Correlation of carbon nanotube dispersability in aqueous surfactant solutions and polymers

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ABSTRACT

In order to assess the dispersability of carbon nanotube materials, tubes produced under different synthesis conditions were dispersed in aqueous surfactant solutions and the sedimentation behaviour under centrifugation forces was investigated using a LUMiFuge stability analyser. The electrical percolation threshold of the nanotubes after melt mixing in polyamide 6.6 was determined and the state of dispersion was studied. As a general tendency, the nanotubes having better aqueous dispersion stability showed lower electrical percolation threshold and better nanotube dispersion in the composites. This indicates that the investigation of the stability of aqueous dispersions is also able to give information about the nanotubes inherent dispersability in polymer melts, both strongly influenced by the entanglement and agglomerate structure of the tubes within the as-produced nanotube materials.

The shape of the nanotubes in the aqueous dispersions was assessed using a SYSMEX flow particle image analyzer and found to correspond to the shape observed from cryofractured surfaces of the polymer composites.

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1. INTRODUCTION

For industrial applications of polymer based composites containing carbon nanotubes (CNTs), like e. g. for static dissipative or conductive parts in automotive or electronic industries, melt mixing is the preferred method for the composite production. In this context, an excellent distribution and dispersion of the nanofillers is an essential precondition for the effective use of the potential of the nanofillers. Remaining primary agglomerates of nanoparticles not only increase the amount of filler needed for percolation (in case of conductive fillers the electrical percolation) but also act as imperfections under mechanical stress.

The processing conditions during melt mixing along with the properties of CNTs themselves influence the resulting properties of the composites, especially the electrical percolation threshold. At this concentration the electrical properties in such composites change from insulator to conductor behaviour. Parameters influencing the electrical percolation threshold, like nanotube length, diameter, waviness, and dispersability of CNTs are dependent on the CNT synthesis conditions, e.g. catalyst, temperature of synthesis, and solvents used. Among these influencing factors the dispersability of nanotubes is a quality which is not commonly considered and difficult to assess. The dispersability of a nanotube material is mainly influenced by the entanglement structure of the tubes within the as-produced primary CNT agglomerates determining also the agglomerate strength. In general, due to strong van der Waals forces CNTs tend to agglomerate or bundle during synthesis but also during incorporation in matrices. In addition, purity and functional groups on the surface of the nanotubes contribute to the dispersability of CNTs in different media due to different impregnation or wetting characteristics. An indication for the importance of the entanglement structure of nanotube materials is given in [1] for epoxy composites. At equivalent surface chemistry a nanotube material having a denser and more entangled network structure resulted in a worse nanotube dispersion and lower enhancement in mechanical properties as compared to a less entangled material.

The investigation of the electrical percolation behaviour of CNTs in polymers is a time-consuming procedure. After melt mixing using different nanotube amounts the composites have to transferred into suitable geometries (like compression or injection moulding to plates) in order to perform electrical measurements. Therefore, it is desirable to estimate the dispersability of carbon nanotube materials in advance using a simpler and faster method. Dispersing nanotubes in a liquid at room temperature and studying the dispersion behaviour and the dispersions stability seems to be suitable for this purpose. Different authors investigated the dispersability of nanotubes in water. It is known that an effective dispersion of carbon nanotubes is possible only with the aid of surfactants. Different surfactants were used to decrease CNT aggregative tendency in water, e.g. anionic surfactant as sodium dodecylbenzene sulfonate (SDDBS) [1-10] or sodium dodecyl sulphate (SDS) [3-6, 11-15], non-ionic surfactant e.g. poly(oxyethylene-8-lauryl ether) [5, 6, 16-18], or cationic surfactant dodecyl trimethyl ammonium bromide (DTAB) [5, 6]. During the dispersion process the surfactants adsorb on the nanotubes surface. An additional ultrasonication treatment of aqueous dispersions may help to debundle nanotubes by providing high local shear, particularly to the nanotubes end. Gaps at the bundle ends or at primary agglomerate's surfaces are formed and are propagated by surfactant adsorption. In the last step, the bundles or agglomerates are separated into individual nanotubes and are kept in homogeneous and stable suspension [1, 19]. The final configuration of SDDBS covered nanotubes was described as a cylindrical micelle with a nanotubes in the centre [1, 20]. It may be assumed that the wetting mechanism of formation of a surfactant micelle around the CNTs in aqueous solution is similar to the wetting behaviour of CNTs by polymer melt chains during the melt mixing procedure.

The stability and quality of an aqueous dispersion can be investigated by UV-VIS-spectroscopy [14] as well as studying the sedimentation behaviour under centrifugation forces [21].

In order to assess the dispersability of CNT materials, in this study carbon nanotubes produced at different synthesis conditions were dispersed in aqueous surfactant solution and the sedimentation behaviour under centrifugation forces was investigated. Additionally, polyamide 6.6 having a surface energy in the same range like the surfactant solution was filled with the carbon nanotubes by melt mixing. The electrical percolation behaviour of these composites was investigated by electrical measurements on pressed plates in order to confirm the applicability of the solvent method for estimating the dispersability. Additionally, optical investigations of the surfactant solutions filled with nanotubes as well as microscopic investigations of cryofractured composites by scanning electron microscopy (SEM) were carried out to observe the shapes of CNTs and CNT agglomerates.

2. EXPERIMENTAL PART

2.1 Materials

The nanotubes in this investigation were either commercial available nanotubes or laboratory products. NC7000 (Nanocyl S.A., Sambreville, Belgium) are multiwalled carbon nanotubes (MWNTs) that were produced in an industrial large-scale chemical vapour deposition (CVD) process. They are characterized by an average diameter of 10 nm, a length of 0.1 up to 10 µm, a carbon purity of 90 %, and a surface area of 250-300 m^2/g [22]. In addition, two different lots of TsNa-MWCnt1 (Tsinghua-Nafine Nano-Powder Commercialization Engineering Center, Beijing, China), delivered at different dates (TsNa1, TsNa2), were used. The diameters are reported to be smaller than 10 nm and the carbon purity is higher than 80% [23]. Another set of CNTs was synthesized at the Leibniz Institute for Solid State and Materials Research Dresden, Germany (IFW). The synthesis of the CNT1 was done using the catalytic CVD method with the so-called fixed bed technology [24, 25]. CNT1 is an equal mixture of single-/doublewalled carbon nanotubes with diameters between 1 and 5 nm and

multiwalled carbon nanotubes with diameters between 4 and 15 nm, and a surface area of around 600 m^2/g [26]. The multiwalled carbon nanotubes CNT2, CNT3, and CNT4 were synthesized using the catalytic CVD method with the so-called aerosol technology [27, 28]. The solvent during the syntheses was cyclohexane for CNT2 and CNT3 and acetonitrile for CNT4. Acetonitrile as solvent leads to CNTs with well-developed bamboo-like structures, caused by the nitrogen incorporation into the shell structure [29-31]. CNT4 contains 86 wt% carbon and 11 wt% nitrogen. The diameters are between 10 and 40 nm, and a surface area of around 125 m^2/g. The synthesis of CNT2 and CNT3 differs only in the temperature of synthesis; the carbon purity was determined to be 96 wt%, the diameters are between 10 and 80 nm, and the surface area is around 160 m^2/g [32].

Since all CNT materials were investigated as synthesized and do not contain functionalization we assume that the surface structure only vary in small ranges and the differences are mainly in nanotube dimensions, nanotube structure (number and perfectness of layers), nanotube shape (e.g. waviness), and entanglement structure between the nanotubes in the powdery material. All CNT materials were characterized by RAMAN spectroscopy using a Bruker FT-Raman spectrometer (excitation at 1064 nm). In order to assess the concentration of defects in the multiwalled nanotubes the intensity ratio D/G between the disorder band at 1284 cm^{-1} (D-band) and the band at 1609 cm^{-1} (G-band) assigned to the in-plane vibrations of the graphitic walls was used, which was found to be between 2.3 and 2.8 for all CNTs. For CNT3 and CNT4 the smallest D-band compared to the other CNTs were found indicating a lower content of amorphous carbon in these samples. Thus, we may assume that dispersability is not mainly influenced by different tube breakage caused by different defect concentrations of the nanotubes, which especially can take place during the melt-mixing.

The polymer used for the melt mixing study was polyamide 6.6 (PA66, VYDYNE, Solutia Inc., Belgium) that is characterized by a melt flow rate of 600 g/10 min (275°C, 5 kg), measured in accordance to ASTM test method D1238.

2.2 Aqueous CNTs dispersion containing surfactants

In preliminary investigations the influence of different surface active components on the stability of aqueous dispersions was analysed: sodium dodecylbenzene sulfonate (SDDBS, Sigma-Aldrich Chemie Gmbh, Munich, Germany) and sodium dodeyl sulphate (SDS; provided by Merck KgaA, Darmstadt, Germany), surfactants with anionic charge, were compared with a technical cationic surfactant Quartolan® (benzyl(dodecylcarbamoyl)methyl) dimethyl ammoniumchloride; DHW Rodleben, Germany). As expected, the dispersion stability was significantly influenced by the surfactant concentration. Stable dispersions were obtained with certain concentrations of all three surfactants, e.g. with 1.0 g/l of SDS. However, the best results were obtained with SDDBS. This is in accordance with results reported by Islam et al. [4] who addressed the high dispersive efficiency to the benzene ring combined with the small head group. However, in opposite to SDS the surfactant SDDBS contains secondary alkyl chains that require more space. In generally, surfactants with secondary alkyl chains show a better wetting behaviour.

According to these pre-investigations, the anionic surfactant SDDBS was used in our study. The carbon nanotubes were dispersed in the following way: 0.0025 g CNTs were added into 35 ml of an aqueous solution of the SDDBS surfactant (0.7 g/l). The stable formation of surfactant micelles is achieved since the concentration of SDDBS at 0.7 g/l is above the critical micelle concentration of 1.2×10^{-3} mol/l [33] (equal circa 0.42 g/l). The low concentration of CNTs was selected in order to ensure so-called swarm sedimentation of CNTs during the centrifugation step. This means that the CNTs do not settle as a particle collectively but move according to their size [21].

In preliminary investigation the influence of sonication power and time was also investigated and partly reported in [34]. In the present study the nanotubes were dispersed in the solutions at room temperature using a sonicator (Hielscher Sonifier 150, frequency 20 kHz, Hielscher Ultrasonics GmbH, Teltow, Germany) for 2 hours at 40 W.

2.3 Characterization of aqueous CNTs dispersion

The sedimentation behaviour of carbon nanotubes in aqueous dispersions containing surfactants under centrifugation forces was investigated using a LUMiFuge 114 Stability Analyser (L.U.M. GmbH, Berlin, Germany). The LUMiFuge is a microprocessor controlled analytical centrifuge that allows determining space and time resolved extinction profiles during the centrifugation of up to 8 samples simultaneously [21]. The centrifugation with high speed results in an accelerated migration of the dispersed particles. Cylindrical glass cell with inner diameter of 10 mm were used. The evaluation of the transmission profiles as measured between the bottom and the fluid level allows the quantification of the dispersion stability. In case of good nanoparticle dispersion, all nanoparticles are wetted with surfactant and the stability of the dispersion is high which corresponds with a low sedimentation rate. In case of bad dispersion remaining agglomerates settle fast. The LUMiFuge experiments were carried out at 3000 revolutions per minutes for 60 minutes at room temperature. To evaluate the dispersion stability the integration of the transmission profiles was performed in the middle region between the positions 100 and 110 mm within the detection region of 89-114 mm. The LUMiFuge experiments are repeatable and the results are based on double measurements.

Optical investigations of different CNTs in aqueous SDDBS solutions were done using image analysis with the SYSMEX FPIA-3000 (MALVERN, Instruments Ltd, UK). This method enables a reliable, repeatable and routine characterization of particle size and particle shape distributions using automated imaging techniques. The particle shape information is generated

from the analysis of a large number of particles. Displays of size and shape data are supported by images of all particles to provide further visual understanding of the measurement data. Particle shape provides an additional parameter to understand the source of manufacturing variations. The measuring range of particle size is 0.8 - 300 μm. The optical investigation was performed with the same dispersions as used for the LUMiFuge experiments at room temperature. From the images, a circularity of the particle shape can be calculated which is the ratio of the circumference of circle of equivalent area to the perimeter of the particle.

The equilibrium surface energy of the used aqueous SDDBS solution (0.7 g/l), determined using the bubble pressure method (SITA online, SITA Messtechnik, Germany) was 32.9 mJ/m^2. Thus, the surface energy of the surfactant containing solution can be regarded to be in the same range like that of the polymer PA66 for which a surface energy of 41 mJ/m^2 was measured in the melt (260°C) using the pendant-drop-method [35].

2.4 Preparation of composites of polyamide 6.6 and CNTs

For the preparation of the composites, powdery PA66 and CNTs were premixed by shaking and then added to the running DACA Microcompounder (DACA Instruments, Goleta, USA) within 30 s. This microcompounder has a capacity of 4.5 cm^3 and consists of two conical co-rotating screws with a bypass allowing the material to circulate for defined periods. The composites were prepared at a melt temperature of 280°C, a mixing speed of 50 revolutions per minutes, and a mixing time of 5 minutes. After the mixing time the material was led out as a strand of about 2 mm diameter using the set speed to air without additional cooling. Before mixing and pressing, both components were vacuum-dried: polyamide at 80°C for 6 hours and CNTs at 120°C for more than one hour.

2.5 Characterization of PA66-CNTs composites

For electrical resistivity measurements thin sheets with a thickness of approximate 0.3 mm and a diameter of 30 mm were pressed from extruded strands at 320°C for 2 minutes between two aluminium plates using press PW40EH (Paul-Otto Weber GmbH, Remshalden, Germany). Rectangular samples (30 x 3 x 0.3 mm^3) were cut from the pressed sheets. A 4-point test fixture (gold contact wires with a distance of 20 mm between the source electrodes and 10 mm between the measuring electrodes) combined with electrometers model Keithley 6517A or DMM 2000 have been used. The values reported are mean values of 4 measurements. With this equipment only resistivity values less than 10^{12} Ohm cm could be measured. The volume resistivity of pure polyamide 6.6 is stated from the manufacturer to be 10^{13} Ohm cm. The composites having resistivities above the measurement limit of the equipment used were also set to this value.

Scanning electron microscopy (SEM) of the composite materials was performed using a LEO 435 (Carl-Zeiss AG Oberkochen, Germany). The composite strands containing 1 wt% were cryofractured in liquid nitrogen and the surfaces were observed after gold sputtering.

3. RESULTS

3.1 Investigation of the stability of surfactant dispersions with carbon nanotubes using LUMiFuge

The aqueous dispersions with the surfactant SDDBS and different kind of CNTs were investigated in the analytical centrifuge LUMiFuge under centrifugal forces. During the centrifugation transmission profiles in dependence on the position and time were recorded (Figure 1). For all dispersions horizontal profiles were observed caused by very broad particle size distribution. These dispersions contain particles which settle separately dependent on their size with their own sedimentation velocity. In all samples an increase in the transmission values with time was observed. However, in case of dispersions with NC7000, TsNa1, CNT3,

and CNT4 only a low increase of the transmission values up to 9 or 10 transmission% took place during the 60 minutes of centrifugation.
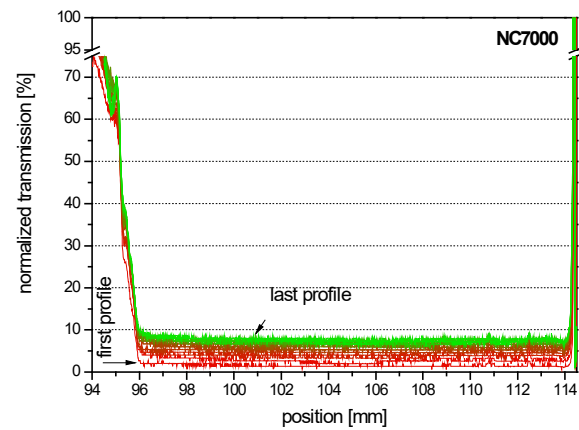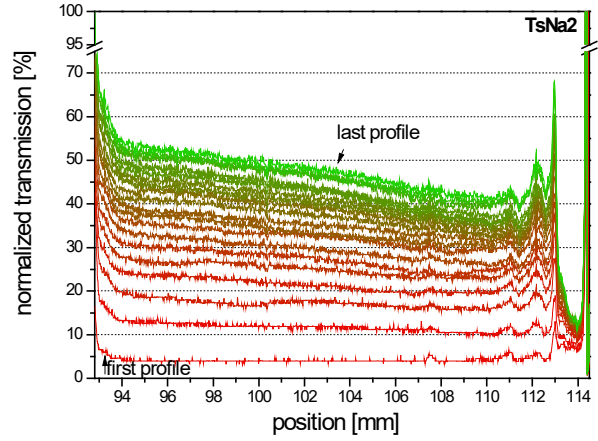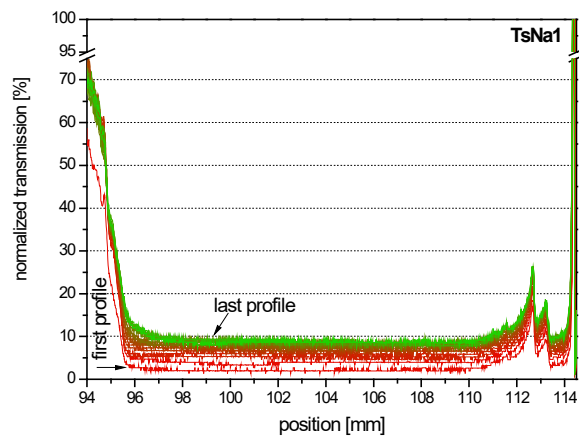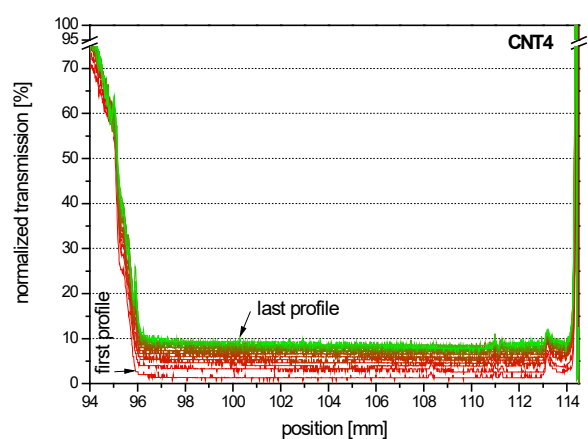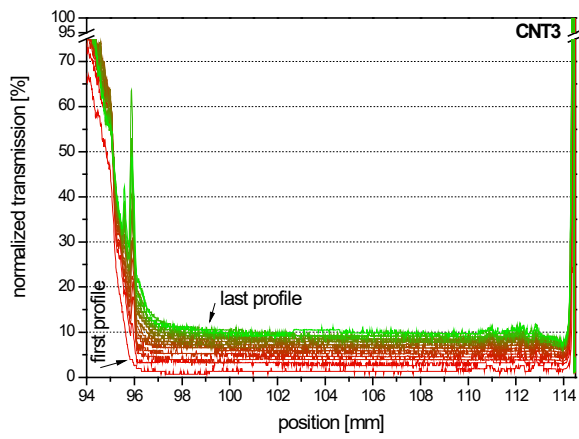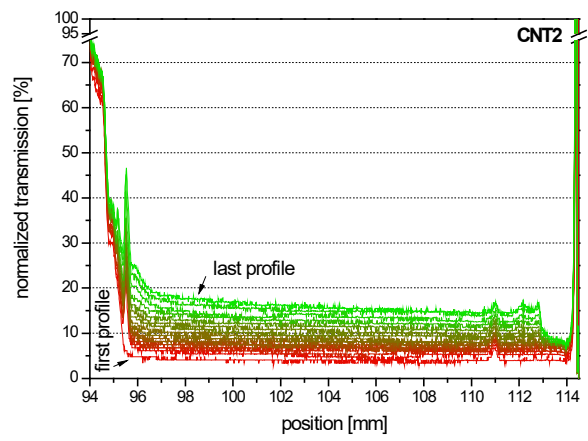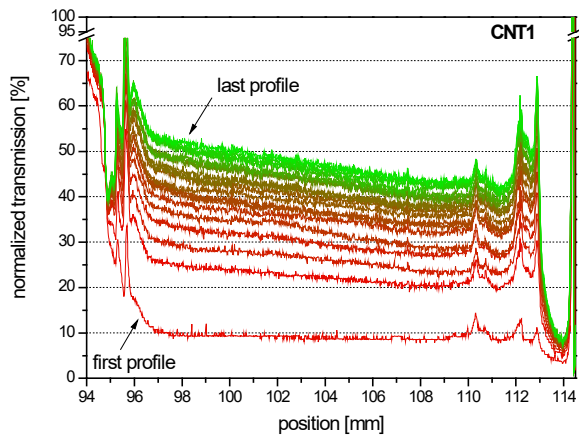
Figure 1: Normalized transmission profiles (LUMiFuge) of SDDBS dispersions (0.0025g CNTs in 35 ml SDDBS, c= 0.7 g/l) at different centrifugation times (0-60 min) at 3000 rpm using different CNTs. a) CNT1, b) CNT2, c) CNT3, d) CNT4, e) TsNa1, f) TsNa2, g) NC7000

Integrating the transmission profiles in the middle position (100 – 110 mm) and displaying these values versus the centrifugation time results in the curves shown in Figure 2. The transmission value at time t=0 indicates the initial value of transmission which is not related to the stability of dispersion. The change in integral transmission versus time is directly related to the dispersion stability and the sedimentation rate. A low initial slope indicates a low sedimentation rate during the measurement corresponding to a high stability of the dispersion [21]. The initial slopes of integral transmission for the dispersion containing NC7000, TsNa1, CNT3, or CNT4 were very low. All four dispersions were very stable under centrifugation.
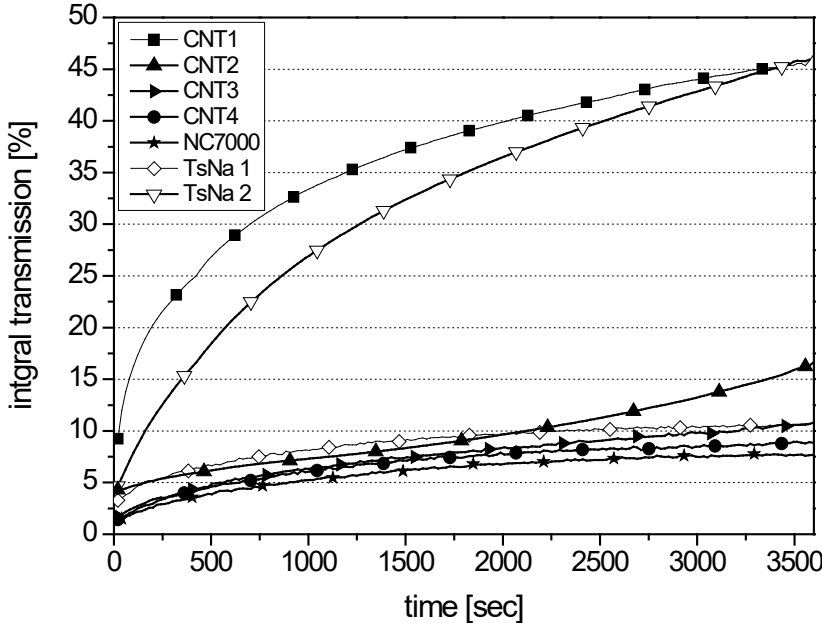

Figure 2: Integral transmission (LUMiFuge) of SDDBS dispersions (0.0025g CNTs in 35 ml SDDBS, c= 0.7 g/l) in dependence on centrifugation time at 3000 rpm

The transmission profiles (Figure 1) and the integral transmission (Figure 2) of the dispersion containing CNT2 show an increase of the transmission values from 3 up to 16 transmission%. The integral transmission curve exhibits only a small increase up to about 30 min comparable to the samples discussed before, however, starting at 30 min the integral transmission increases with a higher slope indicating two-step sedimentation (Figure 2). Additionally, in the transmission profiles (Figure 1) after 30 minutes the formation of sediment was detected. It can be assumed that after this time agglomerates of carbon nanotubes were formed which settle faster. This demonstrates that the stability of the dispersion with CNT2 is lower as compared to the dispersions containing NC7000, CNT3, CNT4, or TsNa1.

The lowest stability was found for the dispersions with CNT1 and TsNa2. The transmission profiles show a considerable increase of transmission with time (Figure 1). During the centrifugation a significant clarification and the formation of sediment already starting at the beginning of the measurements took place. Figure 2 show curves with an increase of integral transmission from 5 or 10 up to 45 transmission% and high initial slopes. These results indicate a high number of remaining agglomerates in relation to dispersed nanotubes already present at the beginning of centrifugation. As a consequence of this bad dispersion in the aqueous surfactant solution they settle with a high sedimentation rate. This is related to a worse dispersability of these nanotube materials after the dispersion step under the selected conditions.

3.2 Electrical percolation in polyamide 6.6

The CNTs were mixed in polyamide 6.6 to evaluate the electrical percolation behaviour of the composites. The electrical volume resistivity of the filled polyamide 6.6 was determined on pressed plates for filler contents between 0.1 wt% and 5 wt% (Figure 3). For pure polyamide 6.6 the electrical volume resistivity is reported to be 10^{13} Ohm cm. In the composites with

CNTs, a considerable decrease of electrical resistivity indicates the electrical percolation threshold.
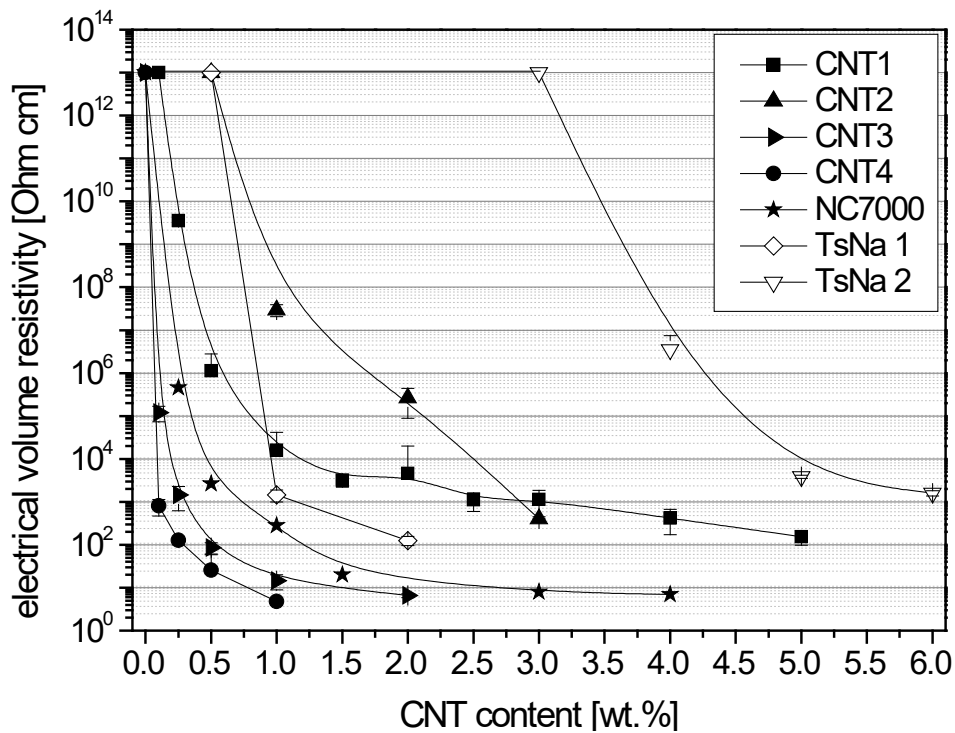

Figure 3: Electrical volume resistivity of polyamide 6.6 versus filler content for different CNTs

Composites of polyamide 6.6 containing CNT3 and CNT4 showed the lowest electrical percolation threshold which was found to be below 0.1 wt%. This finding may be correlated with the results of the RAMAN investigation, where for these two CNTs the lowest content of amorphous carbon was concluded. The electrical percolation concentration of composites filled with NC7000 was between 0.1 and 0.25 wt%. At 0.25 wt% nanotubes the value of electrical volume resistivity of NC7000 composites is three decades higher compared to those of CNT3 or CNT4.

For polyamide filled with CNT1 electrical percolation is observed at 0.5 wt%. With increase in the CNT content the electrical volume resistivity of composites with CNT1 decreased

slowly and the values of electrical volume resistivity were clearly higher than those of composites filled with CNT3, CNT4, and NC7000.

The electrical percolation of polyamide with TsNa1was determined between 0.5 and 1 wt%.

For composites filled with CNT2 electrical percolation could be observed at 1 wt%.

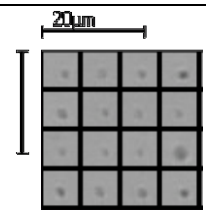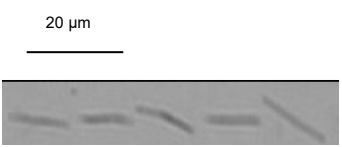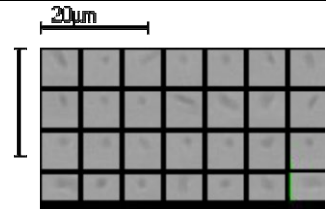The highest electrical percolation threshold was found for the composite containing TsNa2 at 4 wt%.
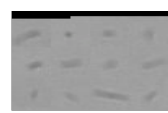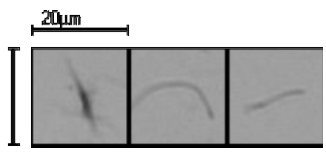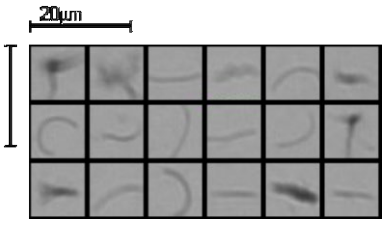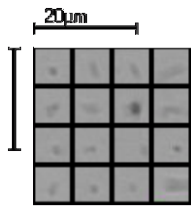
The electrical percolation behaviours of NC7000, TsNa1, and TsNa2 in polyamide 6.6 were found to be different even though the nanotubes exhibit quite similar geometrical dimensions i.e. aspect ratio. The higher percolation composition of TsNa1 as compared to NC7000 could by explained by the lower carbon purity of TsNa1. However, the electrical percolation threshold of TsNa2 was found at much higher filler content than TsNa1 even if geometrical dimensions and purity were identical indicating other structural differences as reason for the worse dispersability.

3.3 Optical investigation of carbon nanotubes dispersions - shape of CNTs

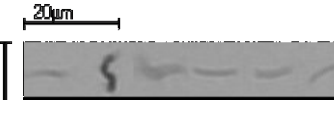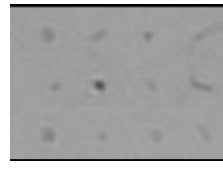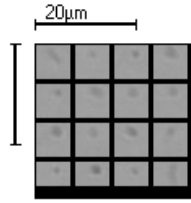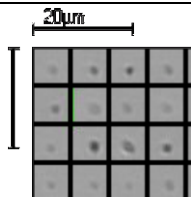The SYSMEX FPIA-3000 Flow Particle Image Analyzer characterizes the size and shape of dispersions with particles in the size range 0.8 µm to 300 µm. Based on the image analysis of surfactant containing dispersions a particle size distribution, a circularity distribution, and SYSMEX images of the particles were obtained. Examples for images as recorded for selected length classes are illustrated in table 1. This method is able to analyse agglomerates of carbon nanotubes; however the optical resolution of the SYSMEX method is too low to observe separated nanotubes. The circularity distribution indicates the general shape of the carbon nanotubes agglomerates. The results of the particle size distribution show that the investigated five CNT surfactant dispersions included 90 % of particles with diameters lower than 1.6 µm. The residual particles of dispersions with NC7000 and CNT1 were determined with a diameter up to 3 µm. Larger particles were detected for the dispersion containing

CNT3 with diameters up to 20 µm and for the dispersion with CNT2 or CNT4 with a diameters up to 15 µm or 10 µm, respectively.

Table 1: Images of the optical analysis using SYSMEX FPIA-3000 Flow Particle Image Analyzer in selected size classes together with the calculated mean circularity

Sample	Class 5: 10-20µm	Class 6: 5-10µm	Class 7: <5µm	Circularity
CNT1				0.97
CNT2				0.78
CNT3				0.75
CNT4				0.83
NC7000				0.97

The particle shape was quantified uses the parameter *circularity*. The value of 1 indicates a spherical particle. A lower value indicates particles with a higher aspect ratio. The detection

limit of the method is a circularity of 0.4 that corresponds to an aspect ratio of 1:20. In table 1 the values of circularity for all dispersions are summarized. In our opinion these values indicate the shape of the agglomerates because a value near 1 is not appropriate for separated nanotubes. For example, NC7000 nanotubes with a mean diameter of 10 nm and lengths between 0.1 and 10 µm exhibit aspect ratios of 1:10 up to 1:1000. Indeed, only if the nanotubes are agglomerated a more spherical formation is possible. Using the SYSMEX analysis, the particle size of the major part of CNTs was determined lower than 1.6 µm (described above) and the circularity was measured with 0.97 corresponding to a circular shape, which suggests the existence of small agglomerates in this dispersion. The SYSMEX images in the class for particles (below 5 µm) do not show a clear shape. In this range of particle size, the optical resolution of the SYSMEX method is too low.

The circularity of NC7000 and CNT1 were determined at 0.97, whereas the agglomerates were detected visually mainly as spherically shaped (table 1). The SYSMEX images of these nanotubes detected only agglomerates in the size class less than 5 µm (table 1). The mean circularity of CNT2, CNT3, and CNT4 was found at 0.78, 0.75, and 0.83, respectively (table 1). That indicates that these three kinds of nanotubes contain longer agglomerates as compared to NC7000 and CNT1. The circularity distribution indicated values between 0.4 and 1. The SYSMEX images show particles in the classes less than 5 µm, 5-10 µm and 10-20 µm (table 1). Especially in the classes 5-10 µm and 10-20 µm CNTs with different shapes were found. For CNT2 straight sticks were visible. Bended nanotubes could be observed in the dispersions containing for CNT3 and CNT4.

The optical investigation of nanotubes dispersion was also used to observe the shape of CNTs agglomerates in dependence on the sonication time. If the aqueous CNT dispersions were sonicated only for 5 or 15 minutes, instead of 2 hours as used for the previous investigations, big agglomerates up to 160 µm were observed. For example, for CNT2 agglomerates with a rectangular appearance like a package of many aligned straight sticks were detected. In case

of CNT3 and CNT4, clew of entangled nanotubes appearing in an oval shape were observed which correspond to the bended nanotubes individualized at longer sonication time. Thus, with increasing sonication time a better individualization of nanotubes could be shown.

3.4 Morphology of PA66 composites - shape of the CNTs on cryofractured surfaces

In order to study the morphology of the composites produced by melt mixing from the five nanotubes lots as described in 3.3 surfaces of cryofractured samples containing 1 wt% CNTs were observed by SEM (Figure 4).
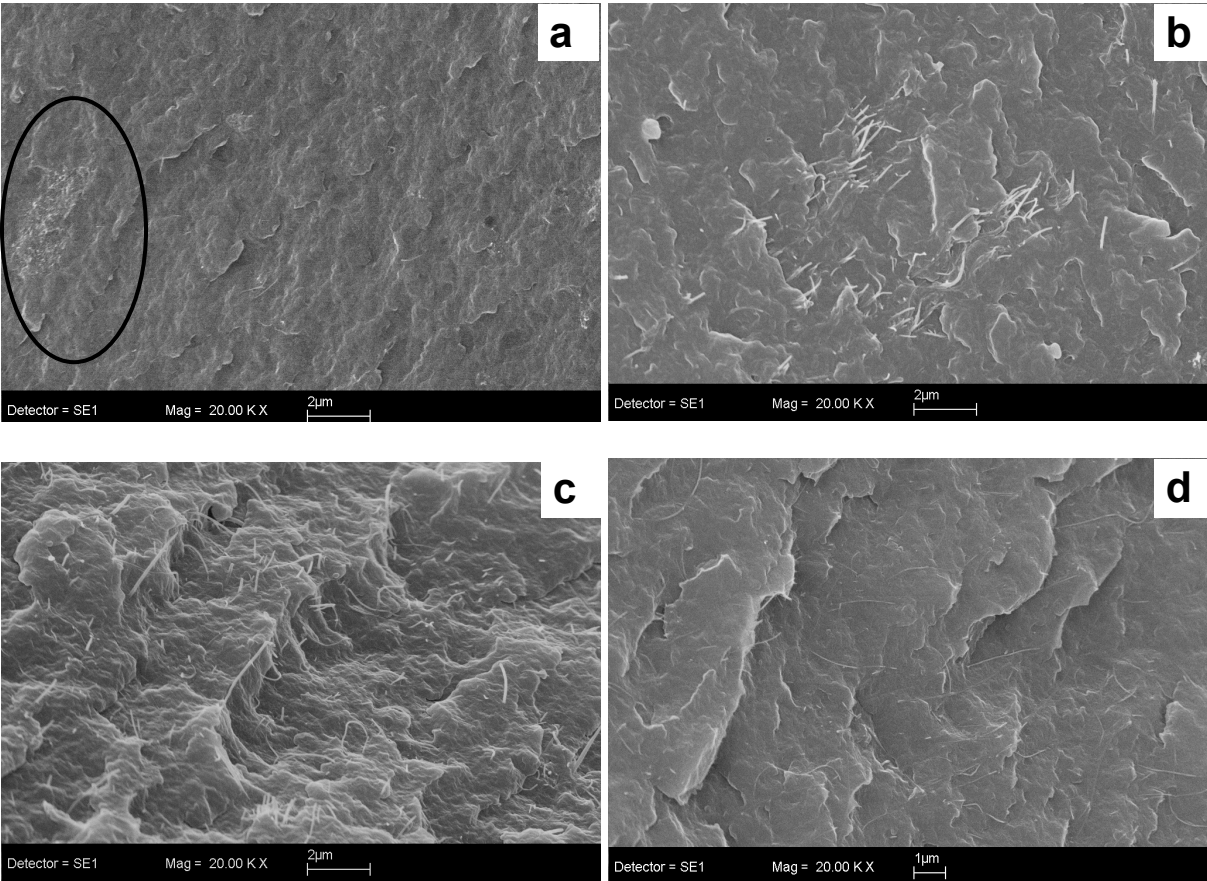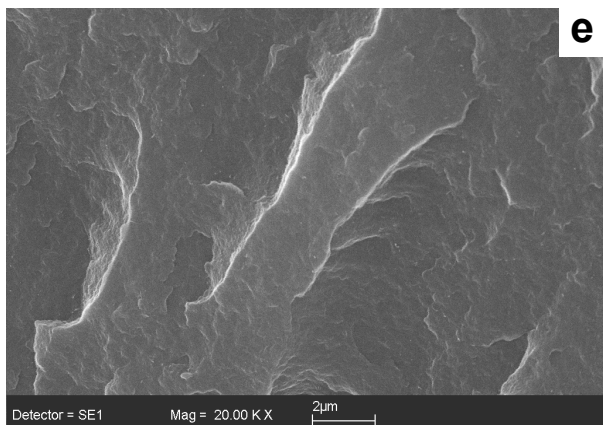
Figure 4: SEM images of cryofractured surfaces of polyamide 6.6. filled with 1 wt% of different CNTs: a) CNT1, b) CNT2, c) CNT3, d) CNT4, e) NC7000.

For the composites containing CNT1 or NC7000 (Fig. 4 a,e) small white dots are visible on the sample surfaces representing broken ends of well embedded nanotubes and indicating quite good phase adhesion. For the polyamide filled with CNT1 the SEM images of the composite with 1 wt% CNT1 illustrate areas with higher concentration of carbon nanotubes (see indication in Figure 4a) which can be assigned to remaining parts of primary CNT agglomerates. These agglomerates were only partially wetted and indicate an insufficient CNT dispersion. On the cryofractured surfaces of the composites filled with CNT2, CNT3, and CNT4 (Fig. 4b-d) relatively long nanotubes up to a length of 2 μm could be observed. In case of CNT2 the nanotubes appear to be quite rigid and are oriented in one direction without good phase adhesion. Areas with higher density of nanotubes can be detected in which the tubes appear to be wetted and separated (Fig. 4b). In contrast, polyamide composites filled with CNT3 or CNT4 indicate well dispersed tubes appearing to be not as stiff as CNT2 and more bended.

4. DISCUSSION

The stability of aqueous dispersions containing different carbon nanotubes and the anionic surfactant SDDBS prepared under defined dispersion conditions was investigated under

centrifugal force using a LUMiFuge. The same carbon nanotubes were mixed in polyamide 6.6 melts using a microcompounder. On the one hand, four kinds of CNTs (CNT3, CNT4, NC7000, TsNa1) showed a very high stability of their aqueous dispersions with low sedimentation rates of the nanoparticles during the centrifugation. For composites of PA66 filled with these carbon nanotubes electrical percolation thresholds below 0.1 wt% or in the range 0.25-0.5 wt% were found. On the other hand, the dispersion with CNT2 indicated lower stability analysing transmission profiles of analytical centrifugation. The lowest stability was observed for dispersions containing CNT1 and TsNa2. The electrical percolation concentration and the values of electrical volume resistivity of the composites filled with CNT1, CNT2, and TsNa2 were significantly higher than those of composites containing CNT3, CNT4, NC7000, or TsNa1. The comparison of the two different lots of TsNa and NC7000 shows that nanotubes with a quite similar geometry can exhibit a completely different sedimentation behaviour in aqueous dispersion as well as electrical percolation behaviour after melt mixing.

These results indicate a correlation between the stability (velocity of settling) of CNTs surfactant dispersions and the electrical percolation threshold of CNT/PA66 composites, both being related to the dispersability quality of the starting nanotube material. A high stability of surfactant CNT dispersion under centrifugation indicates that the surfactant is able to wet separated nanotubes, to stabilize the dispersion, and to prohibit reagglomeration of dispersed CNTs. In case of CNT1 and TsNa2 the surfactant wets to a higher amount nondispersed agglomerated structures resulting in a faster sedimentation. Under the dispersion conditions used, these nanotube materials could not be dispersed appropriately in the aqueous surfactant solution that indicates an inherent worse dispersability as compared to the other nanotube materials studied. This worse dispersability can be mainly addressed to a more entangled structure within the primary agglomerates of the nanotube material and is also reflected after melt mixing, even if different shear conditions were present as compared to those during

solvent dispersion. For the composites filled with CNT1 or TsNa2 correspondingly a higher electrical percolation threshold was found as compared to NC7000, CNT3, CNT4, or TsNa1 which implies that during melt mixing only an ineffective dispersion of nanotubes was obtained. Additionally, the SEM images of the composite with 1 wt% CNT1 illustrate areas with higher content of carbon nanotubes which can be assigned to remaining parts of primary CNT agglomerates which were only partially wetted. For CNT2 where a steep increase of sedimentation rate and the formation of sediment were observed during the sedimentation study of aqueous surfactant dispersions, the cryofractures of the composites indicate also areas with a higher density of nanotubes. In contrast, for composites filled with NC7000, CNT3, or CNT4 well dispersed nanotubes were observed in the SEM images (Figure 4c-e). The samples with CNT1 represent an exception from the general tendency that was found as follows: as better aqueous dispersion stability, as lower electrical percolation threshold, and as more homogeneous nanotube dispersion in the composites. Even if CNT1 had the worst dispersion stability, the electrical percolation in the composites occurred at a relatively low value of about 0.5 wt%. It has to be reminded that this nanotube material had a different structural characteristic, namely containing beside multiwalled also single- and doublewalled nanotubes. Possibly the MWNT part is responsible for fast sedimentation, whereas single- and doublewalled CNTs help to achieve low electrical percolation.

The results obtained in this study agree very well with previous investigations on polycarbonate with NC7000 and TsNa (first and second lot) [34] where slightly different conditions of preparation of aqueous surfactant containing nanotube dispersions and centrifugation using LUMiFuge were used. In this reference, only the nanotubes having similar dimensions and purity were compared. NC7000 and TsNa1 showed a high stability of the surfactant stabilised dispersions by analytical centrifugation and low electrical percolation thresholds between 0.5-1 wt% after melt mixing in polycarbonate. The third type of CNTs (TsNa2) was very instable in the surfactant dispersion (pronounced sedimentation) and the

electrical percolation threshold of these polycarbonate composites was as high as 4-5 wt%. Additionally, the morphological investigation using transmission electron microscopy illustrated that in the composite with the high percolation threshold the CNTs contained remaining primary agglomerates. In contrast, the nanotubes NC7000 and TsNa1exhibiting low percolation threshold of the composites were well dispersed. It was concluded already from that study that the possibility of individualization of TsNa2 was significantly reduced by strong attractive force originating from high van der Waals forces and entanglements within the more compact primary CNT agglomerates. Interestingly, the order in electrical percolation composition is the same like in the composites with polyamide 6.6 presented here, even if the surface energy of molten polycarbonate (30 mJ/m^2 at 280°C [35]) is 11 mJ/m^2 lower than that of polyamide 6.6 (41 mJ/m^2 at 260°C [35]) and is more similar to the surface tension of the surfactant solution (32.9 mJ/m^2). This implies that a similarity of surface energy of surfactant solutions and molten polymer may not be required for the estimation of dispersability by studying the sedimentation behaviour of aqueous surfactant dispersions if the surface nature between the nanotube materials does not differ much. It is planned to extend the study also towards polymers having higher differences in surface energy with the surfactant solution, like polyolefins. In addition, the finding of pre-investigations using other surfactants like SDS and Quartolan® on selected samples may support this assumption. It was found that the order in intensity changes in the transmission curves between different nanotubes was always the same even if the ranges of intensity changes during sedimentation differed and were maximal when using SDDBS solutions. This implies that the sedimentation velocity as characterized by the LUMiFuge is more influenced by the dispersability caused by the entanglement structure within primary nanotube agglomerates and the (shear) strength of agglomerates than by the chemical surface nature. However, functionalization of nanotubes may change the surface characteristic of nanotubes significantly leading to deviations from the observed correlations.

The dispersions as used for the LUMiFuge investigations were also investigated using the SYSMEX Flow Particle Analyzer. Interestingly, similarities were found between the appearance of images obtained from the starting nanotube material, the optical images as obtained by SYSMEX, and the appearance of the nanotubes on cryofractured composite surfaces. SEM images and transmission electron micrographs of the pure CNTs materials [22, 23, 26, 32] indicated the different diameters of the nanotubes but no significant differences in the appearance of the bended nanotubes. In such micrographs it is quite difficult to observe a certain nanotube in full shape due to the high aspect ratios and the existence of intertwined structures. Therefore, the investigation of the shape of CNTs by optical investigation of the surfactant dispersions as performed using the SYSMEX Flow Particle Analyzer may have some advantages. The images were compared with the nanotube appearance on SEM micrographs of the cryofractured PA66 composites.

The dispersions with NC7000 and CNT1 contained only small particles in the size class below 5 µm that were characterized as rather spherical. The SEM investigation of the composites filled with these two types of CNTs indicated well dispersed and embedded nanotubes. In contrast, the surfactant dispersions with CNT2, CNT3, and CNT4 contain next to mainly short CNTs a small part of CNTs with lengths up to 20 µm. In the SEM images of the cryofractured composites relatively long nanotubes up to a length of 2 µm could be observed. Using both methods, CNT2 were detected as straight sticks and the CNT3 und CNT4 appeared to be more bended. These similarities between the observations on aqueous surfactant dispersions and cryofractured surfaces indicate that the shape of different nanotubes can be assessed to a certain extent using SYSMEX characterization of the surfactant dispersions.

5. CONCLUSION

Our results proved that investigations of the sedimentation behaviour of nanotubes dispersed in aqueous surfactant solutions using the LUMiFuge Stability Analyser are suitable in order to characterize the dispersability of as produced carbon nanotube materials. From the stability of the aqueous dispersions, estimations could be drawn towards the dispersability of nanotubes in polymer melts as shown for polyamide 6.6 and in previous investigations for polycarbonate [34]. Nanotube materials with a good stability of their aqueous dispersions also showed a homogeneous dispersion in the melt state as indicated by morphological investigations and exhibited low electrical percolation thresholds in the composites. In extension to previous results from our group obtained on nanotube materials with the same structural characteristics [34] the new results were obtained on a variety of nanotubes prepared under different synthesis conditions leading to different diameters, lengths, and their distributions as well as shape and curvature/waviness. The results were consistent within materials containing multiwalled carbon nanotubes only, which may be not directly comparable with nanotube materials containing mixtures of multi-, single-, and doublewalled CNTs as it was indicated by the behaviour of CNT1.

A direct correlation between the stability of aqueous dispersions and the electrical percolation threshold is naturally not possible, since the electrical percolation behaviour also depend on other influencing factors; mainly nanotube length and diameter, curvature, and surface structure but also interactions to the polymer and processing conditions (see e.g. [36]). In addition, the electrical percolation behaviour is influenced by the structuring process during the polymer crystallisation that may be altered by the nanotube nucleation effects which in terms depend on the state of nanotube dispersion. However, in our results a quite good correlation as described above was found when using constant melt mixing conditions even if the nanotubes differed in diameters and lengths and internal structure. The rating between the different as produced nanotube materials was comparable even when using different

surfactants and conditions of dispersion preparation or using different matrices of the composites (polyamide 6.6. and polycarbonate). Hence, even if these factors change the quantitative results of the sedimentation study, the tendencies in distinguishing between nanotube materials with differences in entanglement and agglomeration structure and, thus, dispersability were found to be the same.

By this method it is possible to perform a time saving pre-selection of nanotube materials and to eliminate lots of CNTs with bad dispersability before time and material intensive melt mixing experiments have to be carry out. The method is also suitable for quality control of different lots (see example for the two lots of TsNa). In addition, meaningful sonication conditions for solvent based composite production methods can be selected. It is expected that the method can be also used to estimate the effect of nanotube purification and modification steps on the nanotube dispersability.

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Figures

Figure 1: Normalized transmission profiles of SDDBS dispersions with different CNTs using LUMiFuge at 3000 rpm and 60 minutes (0.0025g CNTs in 35 ml SDDBS, c= 0.7 g/l). a) CNT1, b) CNT2, c) CNT3, d) CNT4, e) TsNa1, f) TsNa2, g) NC7000

Figure 2: Integral transmission in dependence on time for SDDBS dispersions with different CNT using LUMiFuge at 3000 rpm and 60 minutes (0.0025g CNTs in 35 ml SDDBS, c= 0.7 g/)

Figure 3: Electrical volume resistivity of polyamide 66 filled with different CNTs in dependence on filler content

Figure 4: SEM images of 1 wt% CNTs filled polyamide 66 with different CNTs: a) CNT1, b) CNT2, c) CNT3, d) CNT4, e) NC7000.

Tables

Table 1: Images of the optical analysis using SYSMEX FPIA-3000 Flow Particle Image Analyzer in selected size classes together with the calculated mean circularity