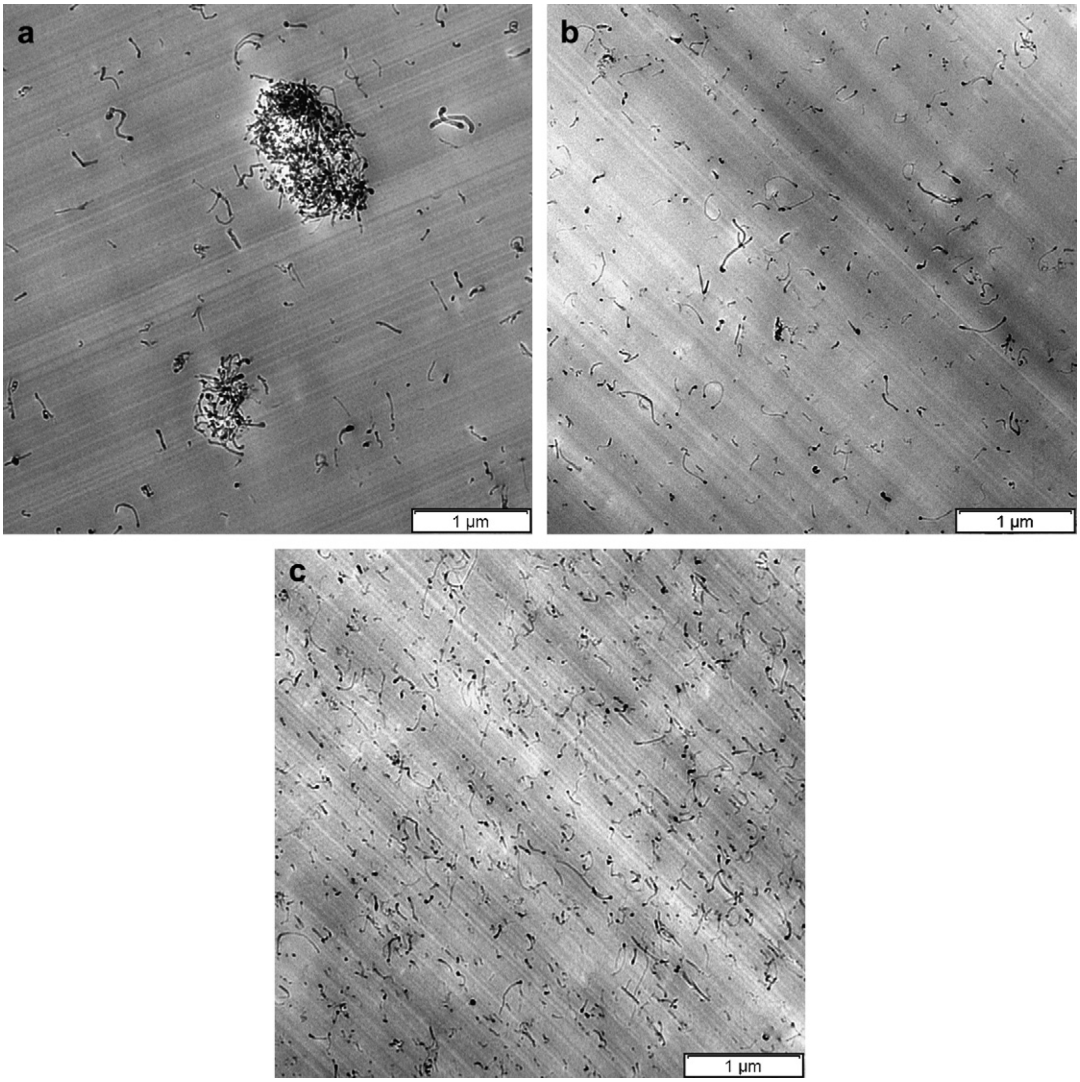

Fig. 2. TEM micrographs of pressed plates illustrating the dispersion of 1 wt% MWNT directly incorporated in polycarbonate: (a) the main fraction of TsNa-Cnt1 (2nd charge) is concentrated in relatively big agglomerates; (b) the 1st charge of this MWNT shows a better dispersability; therefore more individual tubes can be found in the matrix; (c) MWNT Nanocyl 7000 are well dispersed.

surface of the individualized tubes. In the case of the second charge of TsNa-Cnt1 the primary agglomerates can only break down to a certain limit. The MWNT remain in big agglomerates with a very high segregation rate. Instead of SDDBS also some other surfactants were investigated, however, the characteristics remained the same. The stability of Nanocyl 7000 and TsNa-Cnt1 (1st charge) dispersions is much higher compared to the dispersion of TsNa-Cnt1 (2nd charge). Furthermore, the sonication procedure seems to have no significant influence on the sedimentation behaviour. The curves are very close, independently, whether the sonication was carried out for 5 min at high power or 2 h at low power.

The comparison of the dispersion behaviour of the three investigated MWNT in aqueous solutions and in polycarbonate reveals an analogy (see Figs. 1 and 3). Thus, investigations of the segregation behaviour of MWNT in aqueous solutions provide a comparatively easy way to quantify the dispersability of different products and charges. However, to obtain comparable results with other studies, the development of test

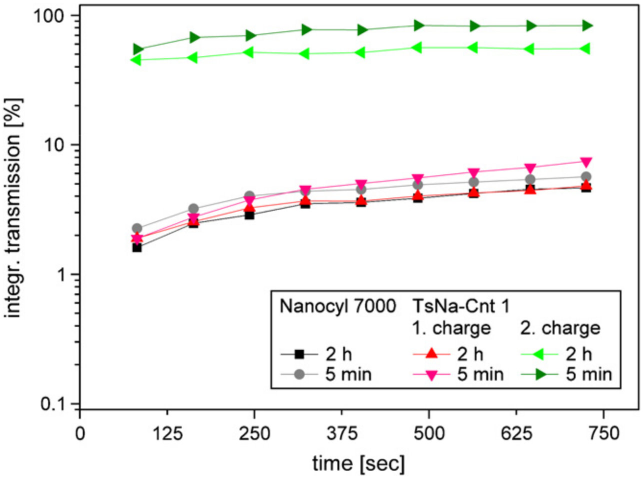

Fig. 3. Integrated optical transmission of aqueous MWNT dispersions in an analytical centrifuge at 3000 rpm vs. time. The stability correlates with percolation behaviour in PC (compare Fig. 1).

standards has to be future work. The basic idea is the characterization of MWNT individualization in a dispersion agent with good stabilization properties. In this manner the influence of interfacial tension between nanotubes and solvent can be more or less excluded and mainly the strength of primary agglomerates, caused by entanglements and van der Waals forces, is responsible for remaining agglomerates.

3.1.2. MWNT dispersion by masterbatch dilution

By using the masterbatch dilution technique the steps of disintegration of primary MWNT agglomerates and wetting the nanotubes by the polymer are already carried out by the masterbatch supplier. In the masterbatch, the MWNT ideally are arranged homogeneously dispersed in a dense network within the polymer matrix. Thus, the incorporation process consisting of mixing the masterbatch with pure polymer should have a more distributive character with corresponding processing condition. However, up to now no systematic studies about the relationships between processing conditions and MWNT dispersion by means of masterbatch dilution are available. The influence of the processing conditions on the electrical properties of the same material system, as reported in Ref. [17], suggests a significant influence on the level of dispersion or distribution. However, one has to take into account the additional processing step of hot pressing which was performed in order to get the samples for the electrical measurements. In the following the effect of selected processing parameters on MWNT dispersion and distribution will be treated independently.

Firstly, the influence of mixing temperature on MWNT dispersion was investigated. In Fig. 4 TEM micrographs of two composites containing 0.875 wt% MWNT are presented. The materials were mixed with 50 rpm for 15 min at 250 or at 300 °C. The cuts were prepared from the core of the extruded strands. The influence of the mixing temperature on the dispersion is obvious. Mixing at 250 °C yields to a much better MWNT dispersion (Fig. 4a) as compared to mixing at 300 °C (Fig. 4b). A reason for this could be the higher viscosity at 250 °C.

To describe the MWNT dispersion process one can use the interpretation of Rwei et al. proposed for carbon black [24] since similar mechanisms can be expected here.

For the dispersion or distribution process the external forces have to be strong enough to rupture the remaining agglomerates or to erode individual MWNT or fragments from the agglomerate surface. The stress τ exposed to agglomerates (which can be treated as particles) under simple shear in Newtonian liquids can be estimated by [25]:

$$\tau = k\eta\dot{\gamma} \tag{2}$$

where $\dot{\gamma}$ is the shear rate and the constant k is related to the particle shape and the flow field. It is worth to mention that k becomes equal to 2.5 for spherical particles [26] and τ is independent of the particle size. Thus, the stress exposed to the agglomerates increases linearly with the viscosity. For our material it is around six to seven times higher at 250 °C as compared to 300 °C (see Table 1). This supports the assumption that the rupture of agglomerates is mainly due to the differences in viscosity.

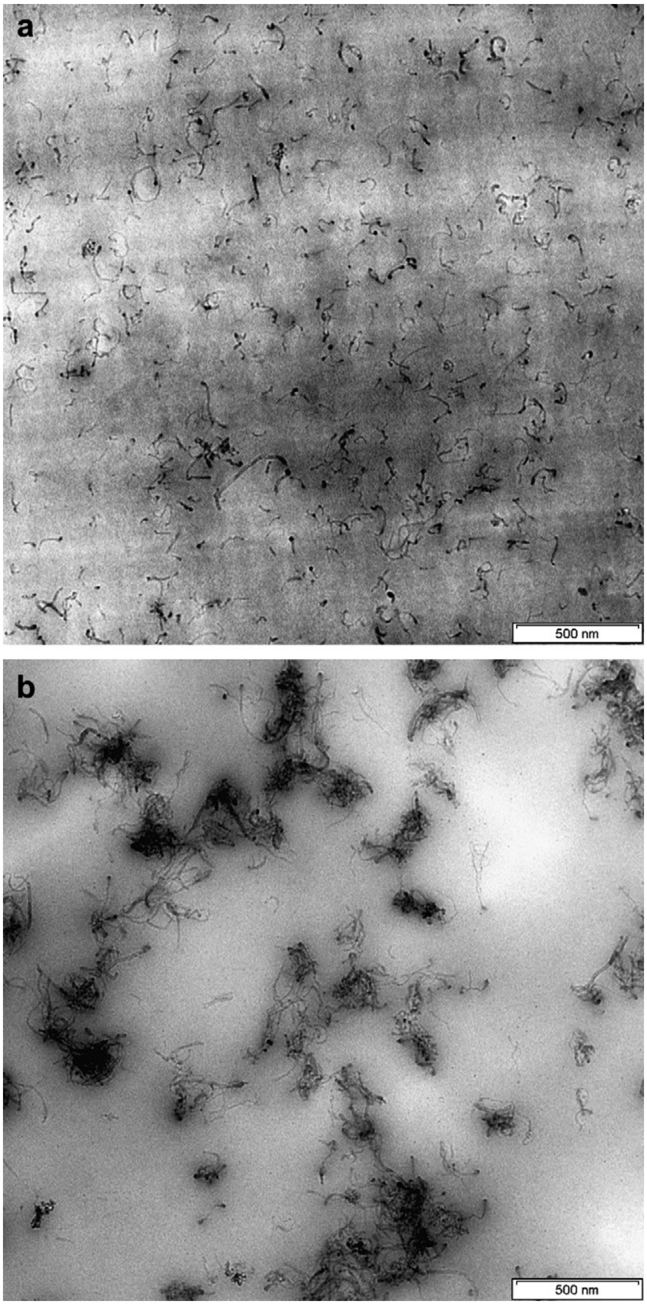

Fig. 4. TEM micrographs of extruded strands (PC + 0.875 wt%, obtained by masterbatch dilution): (a) mixed at 250 °C, 50 rpm, 15 min, (b) mixed at 300 °C, 50 rpm, 15 min. Melt mixing at low temperature leads to an obvious better dispersion.

However, another possibility for the presence of agglomerates at 300 °C is a secondary agglomeration during the melt mixing process (see next chapter).

3.1.3. MWNT agglomeration during melt mixing

To investigate the origin of agglomerates which were observed at high mixing temperatures two other masterbatch dilution experiments were carried out. Both experiments started with the masterbatch dilution at 250 °C and 50 rpm for 15 min

Table 1
Rheological properties of the polymers used in the masterbatch dilution process

Material	E_0 (kJ/mol)	$\eta_{0,250\,^\circ\mathrm{C}}$ (Pa s)	$\eta_{0,300\,^\circ\mathrm{C}}$ (Pa s)
PC Hyperion	101	2067	288
PC Lexan 121	96	1585	260

The activation energies were obtained by fitting the data to the Arrhenius equation (1).

to obtain a good MWNT dispersion as seen before (Fig. 4a). For the first experiment the mixture was subsequently heated up to 300 °C. During the heating period of around 2 min the screw speed was 50 rpm. After the mixture has reached 300 °C mixing was performed further 5 min at 50 rpm. In the second experiment the mixing was performed at 250 rpm for 5 min after reaching 300 °C. In Fig. 5 TEM micrographs of the extruded strands for both mixtures are presented.

In both samples the MWNT appear to be agglomerated. However, the sample mixed with a speed of 50 rpm exhibits much larger agglomerates as compared to that one prepared at 250 rpm. Since the dispersion was very good after mixing at 250 °C, the agglomerates must have been formed during the second mixing step. The observation of secondary agglomeration is of importance and has to be considered for melt processing of carbon nanotube composites. Recently we reported on the kinetics of secondary agglomeration on a PC/MWNT composite by a combined rheological and electrical conductivity study and provided a simple model for agglomeration [27]. In principal, secondary agglomeration occurs in other polymer matrix systems (e.g. for polypropylene [18]) as well, independently whether the MWNT are incorporated directly or by masterbatch dilution.

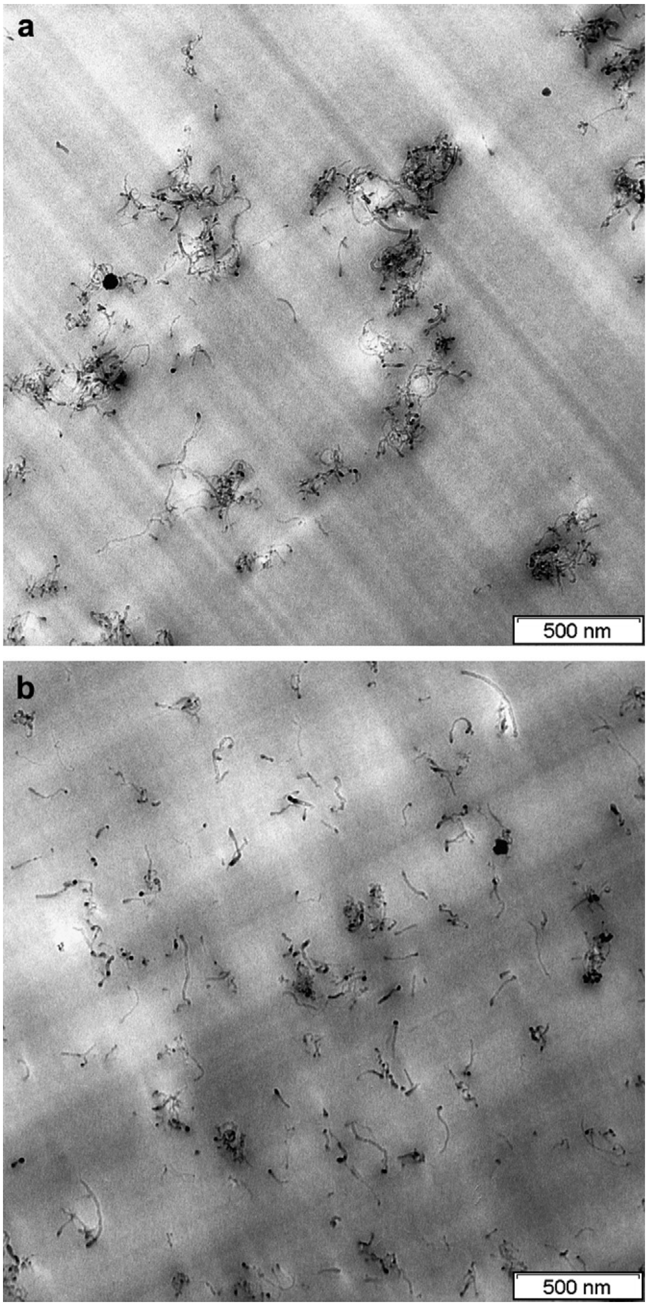

Fig. 5. TEM micrographs of extruded strands (PC + 0.875 wt%, obtained by masterbatch dilution): secondary agglomeration of MWNT in polycarbonate melts with mixing cycle: (a) 250 °C; 50 rpm, 15 min → 300 °C; 50 rpm, 5 min, (b) 250 °C; 50 rpm, 15 min → 300 °C; 250 rpm, 5 min. A higher mixing speed in this subsequent mixing step leads to smaller secondary agglomerates.

An important conclusion that can be derived from the experimental results is that in case of secondary agglomeration prolonged mixing cannot promote the dispersion. In this investigation the final agglomerate size depends rather on the mixing speed which is related to the shear rate. The correlation between the agglomerate size distribution and shear rate can be explained by parallel agglomerate destruction and formation. To rebuild agglomerates, the MWNT have to migrate towards each other or another agglomerate. Without shear the movement of the CNT is caused by Brownian motion and van der Waals interactions (driving force). With the application of shear an additional external force has to be considered. On the one hand side, an increasing shear rate increases the probability of MWNT agglomerates or individualized MWNT getting in contact to each other. If the MWNT coming close to each other van der Waals, depletion forces, or other short range force can enhance the bonding. On the other hand, with increasing shear rates the release rate of MWNT or the break up of agglomerate fragments increases. At sufficient shear stresses, which can be caused by mixing at low temperatures or at high speed the agglomerate size decreases down to individualized MWNT. Consequently, the agglomerate size is given by the balance of agglomerate growth and destruction. In this article the observed effects are discussed only phenomenological, however, in the literature more comprehensive studies can be found for other systems with particles dispersed in a fluid. For instance, Spicer et al. [28] used a population balance model to describe the simultaneous coagulation and fragmentation of polystyrene particles in a water solution. It was reported that the flock size decreased with increasing shear as observed in this study.

The correlation between shear and size of emerging MWNT structures can also be found in the upper micron scale. Fig. 6 presents light microscopical investigations of a thin molten film of the composite with 0.875 wt% MWNT (prepared using

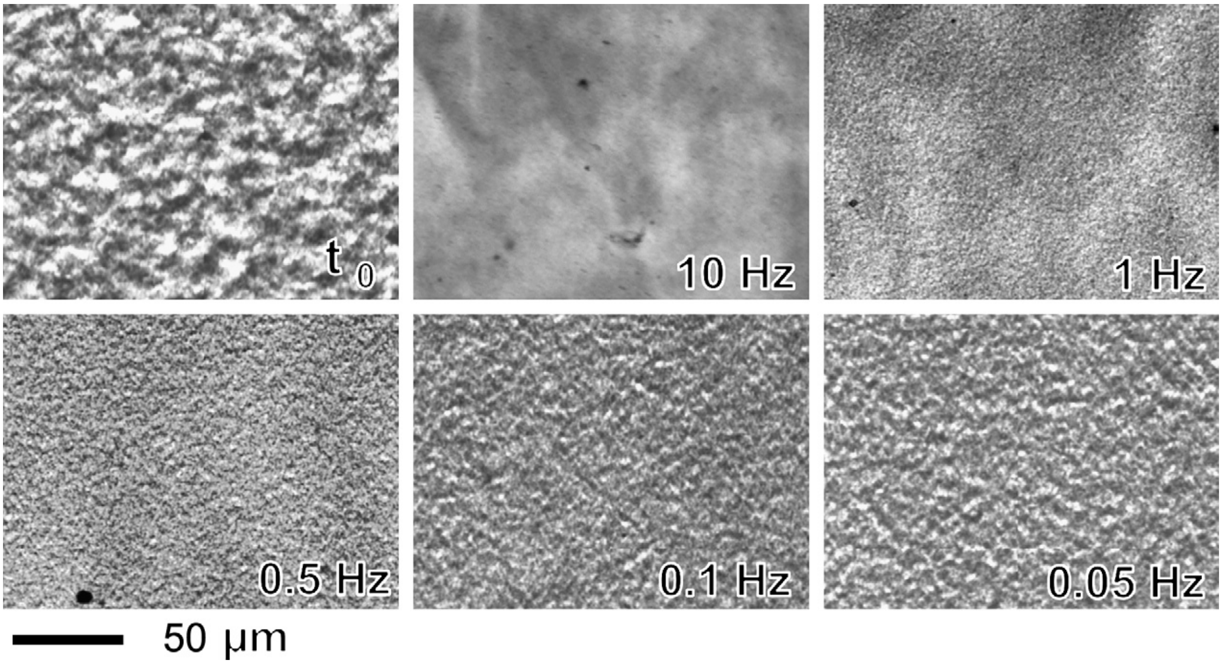

Fig. 6. Light microscopy of thin melt film at 300 °C (PC + 0.875 wt% MWNT obtained by masterbatch dilution). De- and reagglomeration in the micrometer scale initiated by an oscillating shear field at different frequencies (for explanation see text).

50 rpm for 15 min at 250 °C) after different shear treatment. The image at t_0 represents the situation after the sample was placed in the shear system at 300 °C. The morphology seen here is probably caused by secondary aggregation during pressing. After intense oscillating shear with an amplitude of 5 and a frequency of 10 Hz a homogenisation can be observed. The coarse MWNT arrangement disappeared. A subsequent shearing at low frequencies causes the formation of MWNT rich and poor areas. In analogy to the TEM investigations the structure size of the MWNT arrangements is related to the applied shear conditions. Consequently, the agglomerate or network structure can be manipulated by different shear conditions at each length scale with a possible impact on electrical percolation behaviour.

The observations of the present study show an analogy to studies on epoxy systems with carbon blacks and MWNT [29–32]. There, the agglomeration was induced by mechanical stirring and by increasing the ionic strength of the very low viscous epoxy resin. In dependence of the preparation method different network morphologies could be observed by light microscopical investigations. The agglomeration enhanced the electrical properties of the cured material. However, for thermoplastic matrix systems having much higher viscosity the influence of different preparation techniques and the dynamics of MWNT network formation have to be studied more in detail in further investigations.

3.2. Agglomeration and network formation during pressing

For the production of consumer goods many shaping techniques are applied. Injection moulding and extrusion are certainly most commonly used, however, to investigate basic relationships, hot pressing is a simple method and mostly applied in laboratory scale. Thus, most reports on electrical behaviour of polymer–CNT composites are made on hot pressed samples. A first study [18] of the influence of thermal annealing of pressed plates of nanotube filled polypropylene on the electrical conductivity has been published recently. However, the influences of the pressing conditions were not studied in a systematic manner so far.

Here, the influence of pressing speed and temperature on MWNT dispersion and dielectric spectra was investigated. For this study, the composite with 0.875 wt% MWNT prepared by masterbatch dilution already discussed before was used. In difference to the previous experiments, mixing was carried out at 265 °C and 50 rpm for 15 min. TEM investigations (not shown here) reveal an excellent MWNT dispersion within the extruded strands, similar to that one shown in Fig. 4a. Pressing was done at two different temperatures (250 and 300 °C) in each case with two different pressing speeds (0.5 and 6 mm/min).

The results of frequency dependent measurements of real (ε') and imaginary part (ε'') of the complex permittivity and the related AC conductivity (σ') for different pressing conditions are presented in Fig. 7a. The AC conductivity for the sample pressed at 250 °C with 6 mm/min (Fig. 7a, lower graph) shows a frequency dependence typical for the polymer matrix. This is consistently expressed by the low values of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$. The slight frequency dependence of ε' and ε'' is most probably related to relaxation processes in the polymer matrix. In terms of electrical percolation, the system is far below the percolation threshold. This result is surprising since the nanotubes are well dispersed (see TEM micrograph in Fig. 3c) and the aspect ratio of MWNT is rather high. Presumably, the nanotubes in the contact regions are separated by polymer chains [17]. We assume that due to the relatively high viscosity at 250 °C and the short pressing time (6 mm/min) the initially well dispersed state after melt mixing is

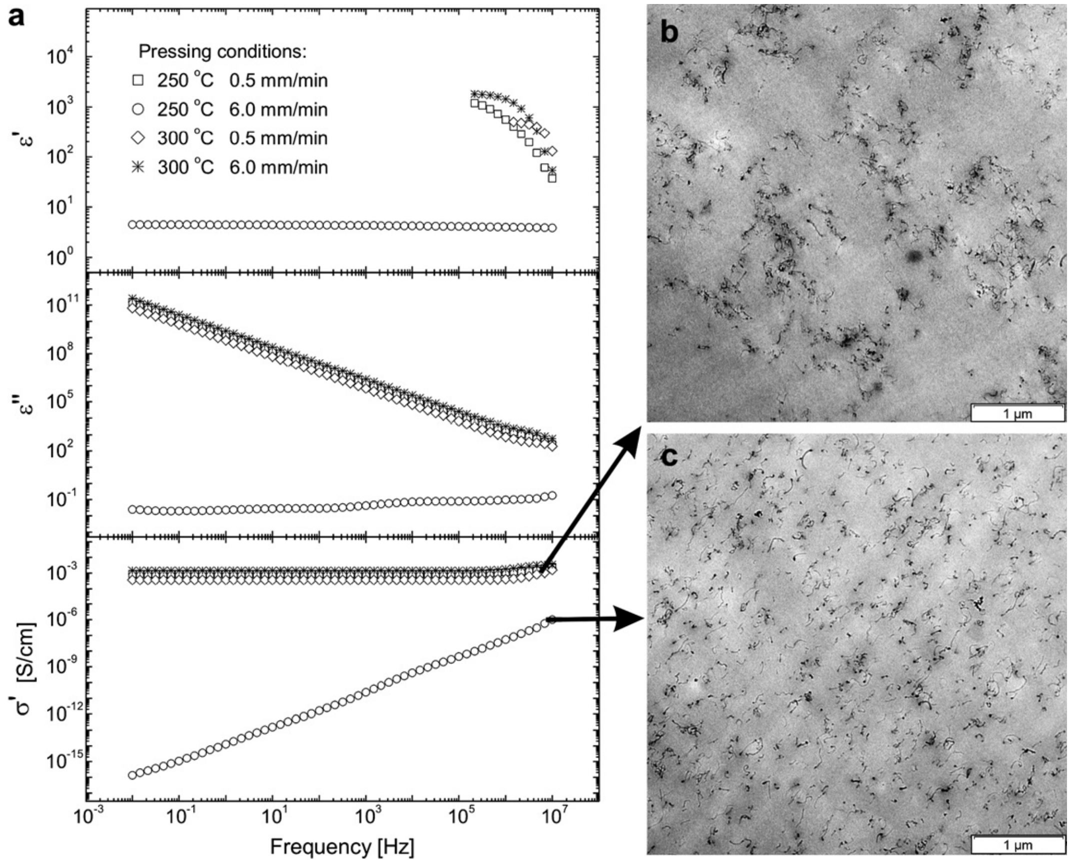

Fig. 7. (a) Frequency dependence of the real (ε') and imaginary part (ε'') of the complex permittivity and the related AC conductivity (σ') for plates pressed at different temperatures and speeds (PC + 0.875 wt%, obtained by masterbatch dilution); (b,c) TEM micrographs of the samples pressed at 300 °C, 6.0 mm/min, illustrating loosely packed agglomerates (b) and 250 °C, 6.0 mm/min, illustrating invidualized nanotubes (c).

preserved. This state was frozen in quite fast, since the temperature difference between 250 °C and the glass transition of PC is relatively small. Orientation of nanotubes parallel to the surface by the squeeze flow cannot be excluded, which also would lead to a lower conductivity.

The σ' curves (Fig. 7a) for the samples pressed at 300 °C with 6 mm/min, 300 °C with 0.5 mm/min, and 250 °C with 0.5 mm/min are several orders of magnitude above that of the sample pressed at 250 °C with 6.0 mm/min and show already at high frequencies σ_{DC} plateaus. The ε' and ε'' curves for these samples are similar to each other as well. Both the frequency dependent conductivity and permittivity are typical for a MWNT network well above the percolation threshold (see Ref. [17] and references therein). The dielectric permittivity curves (ε' and ε'') can be explained by remaining microcapacities in the MWNT network, which are probably caused by polymer layers between neighbouring MWNT as discussed in Ref. [17]. However, the data for ε' (Fig. 7a, upper graph) are on the experimental limit, therefore no values are given for frequencies below 10^5 Hz.

The TEM micrograph as shown in Fig. 7b reveals the formation of agglomerates for the sample pressed at 300 °C with 6 mm/min. Such secondary agglomerates can be formed at low viscosities (higher melt temperatures) and/or longer annealing times (low pressing speed). The agglomerates are assumed to consist of smaller conductive clusters of MWNT which undergo a cluster–cluster agglomeration process (for details see Ref. [27]). Based on this picture one can understand the AC conductivity data as follows: at high temperatures and low viscosities (here 300 °C) the pressing time is sufficient that a conductive pathway is established by cluster formation and aggregation in the viscous matrix. Alternatively, for long pressing times (lower pressing speed) the cluster formation and aggregation process can appear even at higher polymer viscosities (sample pressed at 250 °C and 0.5 mm/min). It has to be noticed that the pressing speed is only an indirect measure of the annealing time. The mobility of nanotubes in the melt (which depends on temperature) and the time before the melt vitrifies at the glass transition are the relevant quantities for these secondary agglomeration processes.

The finding that loosely packed secondary agglomerates originating from well dispersed samples may enhance electrical conductivity of the composite is also in accordance to results obtained by Lin et al. [8], where samples with small aggregates led to lower percolation thresholds. Schueler et al. [30] found the influence of the agglomerate density of carbon black on the percolation threshold in epoxy systems. The carbon black agglomerates were taken as fractal objects and their density decreased with the fractal dimension. Zhang et al. [33] investigated the temperature and time dependency of electrical conductivity for composites of vapour grown carbon fibres and carbon black in multiphase polymer blends. The authors found that with increasing time at high temperatures the electrical resistivity decreased due to agglomeration of the filler particles incorporated in one phase. Model experiments [27] on the cluster aggregation process were recently performed by us in combined rheological and conductivity measurements on the same material as used in this study, where the conductivity recovery with time after short shear deformation was recorded.

The understanding of network formation as a dynamical process also provides a basis for the interpretation of the electrical properties of plastic parts prepared by other processing methods. For instance, in a recent publication [34] our group was able to demonstrate that the network structure and, thus, the electrical properties of injection moulded samples can be enhanced by choosing high processing temperatures as well as low injection velocities. However, in this case additional effects like MWNT orientation have to be considered since the shear rates are several orders of magnitude higher than in the experiments described here.

4. Summary and conclusions

The dispersion and distribution of MWNT in a polymer melt – among other factors – strongly depend on the dispersability of the as-received MWNT material itself. The individualization of MWNT by melt mixing can be hindered by the strength of primary nanotubes agglomerates. The strength can be caused by physical entanglements and van der Waals forces between nanotubes and depends on size, purity, perfectness of the walls, waviness and surface properties. If the MWNT within a composite are concentrated in dense primary agglomerates the electrical percolation threshold is increased. In order to rate MWNT base materials concerning their dispersability a simple method based on the investigation of the sedimentation behaviour of MWNT in aqueous solutions with surfactants was developed. The sedimentation behaviour of the nanotubes in aqueous solutions could be correlated to the network structure in the melt and finally to the electrical conductivity of the composite.

Furthermore, MWNT were incorporated into polycarbonate using masterbatch dilution. In dependence on the processing conditions individualized or agglomerated MWNT could be observed by TEM on extruded strands. Depending on the mixing conditions, evidence of secondary agglomeration during mixing was shown. Additionally, it was illustrated that the structure of secondary MWNT agglomerates can be manipulated at a lower as well as at an upper micron length scale by application of different shear conditions.

It was found that the formation of secondary agglomerates of initially well dispersed MWNT during processing can enhance the electrical conductivity. This was shown by application of different pressing conditions. TEM investigations on pressed plates reveal that pressing with high speed at low temperatures results in samples with individualized MWNT which have a conductivity close to that of the matrix polymer. On the other hand, low pressing speed as well as high temperatures enhance secondary agglomeration and, thus, the formation of a conductive network structure.

The observations reported in this study demonstrate that MWNT show similar aggregates in polycarbonate melts as found before in epoxy resins [30,32]. This is also valid for other polymer melts, like polypropylene [18,35] and can be explained by a combination of cluster aggregation and percolation theory [27].

In order to get plastic parts with a high conductivity at low filler contents in a first step primary agglomerates of nanotubes have to be transferred into individualized nanotubes. In a second step it seems to be favourable to form loosely packed conductive secondary agglomerates. During shaping, vitrification, and/or crystallisation of the plastic parts these conductive network structures have to be preserved.

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