# Dispersability and particle size distribution of CNTs in an aqueous surfactant dispersion as a function of ultrasonic treatment time

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## Abstract

The dispersability of carbon nanotubes (CNTs) was assessed by studying the sedimentation of CNTs dispersed in aqueous surfactant solutions at different ultrasonication treatment times using a LUMiSizer<sup>®</sup> apparatus under centrifugal forces. Different commercially available multiwalled CNTs, namely Baytubes<sup>®</sup> C150P, Nanocyl<sup>TM</sup> NC7000, Arkema Graphistrength<sup>®</sup> C100, and FutureCarbon CNT-MW showing quite different kinetics were compared. In addition, the particle size distributions were analyzed using dynamic light scattering and centrifugal separation analysis. The best dispersabilities were found for Nanocyl<sup>TM</sup> NC7000 and FutureCarbon CNT-MW. To prepare a stable dispersion of Baytubes<sup>®</sup> C150P and Graphistrength<sup>®</sup> C100 a fivefold amount of energy was needed. As a result of the centrifugal separation analysis, it was concluded that Nanocyl<sup>TM</sup> NC7000 and Baytubes<sup>®</sup> C150P were dispersed as single nanotubes using ultrasonic treatment whereas small agglomerates or bundles are existing in dispersions containing FutureCarbon CNT-MW and Graphistrength<sup>®</sup> C100.

# 1. Introduction

Carbon nanotubes are nanofillers with a very high potential in different industrial applications, e.g. for static dissipative or conductive parts in automotive or electronic

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industries. For the effective use of carbon nanotubes (CNTs) an excellent distribution and dispersion is an essential precondition. The CNTs properties like nanotube type (single-, double-, multiwalled), length, diameter, bulk density, and waviness are dependent on the CNT synthesis conditions, e.g. catalyst, temperature of synthesis, and synthesis method used [1]. The purity and functional groups on the surface of the CNTs as well as mainly their entanglements and strength of agglomerates influence the dispersability of CNTs in different media. In addition, due to strong van der Waals forces CNTs tend to agglomerate. Ultrasonication of CNT dispersions is a common tool used to break up CNT agglomerates in solution based processing techniques. Ultrasonication can be done by different ways: using either an ultrasonic bath or insetting an ultrasonic sonotrode into the solvent. The tip of ultrasonic sonotrode oscillates at a fixed frequency and produces a conical field of high energy in the fluid. The solvent within this conical field undergoes nucleated boiling and bubble collapse that is the primary mechanism by which ultrasonic energy disperses particles [2]. This may help to debundle nanotubes by providing high local shear, particularly to the nanotubes ends.

For the preparation of CNT dispersions surfactants are quite often used as additives [3-7]. During the dispersion process the surfactant adsorbs on the nanotubes surface. Gaps at the bundle end or at primary agglomerates surfaces helps in the formation and propagation of surfactant adsorption. Finally, the bundles or agglomerates are separated into individual nanotubes and are kept in homogeneous and stable suspension [8, 9]. The final configuration of sodium dodecylbenzene sulfonate (SDDBS) covered nanotubes was described as a cylindrical micelle with a nanotube in the centre [8, 10].

The destruction of agglomerates in aqueous suspensions using ultrasonic energy was described by different authors [2, 11-16]. Lu et al. [11] reported that multiwalled carbon nanotubes (MWNTs) get shorter with ultrasonic time. Nadler et al. [12] described for aqueous dispersions containing Baytubes<sup>®</sup> C150P agglomerates that with increasing ultrasonic time

(1 minute up to 16 hours) a bimodal agglomerate size distribution pass into a finally monomodal distribution whereas the mean particle size decreased significantly as investigated using a disc centrifuge. These very broad size distributions of the dispersions were explained with the presence of mass fractions of exfoliated CNTs and residual agglomerates. It was not possible to deduce results concerning the carbon nanotubes length using the disc centrifuge. Pohl et al. [15] found for fumed silica suspensions that an increase of energy input leads to a decrease of particle size distribution up to a minimum. Initially, a rupture of agglomerates starts followed by an erosion process. Yu et al. [16] described the dispersion of multiwalled carbon nanotubes in an aqueous sodium dodecyl sulphate solution at different ultrasonic treatment time. With higher sonication energy a better exfoliation and disentanglement of CNTs was found using UV-visible spectroscopy and transmission electron microscopy. The motion and orientation of non-spherical particles in a suspension is also studied detailed in literature. Butler et. al [17] simulated the sedimentation of cylindrical particles in the gravitation field. With time the gravity acts in the downward direction and the particles are oriented perpendicular. Hydrodynamic forces act at the centre of pressure rather than at the centre of mass. The centre of pressure is shifted towards the leading edge of the particle depending on the incidence angle and the aspect ratio [18, 19]. When a gravitational force acts at the centre of mass this induces a torque on the particle that determines its orientation with respect to its moving direction in the continuous phase. An equivalent diameter of short fibres during the sedimentation was calculated by Henn [20]. The settling velocity of a sphere is dependent on its diameter. Due to non exact orientation of fibres in the force direction the settling velocity is influenced by the diameter of the cylinder as well as slightly on its length. In dependence on the aspect ratio the equivalent diameter is slightly higher than the actual cylindrical diameter. Assuming a mean CNT diameter of 10 nm and aspect ratios of 50 an equivalent diameter of the fibres of 21 nm was expected according to these calculation [20].

3/24

The aim of our study is the characterization of the dispersability of CNTs. For this purpose, carbon nanotubes were dispersed in an aqueous surfactant solution containing sodium dodecylbenzene sulfonate (SDDBS) using different ultrasonic treatment times and the time dependent sedimentation behaviour under centrifugal forces was studies. This method was shown to be suitable for estimating the dispersability of CNTs in polymer melts as shown in a previous paper [21] and is extended in this study towards different commercial nanotube grades.

## 2 Methods and Materials

## 2.1 Materials

Four kinds of commercially available multiwalled carbon nanotubes were used: Baytubes<sup>®</sup> C150P (Bayer MaterialScience AG, Leverkusen, Germany), Nanocyl<sup>TM</sup> NC7000 (Nanocyl S.A., Sambreville, Belgium), FutureCarbon CNT-MW (as-grown, FutureCarbon GmbH, Bayreuth, Germany), and Graphistrength<sup>®</sup> C100 (Arkema, Colombes Cedex, France). Despite similar geometrical and purity characteristics the CNTs are different in the strength of the asproduced primary agglomerates. The agglomerates of Baytubes<sup>®</sup> C150P and Graphistrength<sup>®</sup> C100 were synthesised by purpose to contain compact agglomerates in order to enable a safe handling during transport, decanting, and dosage which causes less safety problems and have a higher bulk density as compared to Nanocyl<sup>TM</sup> NC7000 or FutureCarbon CNT-MW. The properties of the four different carbon nanotubes products are summarized in Table 1.

	Nanocyl <sup>TM</sup>	Baytubes®	FutureCarbon	Graphistrength®
	NC7000	C150P	CNT-MW	C100
carbon purity	>90% [22]	>95% [23]	>90% [24]	>90% [25]
diameter	9.5 nm [22]	5-20 nm [26]	not specified	10-15 nm [25]
length	1.5 μm [22]	1->10 μm [26]	not specified	0.1-10 µm [25]
surface area	250-300 m <sup>2</sup> /g [22]	not specified	$\sim 250 \text{ m}^2/\text{g} \text{ [24]}$	not specified
bulk density	$66 \text{ kg/m}^3$	120-170 kg/m <sup>3</sup>	$28  kg/m^3$	50-150 kg/m <sup>3</sup>
(EN DIN 60)	00 kg/m	[23]	20 kg/m	[25]
agglomerate size	not specified	0.1-1 mm [23]	not specified	0.2-0.5 mm [25]

Table 1: Properties of the different CNT products

Sodium dodecybenzene sulfonic acid; sodium salt (Sigma-Aldrich Chemie GmbH Munich, Germany) was used as surfactant with anionic charge.

## 2.2 Characterization of CNT powder

Scanning electron microscopy (SEM) of MWNT materials was performed using an Ultra plus microscope (Carl Zeiss SMT AG, Oberkochen, Germany) on the as received dry powders. The carbon nanotube diameters were determined with transmission electron microscopy (TEM) using a Libra 120 (Carl Zeiss AG, Oberkochen, Germany). The CNTs were suspended in ethanol by shaking, a drop was located on a TEM grid, and the solvent was evaporated. The agglomerate size distribution of the CNT powders was determined by laser diffraction using a Helos/BF particle size analyzer coupled with a RODOS dry dispersion unit and ASPIROS micro dose module (Sympatec GmbH, Clausthal-Zellerfeld, Germany). For the measurements a pressure of 0.5 bar was used. The measurement range is 4.5–875 µm. The volume weighted agglomerate size distributions were calculated in accordance to ISO 13320

using the Fraunhofer diffraction analysis [27-29]. Additionally, the parameters  $x_{10}$ ,  $x_{50}$ , and  $x_{90}$  were calculated indicating that 10%, 50%, and 90% of the particles are smaller than the given value.

The measurements of the mechanical stability of the CNT agglomerates were performed on 100 particles using a Granulatfestigkeitsprüfgerät (GFP, etewe GmbH, Karlsruhe, Germany) at the Fraunhofer Institute for Chemical Technology (ICT) in Pfinztal. During the measurements, the particles which have to be in sizes larger than 100 µm are deformed with an increasing force leading to breakage at a certain pressure in case of brittle particles. However, agglomerates of nanotubes were found to be flexible and did not break under pressure as the deformation behaviour is comparable with that of foams. Therefore, the deformation stress at a deformation of 25% was determined. The crushing force was measured in dependence on the deformation. In the measurement range the force-deformation ratio was constant.

## 2.3 Preparation of aqueous CNTs dispersion containing surfactants

Based on previous investigations [21], the anionic surfactant SDDBS was used in this study. The carbon nanotubes were dispersed in a concentration of 0.07 g/l in an aqueous solution of the SDDBS surfactant (0.7 g/l). The formation of stable surfactant micelles is achieved since the concentration of SDDBS at 0.7 g/l is above the critical micelle concentration of 0.42 g/l [30]. The low concentration of CNTs was selected in order to ensure so-called swarm sedimentation of CNTs during the centrifugation step which means that the CNTs do not settle as a particle collective but move individually according to their size [31]. In the present study 0.0025 g of the nanotubes were dispersed in 35 ml of the SDDBS solutions in a beaker glass at room temperature using an ultrasonic processor UP 200S (Hielscher Ultrasonics GmbH, Teltow, Germany), frequency 24 kHz, 200 watts, equipped with a Sonotrode S14,

made of titanium. The amplitude was adjusted to 20% and the dispersion time was varied (1-30 minutes) to vary the energy input into the dispersion.

## 2.4 Characterization of aqueous CNTs dispersion

The sedimentation behaviour of carbon nanotubes in aqueous dispersions containing surfactants was investigated under centrifugation forces using a LUMiSizer<sup>®</sup> LS611 (L.U.M. GmbH, Berlin, Germany). The LUMiSizer<sup>®</sup> is a microprocessor controlled analytical centrifuge that allows determining space and time resolved extinction profiles during the centrifugation of up to 12 samples simultaneously [31]. The centrifugation with high speed results in an accelerated migration of the dispersed particles. Quadratic synthetic cells (polystyrene) with an optical path 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 particle dispersion, all particles 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 LUMiSizer<sup>®</sup> experiments were carried out at 3000 revolutions per minutes (rpm) for 45 minutes at room temperature. To evaluate the dispersion stability the integration of the transmission profiles was performed in the middle region of the cell between the positions 106 and 124 mm. The LUMiSizer<sup>®</sup> experiments.

## 2.5 Methods used for particle characterization

The particle size distribution of the dispersed CNTs was determined by two different methods. On the one hand, the particle size distributions were determined by dynamic light scattering (DLS, Zetasizer Nano S, Malvern Instr., UK) in accordance with ISO 22412. On the other hand, the centrifugal separation analysis (CSA) of dispersions in a centrifugal force field using LUMiSizer<sup>®</sup> LS611 (L.U.M. GmbH, Berlin, Germany) according to ISO 13318-2 was used. The measurements were carried out about 30 min after ultrasonic treatment at 25°C. From both methods the effective hydrodynamic particle size and particle size distribution can be calculated. However, due to the different methods and kind of data acquisition different aspects concerning the particle size will be obtained. During DLS measurements the particles are subjected to Brownian motion whereas during CSA the particles move due to the centrifugal forces.

Compared with the number of techniques for measuring the size of particles lower than 1  $\mu$ m, there are very few techniques that are able to accurately measure the size of small particles, particularly those less than 10 nanometres. Dynamic light scattering (DLS), based on the same principle like Photon Correlation Spectroscopy (PCS) is a technique able to detect such small particles in dispersion in a fast, routine manner with little or no sample preparation [32]. The theoretical background of PCS in particle characterization is extensively described and discussed for polystyrene particles suspended in water [33]. The intensity weighted particle size distributions based on dynamic light scattering were determined using a Zetasizer Nano S (Malvern Instr., UK) equipped with a monochromatic coherent 4 mW Helium Neon laser ( $\lambda =$ 633 nm) as light source and the so-called NIBS®-technology (Non-Invasive Back-Scattering; patent from ALV GmbH, Germany). All measurements were performed in disposable cuvettes. Twenty autocorrelation functions (ACFs) of 20 seconds data collection time per scan were combined to a mean ACF and evaluated by the DTS (Dispersion Technology Software) 4.00 appendant to Zetasizer Nano S. This Software includes cumulant analysis (in accordance to ISO 13321) and the multimodal size distribution algorithm NNLS (non negative least square). The analysis of the ACF gives the mean diffusion coefficient D<sub>T</sub>. From cumulant analysis it is possible to get the z-average hydrodynamic diameter  $d_{h,z ave}$  of particles and the polydispersity index which is a measure of the broadness of the particle size distribution.

Another method to get particle sizes and particle size distributions of small particles is the centrifugal separation analysis (CSA). The experiments with the LUMiSizer<sup>®</sup> were performed at 3000 rpm and temperature of 25°C. The kinetics of transmission profiles for particle sizing was recorded at a wavelength of 880 nm and time intervals of 10 s. The obtained transmissions values were transformed into extinction and subsequently the velocity distribution as a primary result obtained by means of the Software SEPView. The mode "Constant position" was used and three notes were set at 120, 122, and 124 mm. Based on the velocity distribution the software allows to calculate the particle size distribution. The intensity weighted distribution was used to match the data from DSL experiments. For this calculation, the density of both fluid ( $\rho_F$ ) (water 1 g/cm<sup>3</sup>) and particles ( $\rho_P$ ) (CNT 1.75 g/cm<sup>3</sup>) and the dynamic viscosity of the fluid ( $\eta_F$ ) (water 0.8872 mPa s) are required. As one result of the analysis the average mean value of particle diameter x50 was obtained.

#### **3 Results**

# 3.1 Characterization of CNT powder

The dry CNT powders were investigated to collect additional information on the size and structure of the agglomerates. For the quantitative determination of the particle size distribution the laser diffraction method was used and cumulative distribution curves are given in Figure 1. Table 2 shows the mean values of particle sizes. All CNT powders exhibit agglomerates in the µm-size. The smallest agglomerates were found for FutureCarbon CNT-MW which are between 10 and 100 µm. Slightly higher agglomerate sizes were determined for Baytubes<sup>®</sup> and Graphistrength<sup>®</sup> CNTs which are between 30 and 550 µm. The largest agglomerates were found in Nanocyl<sup>TM</sup> NC7000. Unfortunately, the main part of these particles was out of the measurement range of the equipment used. The smallest agglomerates were about 675 µm whereas only 12 % of the particles were in the measurement range up to 875 µm.

The nanotubes diameters of all four CNTs were determined using TEM to be nearly in the same range. The diameters of Nanocyl<sup>TM</sup> NC7000 were in the range of 6-20 nm, of Baytubes<sup>®</sup> C150P between 6 and 26 nm, of FutureCarbon CNT-MW between 9 and 30 nm, and of Graphistrength<sup>®</sup> C100 between 6 and 20 nm.



Figure 1: Cumulative volume weighted distribution of mean agglomerate size of the different CNT powders using laser diffraction method

Table 2: Determination of mean agglomerate size of CNT powders (dry) using diffraction

laser light

CNT powder	x10 [µm]	x50 [µm]	x90 [µm]	
Nanocyl <sup>TM</sup> NC7000	Not detectable: size > 675 $\mu$ m			
Baytubes <sup>®</sup> C150P	83	314	485	
FutureCarbon CNT-MW	13	29	62	
Graphistrength <sup>®</sup> C100	55	302	501	

The shape of the agglomerates was observed by SEM images of the different powders (Figure 2). For FutureCarbon CNT-MW, Baytubes<sup>®</sup> C150P, and Graphistrength<sup>®</sup> C100 a bird nest structure was found. A combed yarn structure is observed for Nanocyl<sup>TM</sup> NC7000.





Figure 2: Scanning electron microscopy images of CNT powder at two magnifications: (a) Nanocyl<sup>TM</sup> NC7000, (b) Baytubes<sup>®</sup> C150P, (c) FutureCarbon CNT-MW, (d) Graphistrength<sup>®</sup> C100.

The mechanical stability of the CNT agglomerates was determined using a compressive test. The average deformation stress at 25% deformation strain was found to be 0.64 MPa and 0.67 MPa for Baytubes<sup>®</sup> C150P and Graphistrength<sup>®</sup> C100 CNTs, respectively. The value for Nanocyl<sup>TM</sup> NC7000 was determined to be 0.39 MPa. Unfortunately, the size of the FurtureCarbon agglomerates was too small for the measurement of deformation stress because the minimum particle size for this method is 100 μm.

These findings correlate with the bulk density of the materials. Baytubes<sup>®</sup> C150P and Graphistrength<sup>®</sup> C100 show higher deformation stresses which are in good agreement with the higher bulk densities of 120-170 and 50–150 kg/m<sup>3</sup>, respectively. In contrast, Nanocyl<sup>TM</sup>

NC7000 having a low bulk density of 66 kg/m<sup>3</sup> exhibits also a lower value of deformation stress.

# 3.2. Characterisation of CNTs in aqueous surfactant dispersion

#### 3.2.1 Centrifugal separation analysis (CSA)

For all dispersions horizontal transmission profiles in the centrifugal separation analysis were observed caused by their very broad agglomerate size distributions.



Figure 3: Integral transmission in dependence on sedimentation time: Nanocyl<sup>TM</sup> NC7000, Baytubes<sup>®</sup> C150P, FutureCarbon CNT-MW, Graphistrength<sup>®</sup> C100.

In CSA all four dispersions showed decreasing values of integral transmission with ultrasonic treatment time (Figure 3). This is caused by the increase of the amount of individualized nanotubes and very small agglomerate fragments versus the content of remaining bigger

agglomerates, which differ in the sedimentation velocity. However, for dispersions containing Nanocyl<sup>TM</sup> NC7000 or FutureCarbon CNT-MW the amount of dispersed nanotubes increased faster. Already after 2 min ultrasonic treatment stable dispersions were obtained. For dispersions containing Baytubes<sup>®</sup> C150P or Graphistrength<sup>®</sup> C100 10 min ultrasonication were needed to get stable dispersions whereas the transmission values of the Graphistrength<sup>®</sup> C100 dispersion were slightly lower indicating better initial dispersion. Summarizing, Nanocyl<sup>TM</sup> NC7000 nanotubes and FutureCarbon CNT-MW show a significantly better dispersability in aqueous surfactant dispersions. For these CNTs only a fifth of the energy input is necessary to prepare stable dispersions in comparison to Baytubes<sup>®</sup> C150P and Graphistrength<sup>®</sup> C100.

#### 3.2.2 Particle size distribution of CNTs in dispersion

In dynamic light scattering (DLS) the z-average hydrodynamic particle diameter  $d_{h,z ave}$  is obtained from the cumulant analysis of the normalized electric field autocorrelation function. It is calculated by the Stokes-Einstein equation with the diffusion coefficient determined from the decay time of autocorrelation function. In addition there is certain probability that the light scattered by larger particles will swamp the light scattered by smaller particles since the light intensity of a scattered particle is proportional to the diameter in the sixth power. That means that larger particles are overestimated in the dispersions. For this reason the change of  $d_{h,z ave}$ with ultrasonic treatment time shows only a trend in the change of particle size. In contrast, during the CSA the particles are orientated in the centrifugal field so that the sedimentation velocity is dependent on the smallest dimension of the particle. Figure 4 shows the z-average hydrodynamic particle diameter  $d_{h,z ave}$  as well as the particle diameter  $x_{50}$ determined by CSA in dependence of the ultrasonic treatment time. The values of intensity weighted particle size distribution using CSA are generally lower compared to the intensity weighted values obtained by DLS measurements. Thus, it can be assumed that the ultrasonic treated agglomerates are not spherical. Only if the results of DLS and CSA agree a spherical shape of the dispersed particles or aggregates may be assumed. The values of the integral transmission of the particle dispersions obtained by CSA as presented in Figure 3 (section 3.2.1) show the increase in content of dispersed particles with ultrasonic treatment time leading to decreasing transmission values.

Both the z-average particle diameter (d<sub>h,z ave</sub>) from DLS and the average particle diameter (x<sub>50</sub>) from CSA decrease with ultrasonic treatment time for the four nanotubes used, as shown in Figure 4. Regarding DLS, the initial decrease (during first 5 minutes of ultrasonic treatment) of the z-average particle size d<sub>h,z ave</sub> was faster for Nanocyl<sup>TM</sup> NC 7000 and Graphistrength<sup>®</sup> C100 compared to Baytubes<sup>®</sup> C150P and FutureCarbon CNT-MW. After 10 min of treatment the differences in z-average particle diameter between the dispersions of Nanocyl<sup>TM</sup> NC 7000, Baytubes<sup>®</sup> C150P, and FutureCarbon CNT-MW are diminished. However, the z-average particle diameters d<sub>h,z ave</sub> of the Graphistrength<sup>®</sup> C100 were generally found to be higher than those of the other kinds of nanotubes. The polydispersity index obtained by DLS was found to be 0.4 for Baytubes<sup>®</sup> C150P, Nanocyl<sup>TM</sup> NC 7000, and Graphistrength<sup>®</sup> C100 indicating very heterogeneous particles and agglomerates existent in the dispersions. For FutureCarbon CNT-MW a polydispersity index of 0.2 was found showing that these agglomerates are more homogeneous in size.



Figure 4: Z-average particle diameter  $d_{h,z ve}$  (DLS, full symbols) and average particle diameter  $x_{50}$  (CSA, open symbols) in dependence on the ultrasonic treatment time for aqueous CNT dispersions containing different MWNTs.

The particle diameters x<sub>50</sub> determined using CSA show big differences after 1 min ultrasonic treatment for the different CNT dispersions. The initial values vary between 285 nm for Graphistrength<sup>®</sup> C100 and 76 nm for Baytubes<sup>®</sup> C150P. The initial decrease of particle size x<sub>50</sub> (during first 5 minutes of ultrasonic treatment) was fast for FutureCarbon CNT-MW, Nanocyl<sup>TM</sup> NC7000, and Graphistrength<sup>®</sup> C100. In contrast, the particle diameter of Baytubes<sup>®</sup> C150P did not change much up to 5 min of treatment followed by a decrease after 10 min. After 30 min, the average particles diameters x<sub>50</sub> of Graphistrength<sup>®</sup> C100 and FutureCarbon CNT-MW (around 90 nm) were significantly higher than the diameters of Baytubes<sup>®</sup> C150P and Nanocyl<sup>TM</sup> NC7000 (around 30 nm). The results of DLS show that the size of the dispersed Graphistrength<sup>®</sup> C100 nanotube agglomerates was the largest.

For better understanding of the deagglomeration of agglomerates the intensity weighted particles size distributions obtained by DLS and CSA were compared (Figure 5). Especially in the dispersions treated for a short ultrasonic time in the DLS measurements bimodal and very broad distributions were found indicating a heterogeneous particle distribution. With ultrasonic treatment time the dispersions got more homogeneous and size distributions narrowed. The comparison of the particle size distributions obtained by DLS and CSA shows similar results for FutureCarbon CNT-MW and Graphistrength® C100 whereas the particle size distributions of Baytubes<sup>®</sup> C150P, and Nanocyl<sup>TM</sup> NC7000 are very different. As mentioned above in DLS the dispersed particles are subjected to the Brownian motion and larger particles or aggregates are overestimated. It may be assumed that this also applies to non-spherical particles as in our case to the length of the CNTs or CNT agglomerates. In contrast to DLS in CSA the dispersed particles and aggregates are separated by centrifugal force and shear stresses. The particles can be assumed to be orientate in the centrifugal field that means that the sedimentation velocity is related to the sedimentation velocity of a spherical particle with a diameter corresponding to the lowest equivalent diameter of the nonspherical dispersed CNT particles [18-20]. For this reason one will detect with CSA the lower dimension of non-spherical particles and with DLS the higher dimension of non-spherical particles and agglomerates. Therefore, it can be assumed that the particles in the dispersions show a more spherical shape in case of FutureCarbon CNT-MW and Graphistrength<sup>®</sup> C100 whereas the Baytubes® C150P, and Nanocyl<sup>TM</sup> NC7000 particles in dispersion are more rodlike. For CSA, the main part of particles in Baytubes<sup>®</sup> C150P and Nanocyl<sup>TM</sup> NC7000 dispersions according to the highest intensity in the particle size distributions were found in the range of 15-30 nm (Figure 5) which corresponds to the range of the measured nanotube diameters of 6-26 nm. This indicates the presence of separated nanotubes in these dispersions after ultrasonic treatment. The main part of particles in Graphistrength<sup>®</sup> C100 and FutureCarbon CNT-MW dispersions after ultra sonic treatment were found at 70-100 nm

(Figure 5) which is a multiple of the diameters of single CNTs of 6-20 nm for Graphistrength<sup>®</sup> C100 or 9-30 nm for FutureCarbon CNT-MW. This means that after ultrasonic treatment the carbon nanotubes were found to be in small agglomerates or bundles rather than as separated single nanotubes.





Figure 5: Intensity weighted particle size distribution obtained by DLS (lines) and CSA (histograms) for Nanocy1<sup>TM</sup> NC7000, Baytubes<sup>®</sup> C150P, FutureCarbon CNT-MW, and Graphistrength<sup>®</sup> C100.

#### 4 Summary

Four different commercially available carbon nanotube materials were studied with regard to their dispersability in aqueous surfactant solution by varying ultrasonic treatment time. The sedimentation behaviour under centrifugal forces was studied. The particle size distributions of the dispersed nanotubes were analyzed.

The best dispersabilities were found for Nanocyl<sup>TM</sup> NC7000 and FutureCarbon CNT-MW. To prepare stable dispersions of Baytubes<sup>®</sup> C150P and Graphistrength<sup>®</sup> C100 a fivefold amount of energy was necessary. These findings correlate with the values of deformation stress measurements on the primary agglomerates which resulted in lower values for Nanocyl<sup>TM</sup> NC7000 than for Baytubes<sup>®</sup> C150P and Graphistrength<sup>®</sup> C100. In addition, the higher deformation stress of Baytubes<sup>®</sup> C150P and Graphistrength<sup>®</sup> C100 agglomerates is in good agreement with the higher bulk densities of the CNT materials of 120-170 kg/m<sup>3</sup> and 50-150 kg/m<sup>3</sup>, respectively. In contrast, Nanocyl<sup>TM</sup> CNTs having a low bulk density of 66 kg/m<sup>3</sup> exhibit also a lower deformation stress value.

The size of the primary agglomerates in the dry nanotubes powder as evidenced by SEM investigations and laser light diffraction measurements was found to be not related to the dispersability. The investigation of the particle size distributions in the aqueous surfactant dispersions using CSA indicated more rod-like shapes for particles of Baytubes<sup>®</sup> C150P and Nanocyl<sup>TM</sup> NC7000 dispersions after 30 minutes of ultrasonic treatment so that the presence of separated single nanotubes can be assumed. Due to the similarity of the particle size distributions obtained by DLS and CSA for FutureCarbon CNT-MW and Graphistrength<sup>®</sup> C100 after 30 minutes of ultrasonic treatment a more spherical shape of the dispersed small agglomerates was concluded. In addition, the comparison of sizes obtained by CSA with the nanotube diameters obtained by TEM indicates the existence of small agglomerates or bundles rather than single nanotubes. The ultrasonically treated Graphistrength<sup>®</sup> C100

material was detected to contain the largest particles using DLS as well as CSA and therefore it was assumed that the agglomerates were not completely dispersed into single nanotubes. These results help to optimize the processing of composites containing nanotubes. It has to be considered that more energy input is needed to disperse the Baytubes<sup>®</sup> C150P or Graphistrength<sup>®</sup> C100 to a similar dispersion quality like Nanocyl<sup>TM</sup> NC7000 or FutureCarbon CNT-MW. In addition, the information of the particle size and the concluded shape in the dispersions can contribute to understand the electrical or mechanical properties of nanotube composites.

## Acknowledgement

The authors thank Irma Mikonsaari from Fraunhofer ICT Pfinztal for the measurements of deformation stress of agglomerates and U. Geißler, C. Goltzsche, R. Kind, M. Heber, and R. Boldt (all IPF) for their technical support.

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