

# Processing of nanoscaled fibres (CNT) at a pilot plant

Field measurement report No 2

## Imprint

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# 1 Abbreviations and acronyms

A	alveolar
BAuA	Federal Institute for Occupational Safety and Health (in Germany)
CNF	Carbon Nanofibres
CPC	Condensation Particle Counter
CNT	Carbon Nanotubes
DISC	Diffusion Size Classifier
DMA	Differential Mobility Analyzer
ENM	Engineered Nanomaterials
FFP	Filtering Face Piece
HEPA	High Efficiency Particulate Airfilter
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
LEV	Local Exhaust Ventilation
MSDS	Material Safety Data Sheet
MWCNT	Multi-Walled Carbon Nanotubes
NanoGEM	Nanostructured materials – Health, Exposure and Material properties
NAS	Nanoparticle Aerosol Sampler
NSAM	Nanoparticle Surface Aerosol Monitor
PPE	Personal Protective Equipment
SEM	Scanning Electron Microscope
SMPS	Sequential Mobility Particle Sizer
SOP	Standard Operating Procedure
TB	tracheobronchial
TEM	Transmission Electron Microscope
TP	Thermal Precipitator
WHO	World Health Organization

## 2 Summary

Within NanoValid, the BAuA laboratory for nanomaterials assessed and evaluated inhalative exposure to nanomaterials at different workplaces. The aim of these field studies was to check if the installed protective measures were effective and if a risk of the workers was sufficiently reduced. In all studies, the risk assessment combined measurements and a non-measurement approach in terms of an additional inspection of the specific workplace situation. The present report refers to a pilot plant where nanoscaled carbon fibres (CNT) were compounded into polymers by an extruder. The occupational safety and health situation was evaluated both by measurements and by an additional inspection of the specific workplace situation and during activities with nanomaterials.

This report presents:

- an example for a guided dialogue (non-measurement method)
- a detailed measurement report, including morphological analysis of particles
- a conclusion combining the findings of both approaches
- the design of a technical solution for improved handling

The dialogue guide is a short check list with questions that provide an overview of workplace activities, nanoscaled substances and installed protection measures. It covers nanospecific issues as well as general occupational safety and health aspects.

The measurement report summarises results from the measurements during decanting CNTs from a storage hobbock into a smaller container and during handling of that container to load the extruder.

No significant release of CNT aerosols was detected. However, individual single and agglomerated nanofibres were detected on contact samples that were analysed subsequently by SEM (scanning electron microscope). Hence, a limited release of fibrous nanomaterials was assumed. However, a critical exposure of the workplace environment could be largely excluded.

The portioning of CNTs was performed outside of the plant – under open sky – with full-body protection of the workers who poured CNT grains from the hobbock into the container. No technical measures were applied. In order to improve occupational safety and to prevent pollution of the environment, a concept for a closed portioning system was developed by the involved safety experts. The design of that system provides a solution to open a bag containing CNTs inside a closed, glovebox-like enclosing. The CNT fibres are filled into a dosing unit for further processing. Handling from outside the box using installed gloves would help to establish safer working conditions. Since respiratory protection was permanently worn by all employees at the extruder site inside the production hall, it was emphasized that burdensome respiratory protection should be limited to short accompanying activities. Moreover, it is recommended to have the existing local exhaust ventilation running when nanomaterials are handled. Exhaust ventilation should be always positioned near the performed activity.

### 3 Introduction

The manual “Nano to go!” compiles information and training material for people, who are responsible for the implementation of occupational safety and health issues at a company level. It contains valuable information on safe handling of nanomaterials and other advance materials at workplaces.

In general, a specific workplace situation can be assessed either by using exposure measurements or by applying non-measurement methods like comparing the specific situation to standardised work routines and by using control banding tools. Since the reliability of the risk management depends highly on the quality of these approaches, it is important to provide professional advice on how to actually assess the workplace situation and how to perform adequate exposure measurements as potential efficiency control. “Nano to go!” aims to provide such advice in form of field study reports. The field study reports exemplify a way to address occupational safety and health issues when working with nanomaterials.

The present field study was performed at a pilot plant, where nanoscaled carbon fibres (CNT) were compounded into polymers by an extruder. The report includes an exposure measurement and a non-measurement method.

- a) The selection of the **non-measurement method**, here a **guided dialogue** on occupational safety and health aspects, is based on the approach of the brochure, which focusses on safety strategies for occupational safety and health for handling nanomaterials at workplaces. The dialogue guide can also be found among the supplementary items compiled for “Nano to go!”.
- b) The **exposure measurement** was performed according to standard operation procedures (SOP's), which were developed during the project NanoGEM (described in the section 5.3 sampling strategy). The measurements at the respective workplaces were carried out either according to tier 2 (basic assessment) or according to tier 3 (expert assessment) and take the background concentration into account. The aim of this field study measurement was to evaluate the particle number concentration including the particle size distribution and the surface area of the alveolar dust fraction (A-dust) as well as the mass concentration.

## 4 Dialogue guide for occupational safety and health aspects for handling nanomaterials

<b>DIALOGUE GUIDE FOR OCCUPATIONAL SAFETY AND HEALTH ASPECTS FOR HANDLING NANOMATERIALS (NM)</b>		
Company/Institution:	Contact data:	Date:
	Contact person:	

**Question 1: Are NM**

- Produced
  - Processed
  - Released during production / processing
- in your company / institution?

.....

.....

.....

**Question 2: How many employees come into contact with NM in your company / institution?**

- < 10
- 10 to < 50
- 50 to < 100
- ≥ 100

.....

.....

.....

**Question 3: In which form are the NM produced / processed / released?**

- Fibre
- Dust
- Aerosols
- Liquids

.....



.....  
.....

**Question 4: Which NM is (are) produced / processed / released during the working procedures?**

*Carbon nanotubes*

.....  
.....  
.....

**Question 5.1: What is the quantity of NM handled on a daily basis?**

- g/day (ml/day)
- kg/day (l/day)
- t/day (m<sup>3</sup>/day)

.....  
.....  
.....

**Question 5.2: What is the quantity of NM handled on a yearly basis?**

- g/year (ml/year)
- kg/year (l/year)
- t/year (m<sup>3</sup>/year)

**Question 6.1: Are MSDS for the produced / processed nanomaterials available in your company? (Can the MSDS be shown? Can they be delivered? Are they accessible for all employees?)**

- Yes
- No

.....  
.....  
.....

**Question 6.2: Do the MSDS refer specifically to NM?**

- Yes
- No

.....  
.....  
.....

**Question 6.3: Do the MSDS contain the following information?:**

Does the classification of the hazardous properties (see below) refer specifically to the nanoscaled form?

.....  
 .....

Are threshold values for alveolar dust (A- dust) and / or particle number concentration?

.....  
 .....

Morphological information (form, structure, i.e. is it for example a stiff fibre...)

.....  
 .....

Solubility in water (g/l range → well soluble, below 100 mg/l → insoluble)

.....  
 .....

Information about dustiness / dust number

.....  
 .....

Information about human toxicity

Acute toxic (R23, R24, R25; H301, H311, H331)

Chronic toxic (R48)

Carcinogenicity (carc. 3) (R68)

Irritating to skin (R38; H315)

Sensitisation by inhalation (R42, R43; H317)

.....  
 .....

**Question 7: Do you include NM safety information in training courses and occupational-medical and toxicological advice?**

Yes       No

Are there any specials?

*Since no long-term studies exist, a preventive occupational safety approach is followed.*

.....

.....

.....

.....

**Question 8: Which of the following operations are performed on NM?**

**1. mixing and dispersion**  
⋯⋯ **Control guidance sheet 215:** Mixing of solids with other solids or liquids (additional measures)

.....

.....

**2. filling and bagging**  
⋯⋯ **Control guidance sheet 204:** Removing waste from a dust extraction unit (additional measures)

*The filling is performed open in the outdoor area.*

.....

.....

**3. charging and decanting**

*Charging and decanting is performed open in the outdoor area*

.....

.....

**4. weighing**

*Weighing is performed in a capsulated metering device.*

.....

.....

... Control guidance sheet 214: Weighing solids (additional measures)

.....

.....

5. spraying

.....

.....

6. coating (of surfaces)

.....

.....

7. other

.....

.....

... Control guidance sheet 240: Dust workplaces (principles)

**Question 9: Which of the following protection measures are used when handling NM?**

**Technical protection measures – ventilation:**

- Function and efficiency is regularly inspected, at least once per year.
- Before starting work the ventilation is switched on and tested.
- The ambient air movement is across or away from the employee.
- Is data on the amount of alveolar dust (A- dust) and / or particle number concentration at the workplace available respectively does data on the fibre amount exist?
  - Yes
    - How high was the exposure?
  - No → *will be soon performed from particle exposure experts.*

Which of the following technical measures are used when working with NM?:

- Local exhaust ventilation (LEV) → *at the extruder*
- Fume hood
- Glove box
- Safety cabinet

Which of the following technical measures are used when working with NM in form of aerosols:

- Closed facility
- Closed spray booth with automated change of moulded part
- Open spray booth, the spray dusts are captured by exhaust ventilation
- If spraying is performed manually, the spray lance is as long as possible. The drop size is preferably >100 µm (no inhalable mist)

❖ **Control guidance sheet 100:** General ventilation (minimum requirements)

❖ **Control guidance sheet 200:** Local exhaust ventilation (source extraction) (additional measures)

❖ **Control guidance sheet 301:** Glove box (closed system)

.....

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.....

.....

**Technical protection measures - processes:**

- Low-dust drop and dump areas
- Low-dust processing and disposal methods

*Low dust methods are not yet procured, but purchase is planned. Several CNT-manufacturers offer suitable containers for the metering device.*

.....

.....

**Organisational protection measures:**

- Hazardous substances are clearly labelled
- Containers for waste disposal are clearly marked and labelled

→ *Since the CNTs are completely processed, no waste disposal took place yet. In the case concerned, CNTs would not be disposed separately, but in containers for plastic waste.*

- Surfaces are easily cleaned (*partly*)
- Possibilities for dust deposits are minimised. (*unfortunately some dust deposit possibilities exist*)
- Wet cleaning is mandatory. (*with water*)
- Industrial vacuum cleaners are available. (*one special vacuum cleaner for CNTs is present*)

Type of filter: (*not known*)

- M
- H
- Appropriate clean-up equipment for leaking or spilled agents are available and easily accessible.

→ *are disposed separately*

- Cleansing wipes are not kept in pockets.
- Dusty protection clothes are not shaken out or blown off

→ *not applicable, since disposable suits are worn one time and then disposed.*

- In case of dusty activities, only clean filtered air (filter type H) is recycled.
- Bulk goods and open containers are covered.
- Dusty agents are stored in closed containers.
- Basic occupational hygiene standards are adhered to.

❖ **Control guidance sheet 110:** Inhalation - Basic Safety Precautions (Principles)

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**Personal protective measures:**

- Instructions on how to use, maintain and properly store protective equipment, are readily available.
- Chemical-resistant gloves are used.

Type: *nitrile*

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Protective equipment is correctly stored in a dedicated area.

Is protective clothing worn?

Material of protective clothing (if a high amount of material is handled) *100 % polypropylene*

Dust: Type 3 (*not known*)

Aerosols: Type 4

Is a respirator used for short-term activities?

Type of respirator? Type of filter?:

P2      P3

FFP2      FFP3

Other

*The duration of the activity is maximal 2 hours uninterrupted, maximal 4 hours a day. Once a year, the occupational health physician reviews the health.*

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## 5 Exposure measurements of fine and ultrafine dusts and fibres in a pilot plant

### 5.1 General

■ Measuring task:	Workplace measurements in the field - polymer processing plant - extruder
■ Company:	20120911
■ Participants in the preliminary discussion:	Company representatives, BAuA representatives
■ Measurement date:	From 11.09.2012 to 12.09.2012
■ Receipt of samples at:	12.09.2012
■ Sample number:	From AP-2012-09-11-1 to AP-2012-09-12-14 (BAuA dust laboratory Berlin)
■ Analyses carried out by:	BAuA representatives
■ in:	November 2012
■ Preparation of measurement report:	BAuA representative

### 5.2 Description of the measurement procedure

#### **SMPS from Grimm Aerosol Technik<sup>1</sup> – Sequential Mobility Particle Sizer:**

The SMPS detects the particle number concentration in a size range of 10 nm to 1000 nm (LDMA) respectively of 5 nm to 350 nm (MDMA). The pre-impactor removes coarse particles out of the air volume flow before they enter the actual measuring system. With the aid of a neutralizer, the air volume flow is then brought into a state of defined charge distribution (charge equilibration). Subsequently, the particles are separated in the DMA (classifier) according to their mobility in an electrical field (44 size classes). Only particles of the respective charge and size move to the sample air outlet and enter the condensation particle counter (CPC). Within the CPC, the mono-disperse aerosol is directed in a heated saturation tube (N-butanol). The surfeited steam condenses onto the particles by a subsequent cooling. In this way, the particles are enlarged to a size of about 10 µm and counted by a laser beam.

#### **CPC 3007 from the company TSI<sup>2</sup> (Condensations Particle Counter):**

The handheld measurement device detects the particle number concentration time resolved within a size range of 10 nm to 1000 nm. Within the CPC 3007, the particles condense on a saturated isopropanol solution. The measurement system does not classify the particles, but provides a total number concentration for the whole measurement range.

#### **NSAM from the company TSI<sup>3</sup> (Nanoparticle Surface Aerosol Monitor):**

The surface monitor for nanoparticles detects the human lung-deposited surface area of particles (expressed in µm<sup>2</sup>/cm<sup>3</sup>), corresponding to the tracheobronchial (TB) or alveolar (A) regions of the lung.

#### **NAS from the company TSI<sup>4</sup> (Nanoparticle Aerosol Sampler):**

With the nanoparticles aerosol sampler (NAS), samples of charged particles (similar to those from the output of a differential mobility analyser (DMA)) can be transferred on substrate for further analyses.

<sup>1</sup> Manufacturer brand of the company GRIMM Aerosol Technik GmbH & Co.KG

<sup>2</sup> Trademark from the company TSI Incorporated

<sup>3</sup> Trademark from the company TSI Incorporated

<sup>4</sup> Trademark from the company TSI Incorporated



### **Aerosolspectrometer 1.109 from Grimm Aerosol Technik<sup>5</sup> - particles in a size range of 0.25 to more than 32 µm are detected:**

- Aerosolspectrometer 1.109 gravimetric - The measurement device detects the particles in a laser measurement chamber in 30 different size channels and shows the result as particle mass concentration.
- Aerosolspectrometer 1.109 numerical – The measurement device detects the fine particles with a laser measurement chamber in 30 different size channels and shows the result as particle number concentration.

### **TP, prototype device from BAUA (Thermal Precipitator):**

The TP is applied as collection system and works on the basis of thermophoresis. The air flows through two heating plates and precipitates on a cold heating plate, which is laid out as a sample carrier (Si plate). Subsequently, the sample carrier is analyzed with scanning electron microscopy.

## 5.3 Sampling strategy

The sampling is made according to the standard operating procedures generated in the BMBF project NanoGEM. Link:

[http://www.nanogem.de/cms/nanogem/upload/Veroeffentlichungen/nanoGEM\\_SOPs\\_Tiered\\_Approach.pdf](http://www.nanogem.de/cms/nanogem/upload/Veroeffentlichungen/nanoGEM_SOPs_Tiered_Approach.pdf)

A tiered exposure assessment serves as basis. The tiered approach applies as long as no legally binding, health-based limit values for the engineered manufactured nanomaterials (ENM) exist.

### ■ **Tier 1 (Information gathering)**

The task in tier 1 is to clarify, e.g. through on-site inspection, whether nanomaterials are used in the workplace and if they can be released from the corresponding processes. If a release can-not be excluded, a potential exposure has to be determined in tier 2.

### ■ **Tier 2 (Basic assessment)**

As long as no health based limit values exist for engineered nanomaterials, measurements are performed compared to an intervention level. These measurements can either be performed as a short-time screening or a temporary, respectively permanent, monitoring. If the intervention level is exceeded significantly, a potential exposure exists and has to be assessed in tier 3. Exposure measurements in tier 2 are conducted using handheld and easy-to-use devices and are performed to a limited extent. Measurement parameters coming into consideration can be particularly size-integrated particle concentrations, for instance the total number concentration. Typical measurement devices are handheld condensation particle counters (handheld CPCs) and devices based on electrical diffusion charging (DISCmini, nanoTracer, Aerotrak 9000).

### ■ **Tier 3 (Expert assessment)**

Within tier 3, a potential exposure to ENM at the workplace is assessed with extended measurement device expenditure. In this case, measurement devices like the SMPS, CPC, NSAM or Aerosol spectrometer are applied. At the same time, collecting systems are applied, which collect samples for a subsequent analysis by SEM, TEM or ICP-AES.

Measurements in tier 3 always include the determination of the particle background load either by a simultaneous measurement at a representative background location (Two-devices-solution) or by a measurement of the load of the workplace itself before and after the process (One-device-solution).

<sup>5</sup> Manufacturer brand of the company GRIMM Aerosol Technik GmbH & Co.KG

### Quality check of the measurement devices in the laboratory and during the measurements on-site:

Beside the annual calibrations by the producer, the particle number concentrations of the measurement devices are compared with identical measurement ranges before (in the laboratory) and during the measurements (on-site) according to the SOP in order to recognize and if necessary remove deviations. The results of these comparisons are shown in figure 1.

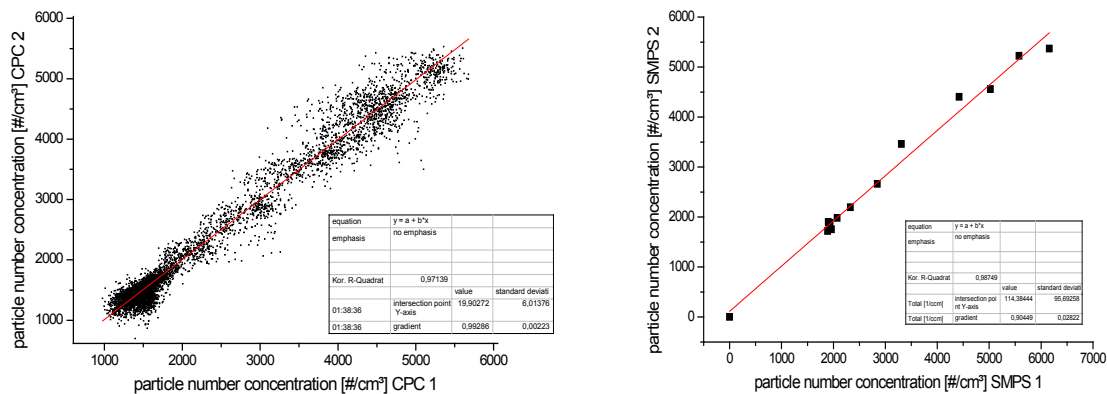


FIGURE 1: COMPARATIVE MEASUREMENT WITH THE CPC (LEFT) AND THE SMPS (RIGHT)

The comparisons of the measurement devices showed good correlations, i.e. the devices work reliably and provide robust and representative measurement results.

## 5.4 Workplace measurements in the polymer processing plant - extruder

### Performance of sampling:

The workplace measurements in the polymer processing (extruder) area were made in accordance to the above-mentioned measurement strategy of tier 3 (expert assessment).

### Description of the workplace:

At the present workplace, CNTs are handled in the area "polymer processing". The activity at the extruder, where CNTs are worked into polymers, is performed in small series production and discontinuously. Several test parameters with different CNT contents and different temperatures were adjusted on the measurement days. During the work process, the employees were located in different relevant areas next to the extruder. In accordance with this, the stationary sampling was performed at the measuring points MP1/MP2 on the stage respectively platform and MP3 (computer worktable) as well as MP4/MP5 in close proximity to the extruder in the lower area (see figures 2 and 3). Two employees performed the activity.

Before the activity at the extruder, the exposure to CNTs was determined during the filling process in the outer area in front of the pilot plant.

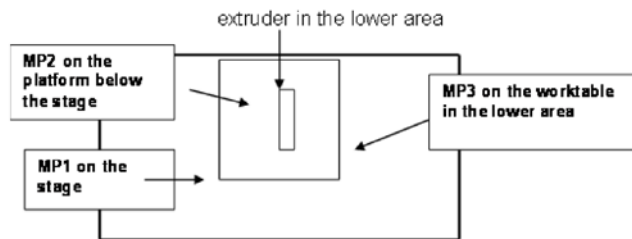


FIGURE 2: SCHEMATIC DIAGRAM OF SAMPLING IN CLOSE PROXIMITY TO THE EXTRUDER (ON THE STAGE)

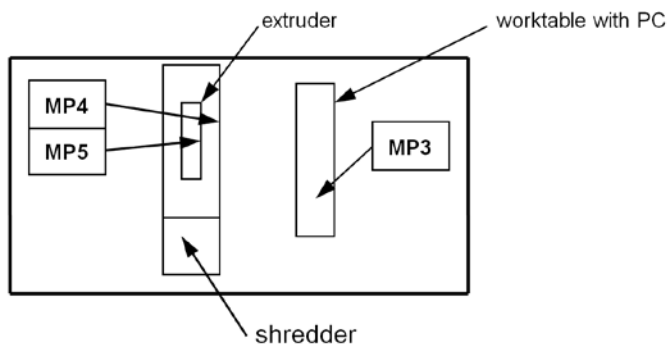


FIGURE 3: SCHEMATIC DIAGRAM OF SAMPLING IN CLOSE PROXIMITY TO THE EXTRUDER (LOWER AREA)

**Room size :** Pilot plant  
approximately 70 x 30 x 10 m<sup>3</sup>

**Ventilation:**

- Pilot plant – closed area
- Exhaust ventilation – directly above the extruder and on the platform
- Doors of the pilot plant partly opened, gates closed (open during the fire alarm)

**Description of the detected substances and preparations:**

During the measurement days, MWCNT (multi-walled carbon nanotubes) were decanted and worked into the polymer within the extruder.

TABLE 1: SAMPLING PROTOCOL FOR THE WORKPLACE – POLYMER PROCESSING – EXTRUDER AREA

DATE	SAMPLE NUMBER	MEASURE-MENT METHOD	MEASUREMENT TASK	VOLUME FLOW l/min	SAMPLING PERIOD		SAMPLING DURATION min	SAMPLING MODE	CLIMATE
					FROM	TO			
11.09.12	AP-2012-09-11-1	SMPS (LDMA)	determination of the particle number concentration before and after the decanting process in the outer area of the pilot plant	0.3	12:03	13:20	77	stationary	measurement in the outdoor area 24 °C, 42% air humidity, clear weather, gusty wind from W
11.09.12	AP-2012-09-11-2	Aerosol-spectr. 1.109	determination of the particle number concentration before and after the decanting process in the outer area of the pilot plant	1.2	12:04	13:20	76	stationary	
11.09.12	AP-2012-09-11-3	CPC 3007	determination of the particle number concentration before and after the decanting process in the outer area of the pilot plant, directly in the breathing zone of the employees	0.7	12:00	13:18	78	handheld	
11.09.12	AP-2012-09-11-4	CPC 3007	determination of the particle number concentration before and after the decanting process in the outer area of the pilot plant, directly in the breathing zone of the employees	0.7	12:00	13:18	78	handheld	
11.09.12	AP-2012-09-11-5	NAS	particle sampling for morphological characterisation of aerosols, which occur during decanting, directly at the decanting barrel	2.5	13:00	13:06	6	handheld	
11.09.12	AP-2012-09-11-6	SMPS (LDMA)	determination of the particle number concentration on the stage (MP1), background measurement before and after the tests	0.3	14:00	17:00	180	stationary	
11.09.12	AP-2012-09-11-7	Aerosol-spectr. 1.109	determination of the particle number concentration on the stage (MP1), background measurement during the tests	1.2				stationary	
11.09.12	AP-2012-09-11-8	CPC 3007	determination of the particle number concentration on the platform (MP2), background measurement and measurement during the tests	0.7	13:51	16:49	178	handheld	

DATE	SAMPLE NUMBER	MEASURE-MENT METHOD	MEASUREMENT TASK	VOLUME FLOW l/min	SAMPLING PERIOD		SAMPLING DURATION min	SAMPLING MODE	CLIMATE
					FROM	TO			
11.09.12	AP-2012-09-11-9	CPC 3007	determination of the particle number concentration at the computer workplace (MP3), background measurement and measurement during the tests	0.7	13:55	17:02	187	handheld	
11.09.12	AP-2012-09-11-10	contact sample	contact sample for morphological characterisation of aerosols attached at the disposable protective clothing during the decanting process						
11.09.12	AP-2012-09-11-11	NAS	particle sampling for morphological characterisation on the stage (MP1), measurement during the test ZE_25_1100-processing only polymer, connection of the CNT barrel on the stage	2.5	15:18	15:35	17	stationary	26 °C, 48%, In the outdoor area:
11.09.12	AP-2012-09-11-12	NAS	particle sampling for morphological characterisation on the stage (MP1), measurement during the test ZE_25_1100-addition of CNT, without exhaust ventilation	2.5	15:39	16:24	45	stationary	24 °C, 42%, clear weather, gusty wind from W
11.09.12	AP-2012-09-11-13	contact sample	contact sample for morphological characterisation from the platform, filler neck at the dosing unit, below the CNT filling						
11.09.12	AP-2012-09-11-14	NAS	particle sampling for morphological characterisation on the stage (MP1), measurement during the test ZE_25_1101 - addition of CNT, with exhaust ventilation	2.5	16:27	17:08	41	stationary	
11.09.12	AP-2012-09-11-15	material sample	material sample of MWCNT which is added to the polymer						
11.09.12	AP-2012-09-11-16	SMPS (LDMA)	determination of the particle number concentration on the stage, background measurement over night	0.3	17:42	08:48	906	stationary	
11.09.12	AP-2012-09-11-17	Aerosol-spectr. 1.109	determination of the particle number concentration on the stage (MP1), background measurement over night	1.2	22:41	08:58	617	stationary	

DATE	SAMPLE NUMBER	MEASUREMENT METHOD	MEASUREMENT TASK	VOLUME FLOW l/min	SAMPLING PERIOD		SAMPLING DURATION min	SAMPLING MODE	CLIMATE
					FROM	TO			
12.09.12	AP-2012-09-12-1	SMPS (LDMA)	determination of the particle number concentration on the stage (MP1), measurement during the fire alarm and the tests ZE_25_002 with exhaust ventilation	0.3	09:01	10:31	90	stationary	
12.09.12	AP-2012-09-12-2	Aerosol-spectr. 1.109	determination of the particle number concentration on the stage (MP1), measurement during the fire alarm and the tests ZE_25_002 with exhaust ventilation	1.2	08:59	10:28	89	stationary	
12.09.12	AP-2012-09-12-3	CPC 3007	determination of the particle number concentration on the platform (MP2), measurement during the fire alarm and the tests ZE_25_002 with exhaust ventilation	0.7	09:07	10:33	86	handheld	
12.09.12	AP-2012-09-12-4	CPC 3007	determination of the particle number concentration at the computer workplace (MP3), measurement during the fire alarm and the tests ZE_25_002 with exhaust ventilation	0.7	09:18	10:38	79	handheld	
12.09.12	AP-2012-09-12-5	thermal precipitator	particle sampling for morphological characterisation on the stage (MP1), measurement during the fire alarm and the tests ZE_25_1102 and ZE_25_1101	2 ml/min	09:32	14:32	300	stationary	
12.09.12	AP-2012-09-12-6	NAS	particle sampling for morphological characterisation on the stage (MP1), measurement during the fire alarm and the tests ZE_25_1102 with exhaust ventilation	2.5	09:34	10:36	62	stationary	
12.09.12	AP-2012-09-12-7	contact sample	contact sample for morphological characterisation directly from the filler neck at the extruder (lower area)						
12.09.12	AP-2012-09-12-8	contact sample	contact sample for morphological characterisation, degasification at the extruder (lower area)						

## 5.5 Measurement results

### General:

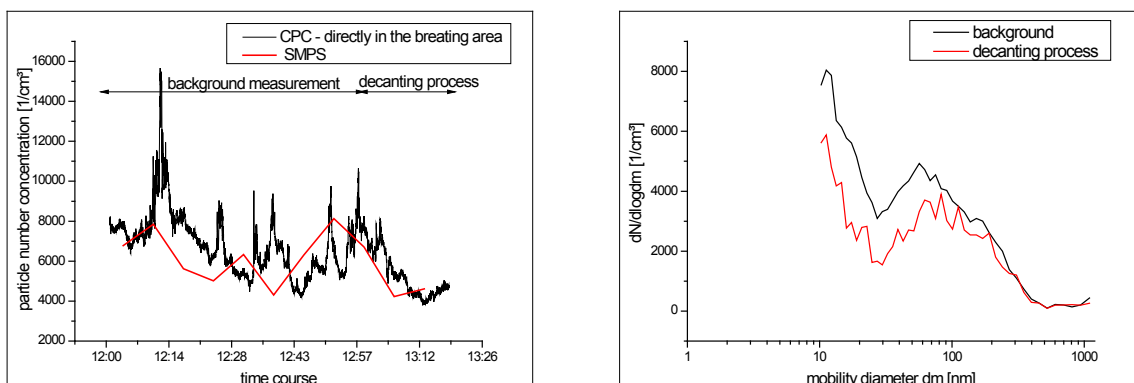
Product-specific particle number concentrations are influenced by emitters of the outdoor area (e.g. increased traffic volume, particles from power plants and sources of domestic fire), weather influences (among others changing wind directions) and further sources in the interiors (smoking, welding, abrasion of electric motors etc.). In the absence of material analysis, the immediate influence of the outdoor conditions (e.g. opened windows, gates) and further background levels in the interiors on the product-specific particle number concentration is generally assumed. Currently, no health-based occupational exposure limit value for ultrafine particles / nanomaterials exists, i.e. a correlation to limit values cannot be given yet. Therefore, all values determined in the present study were measured in relation to a background level, either measured outside or in the respective working area while no activities took place.

### Decanting process:

During decanting, the measurement was carried out directly next to the process and with the CPC 3007 handheld in the breathing area of the employees. Table 2 and figure 4 (left) show the determined particle number concentrations before and during decanting. The mean concentrations as determined with the SMPS and the CPC were comparable. The mean particle number concentrations during the background measurement were higher than during the decanting process. This means that no significant particle number concentration increase during the decanting was observed in the immediate area of the employee. However, the morphological examination showed nonetheless CNT release (see below).

The particle size distribution of the aerosols was determined with the SMPS during the background measurement and the decanting (see figure 4, right). The analysis showed a bimodal distribution, which is typical for an outside air aerosol. Maxima occurred at small particle sizes of 10 nm and at approximately 60 to 80 nm. The geometric mean of the particle size was 45 nm during the background measurement and 49 nm during decanting.

The wider fluctuations of the distribution during the decanting were caused by the shortness of the process (2 scans). There was no significant difference in particle size distribution between the decanting process and the background.



**FIGURE 4: DECANTING PROCESS — TIME COURSE OF THE PARTICLE NUMBER CONCENTRATION (LEFT) AND PARTICLE SIZE DISTRIBUTION (RIGHT)**

**TABLE 2: PARTICLE NUMBER CONCENTRATION DURING DECANTING IN THE OUTSIDE AREA**

	SMPS STATIONARY		CPC 3007 (particles/cm <sup>3</sup> ) HANDHELD	
	particle number concentration	standard deviation	particle number concentration	standard deviation
background	6,338	1,421	6,896	1,562
decanting	4,421	274	5,200	1,028

**Activities at the extruder – stage area:**

Potential exposures to fibrous nanomaterials (CNT) were determined with different test parameters (ZE\_25\_1100, ZE\_25\_1101 and ZE\_25\_1102), with different flow conditions (exhaust ventilation) and at different measurement places / points (see section 5.4). Measurement points MP1 to MP5 were arranged next to the extruder, reflecting working sites of employees.

During the first measurements, the sampling was performed on the stage (SMPS, NAS) and on the platform (CPC). Before starting the tests, the particle number concentration of the “background” above the extruder was determined, i.e. no relevant activities were performed at the extruder. Thereafter, the different tests took place. The results of the measurements are listed in table 3 and figures 5 and 6. The results of the measurements at the PC workplace in the lower area of the extruder, which were performed in parallel to the measurements above the extruder, are listed in table 4.

Values measured with the CPC 3007 were always higher than those measured with the SMPS, which is explainable with the measurement place of the CPC’s on the platform directly above the extruder. It should be noted that the determined concentrations were mainly caused by ultrafine aerosols, i.e. probably emissions from the hot, greased parts of the extruder.

The background concentration of 28,347 particles/cm<sup>3</sup> respectively 71,270 particles/cm<sup>3</sup> was relatively high, and may be explained with further works in the pilot plant. This is supported by results from measurements during the night, when no activities took place at all. Then, particle number concentrations were 9,517 particles/cm<sup>3</sup>.

The particle number concentration increased rapidly with the start of the tests and the temperature increase. However, no difference was observed between tests ZE\_25\_1100 and ZE\_25\_1101, i.e. no significant difference of the particle number concentration was detectable between processing CNT and the test without CNT. Both tests were initially performed without exhaust ventilation. At 16:38 o’clock, the exhaust ventilation at the extruder was switched on and the test ZE\_25\_1101 continued. While doing so, the mean concentration was very clearly below the tests ZE\_25\_1100 and ZE\_25\_1101 (measured both with the SMPS on the stage and the CPC on the platform). This clearly shows, that the exhaust ventilation has a crucial influence on the concentration of ultrafine aerosols (no CNT!) at the different workplaces in the extruder area.

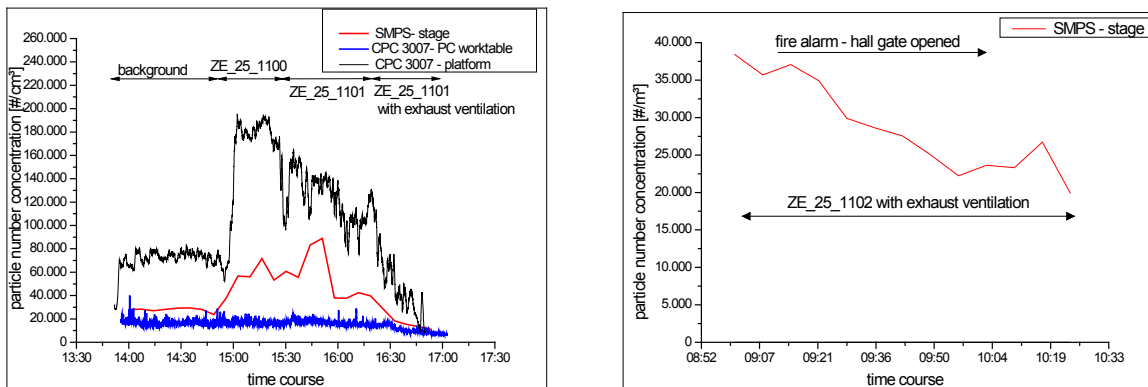
The particle number concentration at the PC worktable in the lower area of the extruder was significantly lower than on the stage or on the platform (see table 4). Additionally, performing the tests seemed to have no influence on the direct concentration at the PC workplace. It can be assumed that only the typical background concentration in the pilot plant had an influence at this workplace. The particle number concentration decreased after switching on the exhaust ventilation.



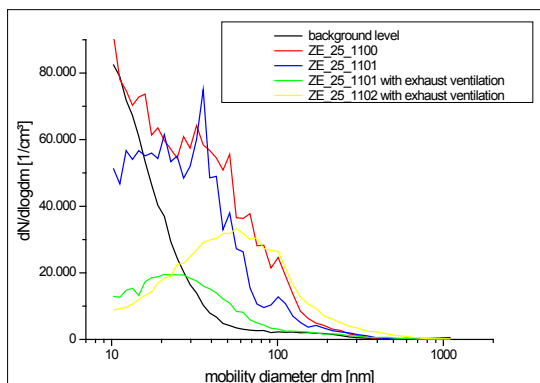
The measurements continued during the test ZE\_25\_1102 on 12.09.12. However, this measurement was influenced by a fire alarm, which was triggered at 09:10 o'clock. Number concentrations were possibly increased by emissions from the neighbour unit and also influenced by the permanently opened gate (different flow conditions in the measurement area).

The particle size distributions given in figure 6 show differences of the tests with ventilation, without ventilation and the background level. Especially the finer particles were captured by the exhaust ventilation. The particle size distribution of the background was also different from the size distribution of the outside air concentration (see figure 4, right) so that one can assume additional emitters of ultrafine aerosols in the pilot plant.

The geometric means of the particle sizes were 18 nm for the background measurement, 27 and 28 nm for the tests ZE\_25\_1100, and ZE\_25\_1101 and 54 nm for the test ZE\_25\_1102 with exhaust ventilation.



**FIGURE 5: ACTIVITIES AT THE EXTRUDER (STAGE, PLATFORM, PC WORKTABLE) — TIME COURSE OF THE PARTICLE NUMBER CONCENTRATION DURING THE TESTS AT 11.09.2012 (LEFT) AND ON 12.09.2012 (RIGHT, STAGE ONLY)**



**FIGURE 6: ACTIVITIES AT THE EXTRUDER (STAGE) — PARTICLE SIZE DISTRIBUTION ,MEASUREMENTS ON STAGE ON 11.09./12.09.2012**

**TABLE 3: PARTICLE NUMBER CONCENTRATION DURING TESTS ON THE STAGE (SMPS) AND ON THE PLATFORM (CPC), MEASUREMENTS ON 11.09./12.09.2012**

	SMPS STATIONARY MEASUREMENT POINT 1		CPC 3007 (particles/cm <sup>3</sup> ) HANDHELD MEASUREMENT POINT 2	
	particle number concentration	standard deviation	particle number concentration	standard deviation
background	28,347	801	71,270	14,138
ZE_25_1100	51,892	14,795	146,106	47,872
ZE_25_1101	51,297	24,202	112,428	35,087
ZE_25_1101 with exhaust ventilation	14,549	3,013	38,670	27,157
ZE_25_1102 with exhaust ventilation	28,697	6,094	46,316	18,232
night measurement	9,516	14,392	--	--

**TABLE 4: PARTICLE NUMBER CONCENTRATION AT THE PC WORKPLACE (CPC) DURING THE TESTS, MEASUREMENTS ON 11.09.2012**

	CPC 3007 (particles/cm <sup>3</sup> ) MEASUREMENT POINT 3	
	particle number concentration	standard deviation
background	16,675	1,977
ZE_25_1100	16,721	1,824
ZE_25_1101	161,61	1,648
ZE_25_1101 with exhaust ventilation	9,562	2,242

#### Activities at the extruder – lower area:

The measurement devices in the lower area were rearranged and the particle number concentration of the background was determined, while no relevant works at the extruder were performed. However, the exhaust ventilation was switched on permanently and the hall gate was open. The measurement devices were positioned directly at the extruder; MP4 and MP5, see section 5.4.

The results, i.e. the mean particle number concentrations are given in table 5. The time course of the particle number concentration is visualised in figure 7, left. Here again it has to be noted that the determined concentrations are mainly caused by ultrafine aerosols, i.e. presumably emissions from hot, greased party of the extruder.

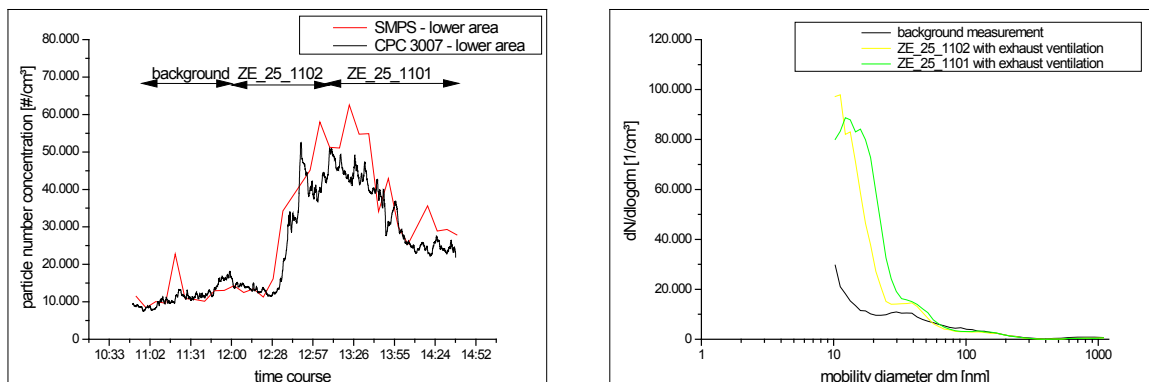
Since the measurement points 4 and 5 lie directly next to each other, the mean values and time courses of SMPS and CPC 3007 were comparable.

When measuring in the lower area of the extruder, a significant increase of the particle number concentration was observed after the actual test started.

For test ZE\_25-1102 with exhaust ventilation, the measurements at the stage (MP1) and at the lower extruder area (MP 4 & 5) showed comparable results. For test ZE\_25-1101, results from the different measurement points were not comparable (concentrations measured in the lower area were higher than on the stage), possibly due to the changed airflow caused by the opened hall gate.

Figure 7, right, shows the particle size distribution during the tests in the lower area of the extruder. The bimodal distribution of the outside air concentration during the background measurement can be explained by to the open hall gate, the geometric mean is about 31 nm and hence a bit higher than during the measurement on the day before. Also the measurements during the actual tests are influenced by the background, as seen by the bimodal distribution. However, the proportion of particles smaller than 30 nm due to the emitters of the extruder is substantially higher than during the background measurement.

The mean particle sizes during the tests ZE\_25\_1101 and ZE\_25\_1102 with exhaust ventilation are approximately 21 and 19 nm.



**FIGURE 7: ACTIVITIES AT THE EXTRUDER (LOWER AREA) — TIME COURSE OF PARTICLE NUMBER CONCENTRATION (LEFT) AND PARTICLE SIZE DISTRIBUTION (RIGHT)**

**TABLE 5: PARTICLE NUMBER CONCENTRATION DURING THE TESTS DIRECTLY AT THE EXTRUDER IN THE LOWER AREA (SMPS AND CPC), MEASUREMENTS AT 12.09.2012.**

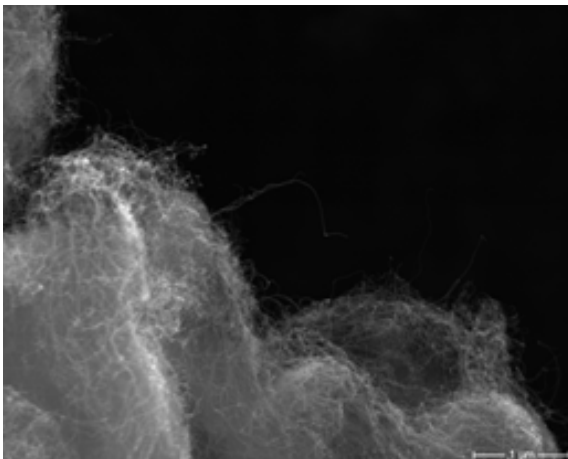
	SMPS (particles/cm <sup>3</sup> ) MEASUREMENT POINT 4		CPC 3007 (particles/cm <sup>3</sup> ) MEASUREMENT POINT 5	
	particle number concentration	standard deviation	particle number concentration	standard deviation
Background measurement lower area	11,996	4,038	11,354	2,830
ZE_25-1102 with exhaust ventilation	28,482	18,814	26,959	14,359
ZE_25-1101 with exhaust ventilation	39,070	12,616	32,894	8,873

**Morphological characterisation of the product particles:**

During the measurement campaign, several air samples were taken with a NAS in accordance with the different processes and workflows in order to perform subsequent scanning electron microscope analyses. The purpose was to state if a release of nanomaterials occurs during the analysed processes, since the online measurement devices (SMPS and CPC 3007) can only register the whole particle number concentration without chemical differentiation. At the same time, contact samples were taken from different surfaces in order to verify potential nanomaterial deposits.

**Decanting process:**

During the decanting process, the sampling was performed in immediate proximity to the worker. High amounts of CNT agglomerates were found on the specimen, i.e. a relatively high amount of CNT fibres was released during the decanting process. Also on the contact samples from the protective clothing of the worker, CNT agglomerates, but also single fibres were found.

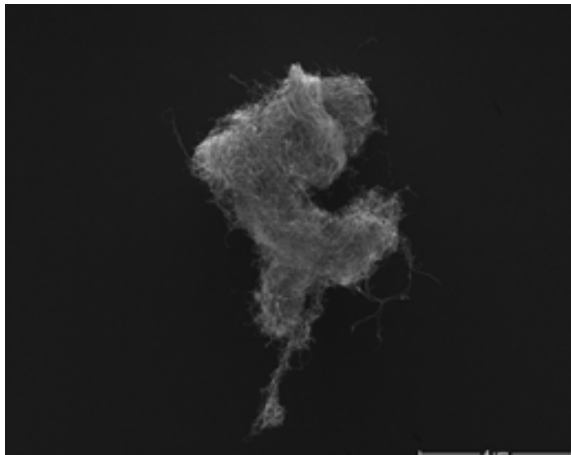


**FIGURE 8: NAS SAMPLE DURING THE DECANTING PROCESS**

**ZE 25 1100:**

The sampling with the NAS was performed on the stage (MP 1). During this time, no fibres were processed inside the extruder, but the CNT barrel was connected to the platform.

Single agglomerates from CNT can be recognized on the specimen. Single fibres could not be detected. It can be assumed that during the connection of the CNT barrel CNT fibres are released or carried away due to the strong thermal differences in the area of the deposited dust (contaminations).



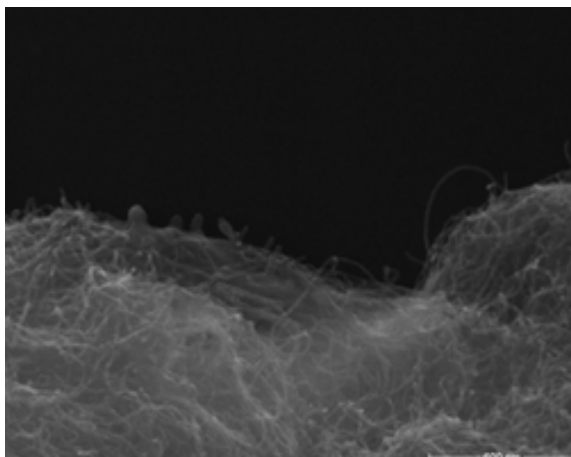
**FIGURE 9: NAS SAMPLE DURING THE TEST ZE\_25\_1100 WITHOUT EXHAUST VENTILATION ON THE STAGE**

#### **ZE 25 1101:**

The sampling with the NAS on the 11.09.12 was performed on the stage (MP 1). No agglomerates or single fibres of CNT were found on the specimen, which were taken during the test course (ZE\_25\_1101) without exhaust ventilation. However, CNT agglomerates were analysed during the tests (ZE\_25\_1101) with exhaust ventilation. Single fibres were not detected.

One has to assume that fibres were also transferred to the stage area due to the exhaust ventilation. No CNT agglomerates or single fibres were detected during the measurements in the lower area during the tests directly at the extruder on 12.09.12.

As expected, the contact sample of the filler neck at the dose unit (below the CNT barrel) shows CNT agglomerates.



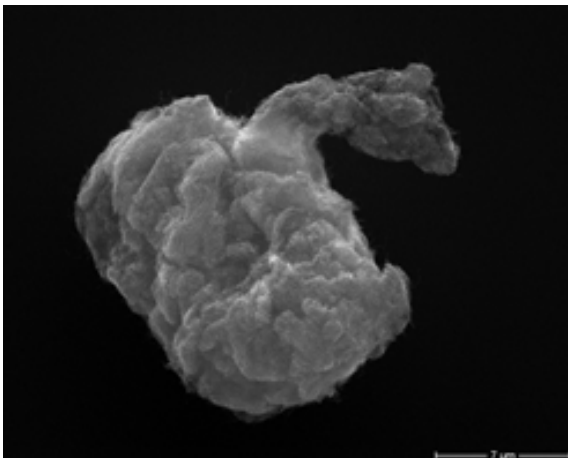
**FIGURE 10: NAS SAMPLE DURING THE TEST ZE\_25\_1101 WITH EXHAUST VENTILATION ON THE STAGE**

**ZE 25 1102:**

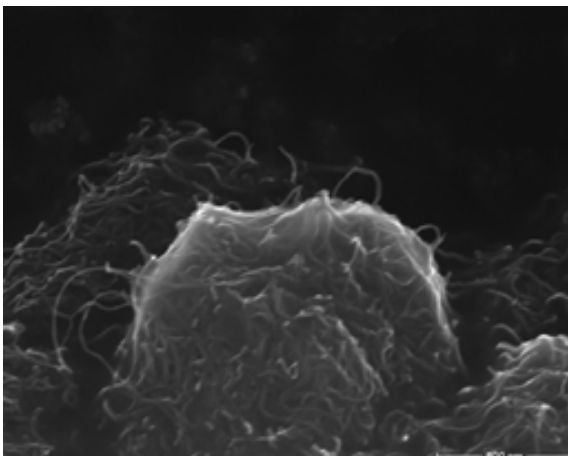
On 12.09.12, the sampling during the tests (ZE\_25\_1102) was performed on the measurement place 1 on the stage and with running exhaust ventilation. CNT agglomerates could be verified during the sampling on the stage (see figure 11). However, during comparable measurements in the lower area, no CNT agglomerates were found.

Here again, it is possible that fibres are carried to the upper area of the extruder by the exhaust ventilation.

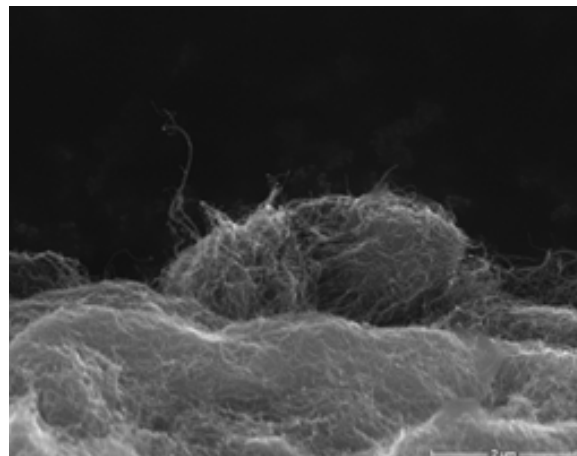
The contact samples from the filler neck in the lower area directly at the extruder showed CNT fibres, which were embedded into a matrix. This was probably a polymer particle with the processed CNT agglomerates (see figure 12). These Polymer particles with CNT embeddings were also visible on the contact sample from the degassing (see figure 13). Especially single fibres sticking out of the matrix were found.



**FIGURE 11: NAS SPECIMEN DURING THE TEST ZE\_25\_1102 WITH EXHAUST VENTILATION ON THE STAGE**



**FIGURE 12: CONTACT SAMPLE FROM THE NECK FILLER**



**FIGURE 13: CONTACT SAMPLE BEFORE THE DEGASSING**

## 5.6 Summary of the measurement results:

- During the outdoor decanting process by an employee wearing disposable protective clothing, respiratory protection, goggles and chemical resistant gloves, no significantly increased particle number compared to the background were measured with the measurement devices.
- Both contact samples, which were taken after the decanting process from the personal protective equipment, and samples from the electro precipitator (NAS) showed the presence of a high amount of fibre agglomerates and also single fibres in the subsequent scanning electron microscopically examination. A comparable material sample with another lot number was available in the measurement laboratory. Both materials showed comparable morphological properties regarding fibre diameter and agglomerate generation.
- The observed increase in particle number concentrations was not caused by MWCNT used in this test, but rather by a release of ultrafine aerosols from the hot and greased parts of the extruder in operation (emitters from the extruder).
- As expected, the particle number load was decreased by an aimed exhaust ventilation above the extruder by more than two thirds of the initial value.
- It is possible that CNTs are carried to the upper area by the exhaust ventilation, which was proved by NAS samples. In the lower area, no fibre release was detected with the air measurements.
- Contact samples taken from the filler neck and the degassing device also showed the presence of agglomerates with the shape seen before. However, the occupancy density on the sampling substrates (Si wafer) was lower than during the decanting process.

As an immediate measure, the outdoor decanting process should be optimised. The experts from the measurement laboratory will submit a proposal to the polymer processing plant, how to design the decanting process more safely.

## 6 Conclusions

### 6.1 Specific conclusions for the fibre processing workplaces in a pilot plant

These conclusions combine the knowledge generated based on the inspection following the dialogue guide and the field measurement.

The test results detected no significantly increased enrichments of the particle number concentrations of nanoparticles at the workplace. Indirect measurements showed fluctuations of particle number concentration and particle size distribution. However, these could not be separated from the background level and process-related influences, for instance they exceeded the mean particle number concentrations in several town atmospheres. Nevertheless, single fibrous nanomaterials and agglomerates were clearly detectable in contact samples by subsequent particle analyses (scanning electron microscope). Hence, a limited release of fibrous nanomaterials has to be assumed. However, a critical exposure of the workplace environment can be largely excluded.

The following safety strategies for handling the nanomaterials are recommended:

#### **Decanting process:**

The protective measures used in present work routine (protective clothes, goggles, FFP3 respiratory mask and chemical resistant gloves) are regarded as sufficient. Nevertheless, since this process implements a significant burden for the employees, the use of a closed filling system is recommended for the future. A putative design of a closed filling system for this specific application is depicted in Figure 14.

For the filling process, the CNT-bag is laid in a system, which is closed afterwards. The CNT-bag is opened with a knife in this closed box (either with a window or in a transparent box). The CNT fibres fall into a dosing unit for further processing. The handling is performed using installed gloves, which are normally found in a typical glovebox. The air is exhausted over a vacuum cleaner respectively by local exhaust ventilation. This airflow can be stopped with shut-off valves (triangle symbol for shut-off valve). The air is flowing over HEPA filter (square with dotted line).



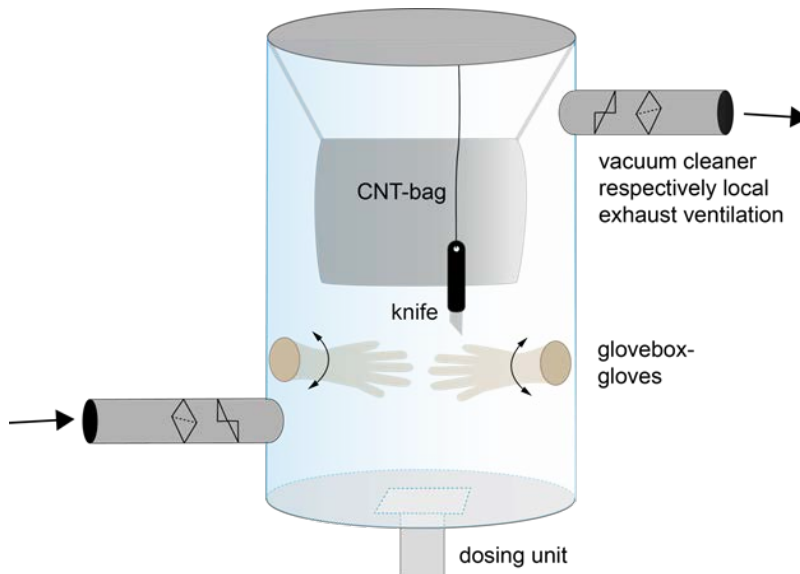


FIGURE 14: DESIGN OF A CLOSED FILLING SYSTEM FOR OUTSIDE USE (REFERENCES: NICO DZIURWITZ AND MARTINA BRANDAU-POLLACK, BAUA)

#### Working at the extruder:

The utilized PPE with gloves, FFP3 respiratory mask, normal work clothing and chemical resistant gloves is regarded as sufficient. The use of respiratory masks shall be limited to short accompanying activities, like connecting the CNT barrel and further work on the stage. The existing local exhaust ventilation should be always used during handling nanomaterials and should be always positioned near the release source.

#### Use of new nanomaterials or changed production process:

According to size, morphology and chemical hazards of the substance, a new risk assessment has to be performed and if necessary, the protection concept has to be adapted accordingly.

## 6.2 General assessment of the nanofibre exposure

The currently available measuring strategy for fibrous nanomaterials has to be critically assessed since the different fibre morphologies can show different efficacy due to their geometry. The relevant properties for fibrous nanomaterials are the solubility and the well-known fibre principle. Fibres which meet the WHO definition (i.e. fibres with a diameter  $< 3 \mu\text{m}$ , a length  $> 5 \mu\text{m}$  and a length-diameter-ratio of  $> 3:1$ ) are especially critical. Single fibres and open clusters composed of single fibres, which meet this fibre definition, shall in particular be regarded critically.

Similarly critical are fibre bundles composed of nanoscaled fibre material with a length according to the WHO definition ( $> 5 \mu\text{m}$ ). A further and new criterion shall be considered for the characterisation of the efficiency of fibrous nanomaterials: the rigidity of the fibres/tubes. When considering different CNT/CNF materials, especially strongly tangled, mostly flexible fibre geometries attract attention in contrast to very straight and stiff fibres/tubes. Pathomechanistical considerations suggest that the stiffness is a relevant hazardous property for the material. For further investigations, it is necessary to develop an adequate level to assess this property.

As mentioned above, the currently available measurement strategies for handling fibrous nanomaterials have to

be regarded critically. The measurement devices applied for determining the particle number concentration (for instance SMPS, CPC) do not provide any information on the fibre morphology. In tier 2 of the tiered approach, samples with subsequent analysis using an electron microscope are described. However, no standardised and statistically valid processes exist for the assessment of compound samples (thermal precipitator, electrostatic precipitator), which resemble the VDI 3492.

## 7 Reference

Control guidance sheets. Available from: <http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/EMKG/Schutzleitfaeden.html> [accessed 10 September 2014].