A method for determination of length distributions of multiwalled carbon nanotubes before and after melt processing

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Abstract

A relatively simple method to determine the length distribution of carbon nanotubes (CNTs) before and after melt processing was developed. This involves the selection of a suitable solvent for dispersing pristine CNTs as well as to dissolve the matrix of melt mixed composites and the choice of an appropriate nanotube concentration. The length of suitably individualized CNTs was visualized using transmission electron microscopy and length distributions were measured using image analysis. Examples are shown for Baytubes® C150HP and Nanocyl™ NC7000 and their melt mixed composites with polycarbonate where the same procedure was applied to both, measuring the initial length distribution and the distribution after recovering from the composites. These results indicated a significant shortening after melt processing up to 30% of the initial length.

1. Introduction

The electrical and mechanical properties of conductive composites based on carbon nanotubes (CNTs) are strongly affected by the properties of the CNTs themselves. Beside the dispersability, surface quality, and waviness also the aspect ratio of CNTs plays an important role for the formation of a conductive CNT network in a matrix. The exact determination of the length of carbon nanotubes is difficult and not often reported in literature. This is mainly caused by the difficulties to individualise nanotubes without any damage in such a way that it

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is possible to observe nanotubes as single tubes in microscopic techniques. Also the entanglements of several nanotubes restrict the individualisation. In addition, due to the huge aspect ratio it is a problem to follow long nanotubes in microscopic observations. For the individualisation of nanotubes, quite often dispersions in solvents or aqueous surfactant solutions are prepared, whereas the advantage of solvent-based CNT dispersions in comparison to aqueous surfactants solutions lies in the much easier removability of most solvents. In both kinds of dispersions the attractive van-der Waals forces between the CNTs and the interactions between CNTs and the solvent or surfactant are involved.

To explain the CNT dispersion state in solvents, in literature Hansen solubility parameters or Hildebrand parameters are used [1-3]. Hu et al. [1], Cheng et al. [2] and Bahr et al. [4] discussed different solvents for CNTs whereas the dispersability in the solvents was found to be different for different CNT materials. Aus outlined in [1], [4] after studying different solvents, e.g. chloroform was suitable for the investigated single-walled CNTs (SWCNTs) [4] or CNTs (without specification, [1]), whereas toluene was only successful in the study of [1]. Cheng et al. [2] concluded after studying a variety of different solvents in combination with SWCNTs (HiPCo) that it is difficult to justify a universal or characteristic solubility parameter for the nanotubes. Bergin et al. [3] estimated Hansen parameters for SWCNTs (HiPCo) to be $\sigma_D = 17.8$ MPa ^{½}, $\sigma_P = 7.5$ MPa ^{½}, and $\sigma_H = 7.6$ MPa ^{½}. However, according to these studies it is not yet fully understood why solvents and nonsolvents exist in the region of Hansen parameter space close to the solubility parameters of SWCNTs. Thus, in summary these studies did not come to conclusive results and could not explain why some solvents act better and others worse. Therefore, it seems to be necessary to find for each CNT type experimentally the solvent with the best dispersability.

For SWCNTs N-methyl-2-pyrrolidone [5-7] or dimethylformamide (DMF) [8] were described to be good dispersion mediums. Furthermore, for multiwalled CNTs (MWCNTs) chloroform

[9, 10], dichloromethane [11], ethanol [12-14] or acetone [15] were found to be suitable dispersion mediums.

Concerning the length distribution of CNTs, some authors report measurements on pristine nanotubes using microscopic methods after dispersing nanotubes in suitable solvents or after dissolving them from a matrix. Albuerne et al. [9] dispersed pristine and functionalized MWCNTs (Baytubes® C150P) in chloroform using ultrasound and placed a drop on a cleaned polished silicon wafer. Scanning force microscopy (SFM) was used for the examination of the nanotubes length distribution on approximately 100 nanotubes. Investigations on nanotubes lengths after incorporation in an epoxy resins were reported by Fu et al. [16] whereby the epoxy matrix was dissolved using DMF and low energy ultrasound. The MWCNTs were put on silicon plates and the measurement of the length of MWCNTs was carried out using scanning electron microscopy (SEM). The length of the initial nanotubes was taken from the CNT producer's datasheet to be 10-20 μm and a shortening up to 1.4 μm was described. Chen et al. [17] measured the nanotubes length after composite preparation by solution-mixing on approximately 150 nanotubes using field-emission scanning electron microscopy. For that, poly(methyl methacrylate)/MWCNT composites were dissolved in tetrahydrofurane (THF) for 48 h and the mixture was dropped on a transmission electron microscopy (TEM) copper grid. The length of the very long pristine CNTs was not measured in the same way, but controlled by the growth time during the nanotube synthesis which was found to be approximately 1 μm per minute, leading to initial nanotubes length between 20 and 100 μm. The comparison between the as-grown and the processed CNT indicated a strong shortening of MWCNTs up to 90% of the initial length during the sonication assisted composite preparation after a nanotubes surface oxidation step. Duncan et al. [18] investigated the fragmentation aspect ratio of differently functionalized MWCNTs in polycarbonate (PC) composites prepared by a solvent precipitation method. For the fractured composites, PC was dissolved in THF and a sample was placed on a TEM grid from which aspect ratio distributions of the partially broken nanotubes are shown based on over 100 tubes. For the initial length of the self-produced carpet-like CNTs 1000 µm were given. Lin et al. [19] determined the MWCNT lengths after melt dilution of a PC based masterbatch using SFM whereby a relatively harsh solvent and ultrasound treatment was used to extract the nanotubes from the PC matrix. The length of the nanotubes before incorporation into the masterbatch was taken from the producer’s datasheet to be between 10-15 µm. Using different small scale mixers a comparable lengths of the nanotubes in the range between 0.4 -0.6 µm was measured. It has to be considered that ultrasonication of nanotube dispersions may lead to mechanical damage and shortening [11] changing the length to be studied.

Krause et al. [20] performed SEM investigations on the remaining nanotubes after pyrolysing small amounts of MWCNT-polyamide composites melt mixed in small-scale under different conditions. By this, changes in the nanotubes lengths after melt compounding using different rotation speed could be estimated. However, a length distribution could not be obtained by that method.

Summarizing the trials to determine CNT length it has to be stated that no investigation discuss the length of pristine CNTs and CNTs recovered from a composite simultaneously using the same preparation and measurement method. Therefore, in our study the length distributions of pristine and processed CNTs were assessed using the same procedure, namely by dispersing both in a suitable solvent, applying TEM on individualized nanotubes and performing image analysis. In this way the obtained results concerning the CNT length are comparable and a method to discuss reliably effects of processing dependent shortening was established.

2. Experimental

Two kinds of commercially available multiwalled CNTs were used as supplied: Baytubes® C150HP (Bayer MaterialScience AG, Germany) and Nanocyl™ NC7000 (Nanocyl S.A., Belgium). Nanocyl™ NC7000 are characterized by a carbon purity of 90 % and a surface area of 250-300 m^2/g [1]. The bulk density in accordance to EN DIN 60 was determined to be about 66 kg/m^3, the outer nanotube diameter is 10±3 nm [10], and the agglomerate size is larger than 675 µm [21]. Baytubes® C150HP are characterized by a carbon purity of about 99 %, a bulk density of 140-230 kg/m^3 [2], an outer diameter of 11±3 nm [10], and a agglomerate size of 10-600 µm [21].

For the dispersability tests of pure nanotubes different solvents were used, namely acetone, ethanol, n-hexane, chloroform, p-xylene, 1-butanol, petroleum ether, 1,2,4-trichlorbenzene, and dodecane (all Merck KGaA, Germany). The MWCNT materials (1 mg) were located in a glass flask and wetted by the solvents (10 ml) at room temperature leading to a concentration of 0.1 g/l. After a short treatment for 3 min in an ultrasonic bath (SONOREX RK100H, BANDELIN electronic GmbH, Germany, frequency 35 kHz, ultrasonic power 80 W), assumed not to shorten the nanotubes length significantly, the dispersions were observed visually. For the nanotubes length investigations, finally chloroform was used to disperse both kinds of the pristine nanotubes using the ultrasound conditions described above.

In order to investigate the nanotubes length distribution after processing, two melt mixed composites based on PC with Nanocyl™ NC 7000 or Baytubes® C150HP were used for extracting the MWCNTs. The first composite was processed by diluting a masterbatch containing 7.5 wt% Nanocyl™ NC 7000 in PC (Lexan™ 141R, Sabic Innovative Plastics, The Netherlands) towards a composite with 2 wt% MWCNTs as it is described in [22]. Both processing steps were performed using a co-rotating twin-screw extruder ZE25 (Berstorff, Germany) at a mean barrel temperature of 260°C, 500 revolution per minutes (rpm), a

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[1] Nanocyl. Data sheet Nanocyl 7000. Edition 2007-02-05. Sambreville, Belgium; 2007.

[2] BayerMaterialScienceAG. Data sheet Baytubes® C150HP. Edition 2007-05-14. 2006.

throughput of 5 kg/hours and an optimized screw configuration (SC5 in [22]). The second composite was prepared by direct incorporation of 1 wt% Baytubes® C150HP in PC (Makrolon 2600, Bayer MaterialScience AG, Germany) using a DACA microcompounder (DACA Instruments, USA) having two conical co-rotating screws operating at 280°C, 300 rpm, and 5 minutes mixing time as described in [23]. The materials were fed simultaneously in the hopper of the compounder, where the predried PC granules and as- received CNT powder were added alternatively in small portions within about 1 min.

For the evaluation of the nanotubes length distribution in these composites, small pieces of the extruded strands as received from the extruder or the microcompounder were dissolved in chloroform at room temperature without any additional treatment for 1 hour and the dispersions were afterwards treated for 3 min in an ultrasonic bath using the already mentioned conditions. The nanotube concentration in the dispersions was selected to be again around 0.1 g/l.

For the TEM investigations a drop of the freshly prepared dispersion with 0.1 g CNT/l, either received from the pure or the nanotubes recovered after melt processing, was placed on a TEM grid with a carbon coating and dried at air. In the TEM images collected with a Libra120 or a Libra200 (Carl Zeiss GmbH, Germany) the nanotube lengths were measured on approximately 400 particles applying the software SCANDIUM 5.1 (Olympus Soft Imaging Solutions GmbH, Germany) using the full visible length of each separated nanotube not touching the edge of the image by applying the *polyline* function. In order to measure the length of very long nanotubes in some cases several images were stitched together. The results are given as number distributions with class sizes of 100 nm. To quantify the nanotubes length distribution, the typical distribution parameters x_{10}, x_{50} and x_{90} were calculated indicating that 10%, 50%, and 90% of the nanotubes lengths are smaller than the given value.

3. Results

In order to find a suitable solvent for the dispersion of pristine MWCNTs, different solvents were tested, namely acetone, ethanol, n-hexane, chloroform, p-xylene, 1-butanol, petroleum ether, 1,2,4-trichlorbenzene, and dodecane. For investigations of the dispersability in the different solvents the MWCNT materials were wetted by the solvents. Immediately, the CNTs settle on the bottom of the glass flask and the remaining supernatant appears transparent. After a short ultrasonic treatment for 3 min, assumed not to shorten the nanotubes length significantly, the dispersions showed different appearances as summarized in Table 1. The three different kinds of dispersions are illustrated in Figure 1 and can be described in the following way:

- “dispersed”: The nanotube dispersion is black within which CNT agglomerates with increased agglomerate volume could be observed.
- “swollen”: The nanotube material settles on the bottom of the flask. A significantly increase of the volume of CNT agglomerates can observed. The high of the sediment rise in comparison to *sedimented* CNT dispersions.
- “sedimented”: The nanotube material settles on the bottom of the flask. No changes of the volume of CNT agglomerates could be observed.

Table 1: Description of CNT dispersions in different solvents (0.1 g/l CNT after 3 min ultrasonication)

solvent	**Baytubes® C150HP**	**Nanocyl™ NC7000**
acetone	+	+
ethanol	-	+
n-hexane	+	+
chloroform	++	++
p-xylene	+	-
dodecane	-	-
petroleum ether	+	+
1-butanol	-	-
1,2,4-trichlorbenzene	-	-

++) dispersed; +) swollen; -) sedimented

dispersed swollen sedimented

Figure 1: Different states of CNT dispersion

The best dispersion as observed by optical observation for both types of CNT was achieved in chloroform. The CNT agglomerates were swollen and the supernatant appeared as a homogeneous black dispersion. Swollen agglomerates of Baytubes® C150HP and Nanocyl™ NC7000 below a transparent supernatant were found in acetone, n-hexane, and petroleum ether. Nanocyl™ NC7000 agglomerates swelled in ethanol. In contrast, Baytubes® C150HP material sedimented in ethanol and was swollen with a transparent supernatant after one week. In p-xylene only agglomerates of Baytubes® C150HP swelled with a transparent supernatant, whereas Nanocyl™ NC7000 sedimented. The initial swelling of the nanotubes agglomerates by solvent infiltration and interaction has to be considered as a crucial precondition to individualise nanotubes in additional steps, like further sonication. Thus, dodecane, 1-butanol, and 1,2,4-trichlorbenzene were found to be not suitable to disperse both investigated nanotube materials.

Based on the dispersability tests, chloroform was used to disperse the pristine nanotubes using the ultrasound conditions described above. In Figure 2 the length distributions of pristine Baytubes® C150HP and Nanocyl™ NC7000 are shown. Nanocyl™ NC7000 nanotubes are found to be significantly longer than Baytubes® C150HP. In addition, for Nanocyl™ NC7000 a very broad length distribution was found with several nanotubes up to 10 µm.

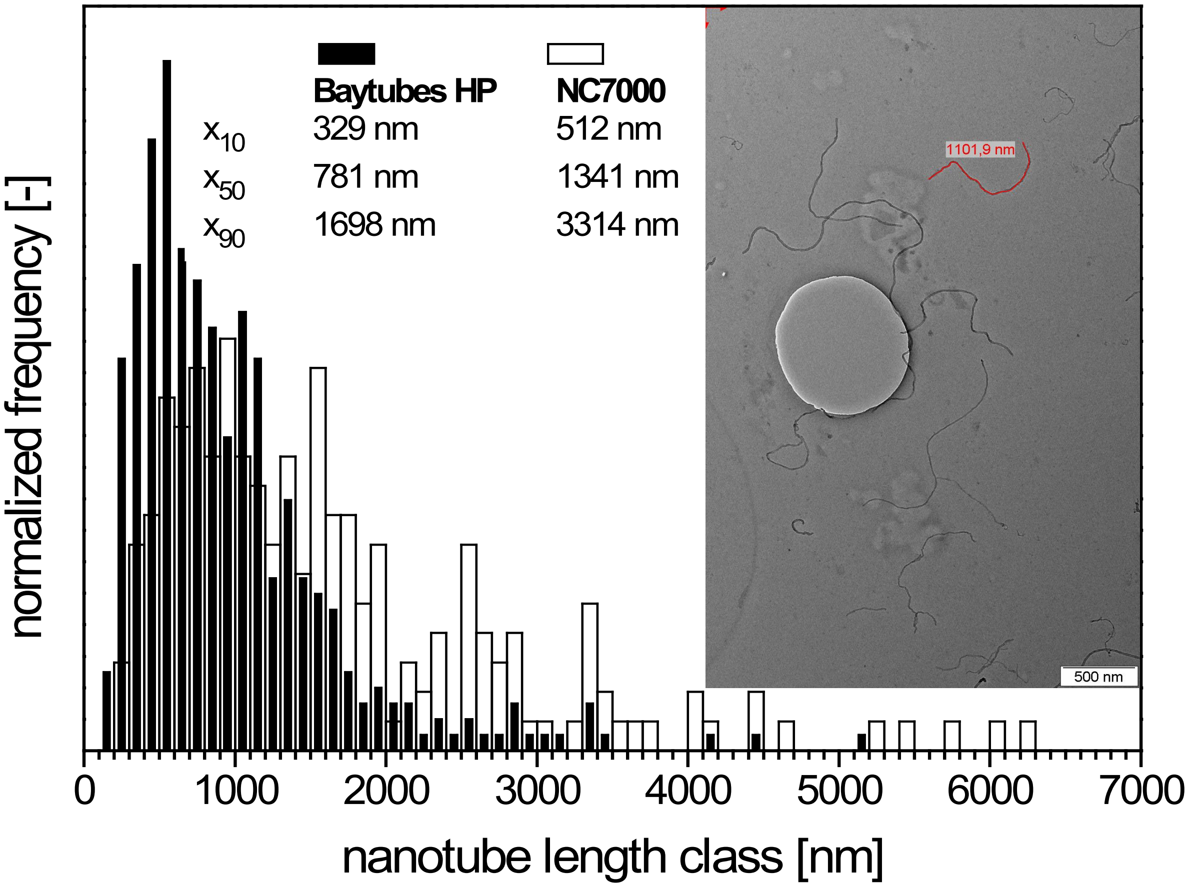

Figure 2: Length distribution of Nanocyl^{TM} NC7000 and Baytubes$^{®}$ C150HP (total number of particles: 402 (Baytubes), 314 (NC7000)), including a TEM image of NC7000 combining 2 images with an exemplary length measurement of one MWCNT

For exemplarily measuring the nanotubes length after processing two MWCNT filled polycarbonate (PC) composites were selected. The examples were chosen to demonstrate that the method works independent on the special grade of the polymer (here polycarbonate), carbon nanotube type, and the specific processing conditions. Figures 3 and 4 show the comparison of length distributions of both nanotube materials before and after melt processing in the polycarbonate composites. Due to the different quality of the nanotubes, composite concentrations, and compounding conditions the degree of shortening is not comparable between both composites. In case of the composite containing 2 wt% Nanocyl^{TM} NC7000 (Figure 3) produced by the two-step melt processing and using the initially longer nanotubes a more significant shortening of the nanotubes length to about 30% (related to x_{50} -value) was observed.

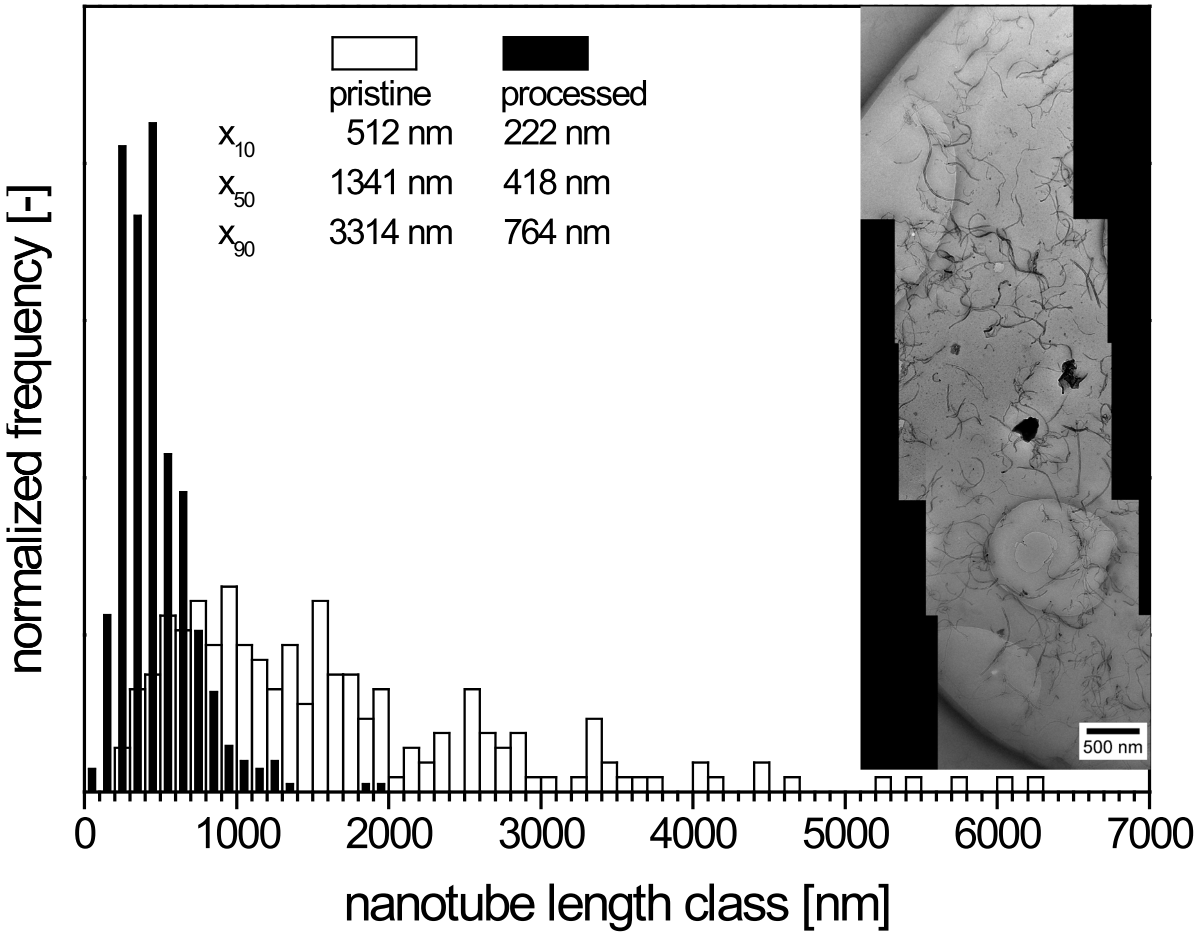

Figure 3: Comparison of length distribution of Nanocyl^{TM} NC7000: before (pristine MWCNTs) and after processing (as recovered from a melt processed PC composite with 2 wt% MWCNTs) (total number of particles: 314 (pristine NC7000), 409 (processed NC7000)), including TEM images of processed NC7000 combining 5 images

The comparison of nanotubes length distribution of Baytubes® C150HP before and after melt processing into composites containing 1 wt% is shown in Figure 4. Under the conditions selected the Baytubes® C150HP were shortened to about 50% of their initial length (related to x_{50}).

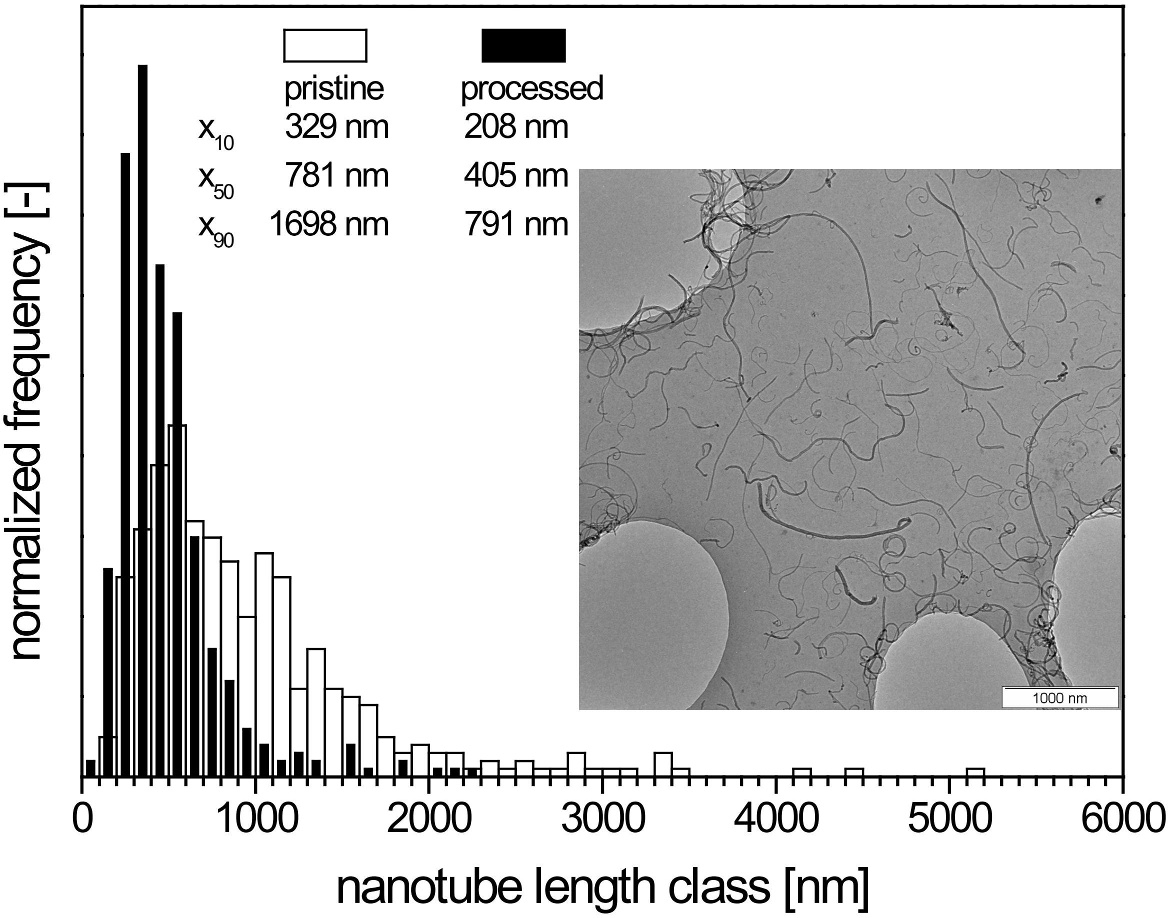

Figure 4: Comparison of length distribution of Baytubes® C150HP: before (pristine MWCNTs) and after processing (as recovered from a melt processed PC composite with 1 wt% MWCNTs) (total number of particles: 402 (pristine Baytubes® C150HP), 402 (processed Baytubes® C150HP)), including TEM images of pristine Baytubes® C150HP

In the TEM images (see e.g. Figures 3 and 4) a good individualisation into single nanotubes is visible again indicating that chloroform is a good dispersing agent for the pristine CNTs but on the same time also a good solvent for PC.

The presented principle to dissolve CNT from composites using suitable solvents and to work with suitable concentrations of nanotubes when preparing the samples for TEM also can be applied to other polymeric matrices. A precondition is that the solvent used for dissolution of the matrix should be also a good dispersion agent for the CNTs. If this cannot be achieved, a combined strategy using different solvents for dissolving the matrix and dispersing the extracted nanotubes as presented in [19] may be used.

For the investigated industrial nanotubes recommendations can be given based on the dispersability tests presented. For example, for composites containing Baytubes® C150HP in polyethylene it should be favourable to use p-xylene or n-hexane as compared to 1,2,4-trichlorbenzene to disperse the nanotubes and extract them from composites.

Summary

In this paper, a relatively simple method is presented which allows determining the nanotubes length distributions of as received MWCNTs as well of the same nanotubes recovered from processed composites using the same methodology. The method consists of the selection of suitable dispersion media for the pure nanotubes, which were shown to differ when using two commercial nanotubes materials. The investigation of the dispersability in different solvents gave the best results for both kinds of MWCNTs, namely Baytubes C150HP and Nanocyl™ NC7000, in chloroform. However, the dispersability in ethanol and p-xylene differed with the type of MWCNTs. The method also includes the choice of a suitable concentration for preparing dispersions leading to individualized and thus measurable nanotubes after deposition on a TEM grid, which was found to be 0.1 g CNT/l solvent. The method also encloses the use of the same solvent for nanotube dispersion in order to recover processed nanotubes from composites. In the presented examples, polycarbonate based composites were dissolved in chloroform. In this way the results concerning the CNT length obtained using image analysis on TEM images are obtained under comparable conditions and therefore can be directly related. The focus of the paper was to develop a method for the characterization of CNT length distribution. In order to show the applicability, two examples of melt mixed composites based on polycarbonate and the two different nanotubes are presented illustrating the obviousness of the results. On both examples a significant nanotube shortening after melt processing up to 30 % of the initial values could be demonstrated which to our knowledge was not quantified before.

Based on the method, now systematic studies on the nanotubes shortening in dependence on mixing procedures, mixing conditions, nanotube properties, nanotube pre-treatments and others are possible and will be presented in further studies.

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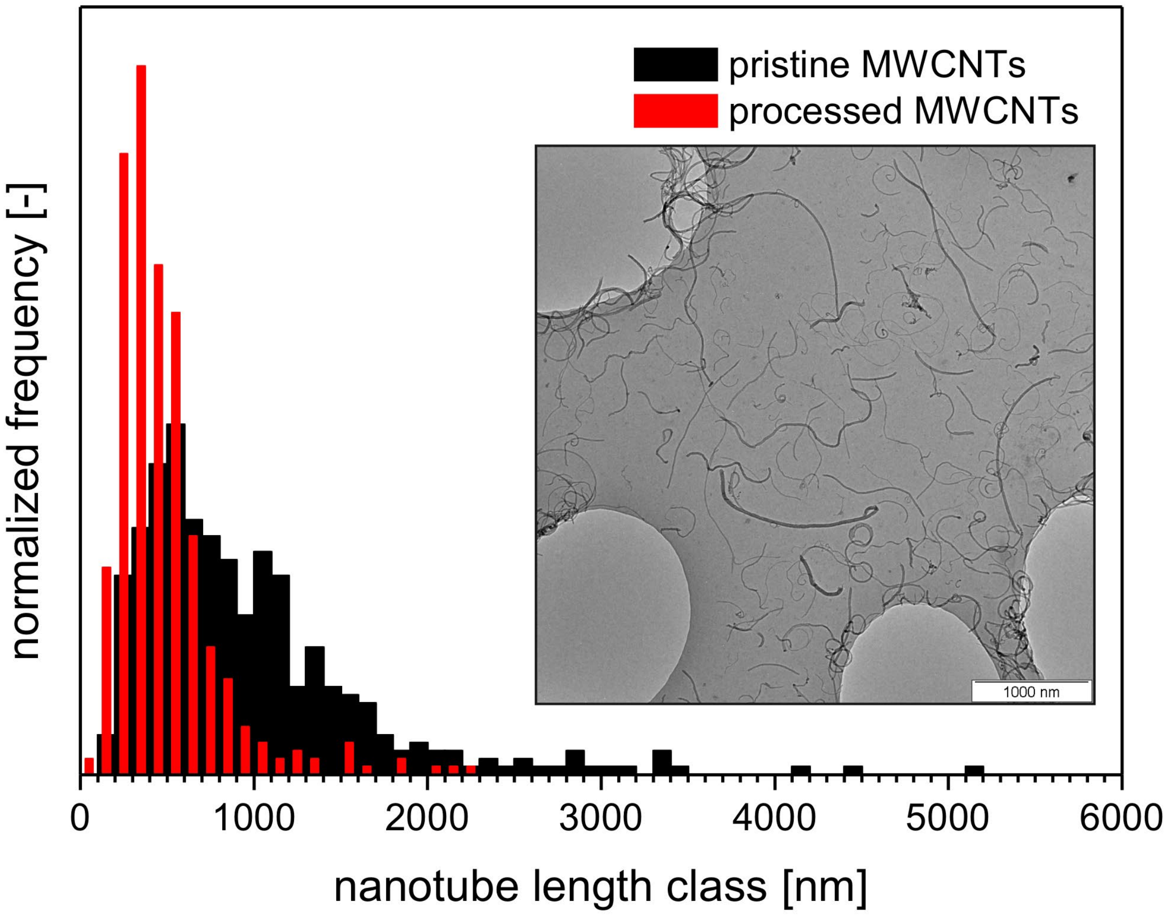
Graphical Abstract



A method to determine the length distribution of carbon nanotubes (CNTs) before and after melt processing was developed. This involves the selection of suitable solvents for dispersing pristine CNTs as well as dissolving the matrix of composites, the length visualization using transmission electron microscopy, and the quantification using image analysis.