Inno.CNT
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CARBON NANOTUBES

Inno.CNT Workshop

Metrology and Exposure Assessment of Carbon Nanotubes

29-30 November 2011

Schloss Burg, Germany

Workshop Report

Content

1. Executive Summary

The development of Carbon Nanotube (CNT) related technologies and applications is a highly topical area of research worldwide. However, for the responsible development of sustainable CNT based applications the appropriate consideration of safety issues is of key importance. In fact safety related research has to be an essential integral part of the innovation strategy.

Due to highly diverse morphologies and structures of different kinds of CNT, a costly and time consuming detailed case by case consideration of their specific interactions with biological systems is needed. On the other hand the evaluation of potential risks of CNT based products requires in parallel the assessment of potential release and exposure scenarios during production, processing, use and at the end of product life.

Therefore, it is essential for any further risk assessment to be able to detect and characterize on one hand CNTs as produced and modified. On the other hand it must be possible to measure the potential release of particles accurately in order to:

- estimate resulting CNT exposures of staff at workplaces during production and processing,
- assess the risk for consumers during use of the product and
- determine the impact of end-of-life phases on fauna and the environment.

The need to measure CNT release and exposure from products in different phases of their life cycle is an issue that needs to be addressed free from competitive pressures in a more global overarching manner. The aim of the workshop was to conduct an international exchange of experience via results and discussion to identify opportunities and initiate further scientific technical work on the following topics:

- Metrology, i.e. detection and characterization methods for CNT
- Release and potential exposure during
    - the production of CNT
    - the processing of CNT-containing products
    - the use of CNT-containing products
    - the end-of-life phase of CNT-containing products
- Transport and fate of CNT in the environment
- Life cycle aspects of CNT-containing products

With 25 international experts from ten countries, the workshop brought together a unique and prestigious field of participants. The workshop participants have derived specific recommendations related to above listed potential topics for further research and have classified these by their importance and urgency.

This workshop report summarizes results from these discussions and can be used by organizations and authorities who are interested in this topic to initiate further research activities regarding CNT metrology, release and exposure at different stages within the lifecycle of CNT-based products.

2. Results

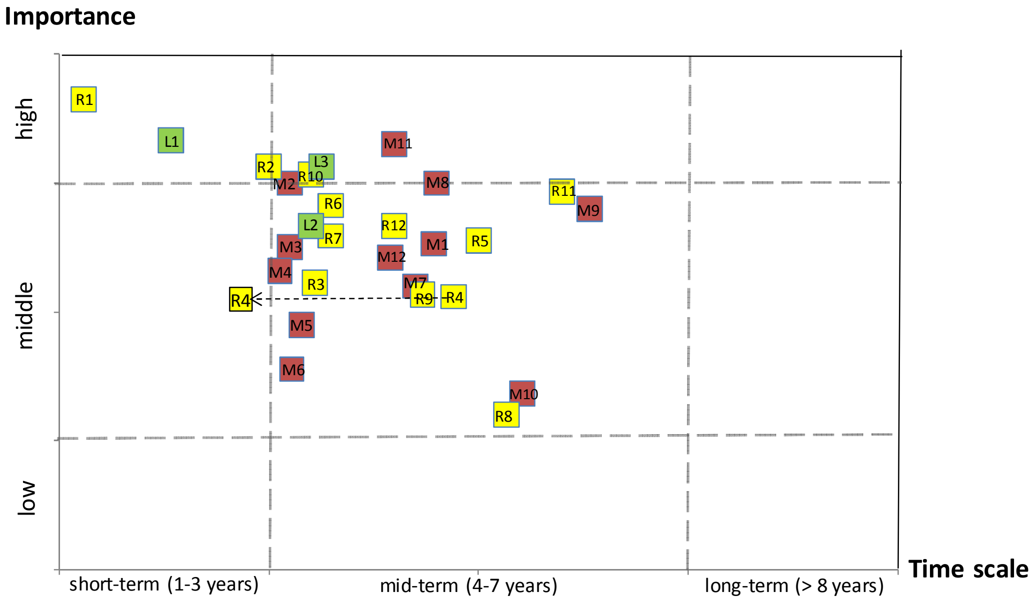
The workshop has been structured in three sessions:

M Metrology

R Release and potential exposure during the production of CNT and processing of CNT-containing products

L Life Cycle Analysis of CNT-containing products

In each session participants raised issues they perceived as being important and these were subsequently evaluated by all involved with regard to importance and urgency. The overall distribution of topics is given in the graph below. All topics identified were found to be located in the region from middle to high importance and should be addressed within a time frame of less than seven years. Details of the topics and their valuation are described in the following sections of this report.



Remark: Topic R4 (Standard materials for release measurement) has been shifted in the discussion to an earlier time scale.

2.1 Metrology

Selectivity of detectors for CNTs vs. background

M1. Couple classification + online spectroscopy

The classification of CNT in online measurement equipment is often based on the electrical mobility diameter as an equivalent diameter. This equivalent diameter is a function of the CNT’s length and diameter as well as of particle charge. For electrical mobility analysis, the classification process is usually followed by a particle counter acting as detector. In order to derive information on the CNTs diameter and length, the combination of different measurement signals, e.g. mobility diameter plus surface area, has to be developed. This is especially important for a distinction from other particles having the same mobility diameter.

M2. Collector + automated image analysis

Sampling and subsequent electron microscopic analysis (TEM or SEM) of CNT is crucial to identify also small amounts of CNT present in the airborne state. Different kinds of samplers applying a wide variety of substrates exist, but often with unknown sampling efficiencies, especially in view of CNT. Image analysis requires high quality images with evenly distributed contrast values and without perturbations from charge effects. Based on length, diameter and aspect ratio, an automated image analysis must be capable of identifying CNT on different kinds of substrates and possibly while attached to a matrix material. Unambiguous automated identification of agglomerated CNT will most likely not be achievable within the next decade. An evaluated and standardized method for automated image analysis has to be developed.

M3. Labeling vs. natural / non-CNT background (not only aerosol)

For easy detection of CNT without using electron microscopic methods it is possible to label CNT by chemically attached markers. After production of the CNT, a certain amount of marker material is attached. This marker could e.g. be cobalt, which is detected easily because it is not an abundant element in the environment. If iron or nickel were used as markers, a positive identification would be impossible, because these elements are very common in working environments as well as elsewhere. For scientific research (transport behavior, life cycle analysis, etc.) a radioactive labeling is very useful due to the high sensitivity and selectivity. A method of chemical labeling is needed that is suitable for the production environment (see also M10).

M4. Distinguish HARN vs WHO fibers

According to the World Health Organization (WHO) fibres are defined to have a length above 5 µm, a diameter below 3 µm and an aspect ratio (length to diameter) above 3:1. For the assessment of number concentration, e.g. for asbestos analysis, fibres are sampled onto filters under defined conditions and analyzed with an optical method covering typically only fibers with a diameter above 200 nm. High Aspect Ratio Nanoobjects (HARN) are usually covered by the WHO definition if the length of the object is above 5 µm, which is not necessarily the case for more rigorously processed materials. For a correct assessment of airborne HARN a method is necessary to distinguish morphologically and chemically between the classical WHO fibres and the new nanoobjects.

Standards

M5. To generate predefined CNT aerosols

Today, nearly all instruments available for the measurement of airborne particles are only calibrated with spherical particles of known size and density. Furthermore, no standard exists yet for a calibration of particle number concentration. For the calibration of instruments used for measuring CNT aerosols there is therefore a need to generate aerosols of airborne CNTs with well-defined properties for an accurate determination of properties. These CNTs must at least be defined in diameter and length. Fully characterised CNT aerosols are also needed for the calibration and validation of particle samplers to check proper functioning.

M6. Calibration for elemental carbon

A method suitable for the detection and quantification of CNT is the thermooptical analysis of organic and elemental carbon (OC/EC analysis). The NIOSH protocol 5040 is used as a standard in occupational hygiene, but modifications to the temperature protocol have been made by users to better distinguish CNT from carbonaceous background aerosol. Instruments are calibrated for total carbon (TC) by using CO2 or an organic standard (e.g. sucrose). Unfortunately, there is no clear definition for the distinction of OC and EC, and hence there is no standard available for the calibration of OC or EC concentrations. Therefore, a standard method for OC/EC analysis including a suitable temperature protocol and calibration method has to be developed.

Selectivity for different types of CNTs

M7. By length / MMAD / shape

The primary morphology of a CNT can be described by its diameter and length, which are usually determined by electron microscopy. But since CNT can reach extremely high diameter to length aspect ratios of several 10,000 it is important to take into account a secondary morphology, whereby the fiber is bent onto itself to form structures such as pills and tangles, or forms agglomerates with other CNT to form bundles. It is the secondary morphology that governs predominantly the propagation behavior of CNTs, which is determined by the majority of particle sizing instrumentation in the form of a Mass Median Aerodynamic Diameter (MMAD). The MMAD represents a characteristic of the particle size distribution that splits the fine and coarse size fractions in equal shares by mass. The density of the CNT “particle” is generally much lower than that of graphite because the secondary morphology introduces a high level of porosity. A complete set of parameters describing the whole morphology has to be defined.

M8. By chemistry/surface functionalization → persistence, fate

CNT are grown in pristine form as pure hexagonal carbon but are often grafted with other chemical groups, e.g. during purification (catalyst removal) or deliberately to achieve different chemical properties such as hydrophilicity. Covalent attachment of chemical groups always leads to defects in the wall of a CNT because the associated hybridization change from hexagonal to cubic puts the tube structure under enormous strain. Such defects are conducive to promote further functionalization and the generation of polar or ionic groups that increase CNT solubility in water and make these structures more susceptible to chemical cleaving, hence less persistent in biological systems. A detailed understanding of the relationship between structure and chemical modification of CNT and its behavior in the environment has to be established.

M9. By chemistry/surface functionalization → toxicology

The toxicological potential of processes involving CNT in biological systems is varied and in many ways still unexplained. Factors include a fibrous morphology in conjunction with a minimal length (asbestosis, macrophages), chemical toxicity of catalytic contaminants or grafted functional groups and persistence coupled with the capacity to penetrate semipermeable barriers (cell walls). A better understanding of the relationship has to be worked out.

M10. Precursor particles as tracer for CNTs

Metallic catalysts are used for assembling CNTs atom by atom. Some processes allow for the catalyst nanoparticle to be subsequently detached from the rest of the CNT. It is also possible to remove the catalyst by dissolving it chemically, but there are some processes where the catalyst remains strongly associated with the CNT. This metallic signature is easily detected by various methods, quite contrary to the pure carbon composition of pristine CNT, and allows a proportional quantification of CNT presence. A generally recognized method for the identification of tracer particles has to be established (see also M3).

M11. Continuous (low-cost) monitoring (not always HARN)

Continuous monitoring of aerosols in clean rooms or the environment is carried out by mass based densitometry or by counting particles using optical diffraction.

Measurement of particle mass is affected heavily by coarse particle background, because ultra-fine particles contribute very little to collected mass. Another contributing factor is that the optical absorption of particles with dimensions smaller than the wavelength of the light used for detection may not follow standard electro-dynamic principles, as described by the Kramers-Kronig relationship. The sensitivity of the technique can however be increased very substantially by using analyzers capable of distinguishing between organic (organic compounds) and elemental carbon (graphite, fullerenes, CNT).

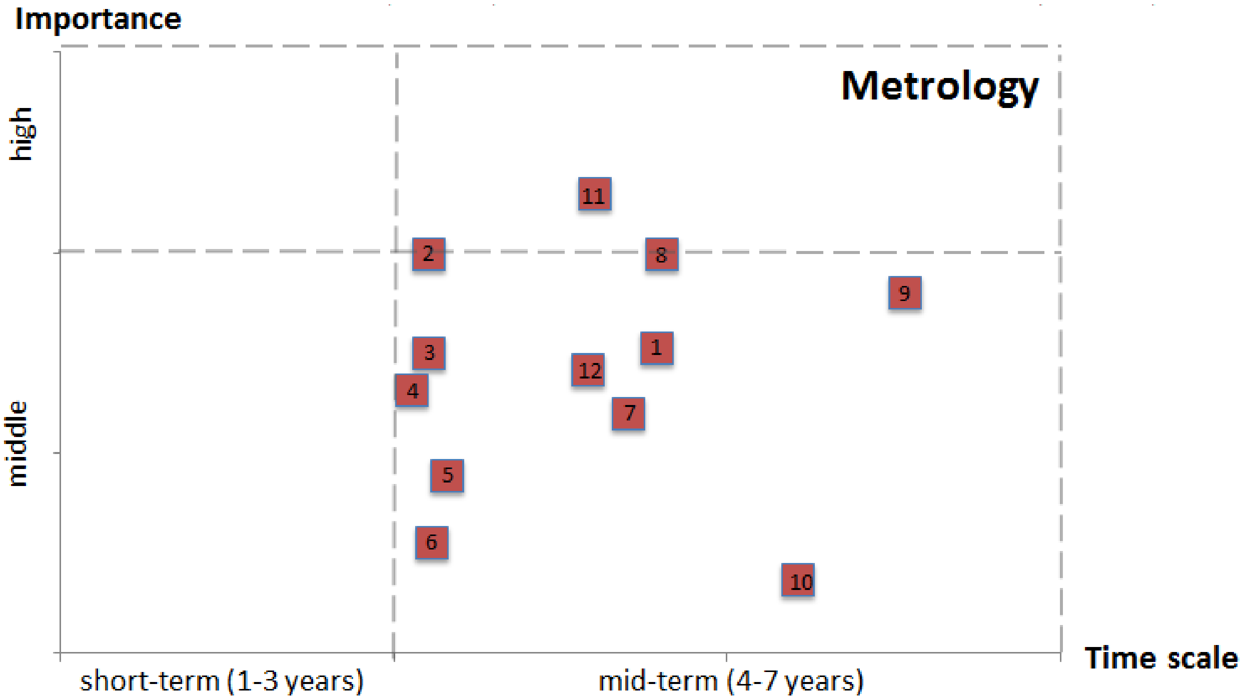
Results from optical particle counters are affected heavily by naturally occurring particle background, which cannot be discriminated from the signatures of CNTs. It is furthermore important to observe the coincidence loss limit of optical particle counters to ensure accurate operation of the instrument in different environments. The use of condensation particle counters is currently less common in continuous monitoring, but is possible and provides useful information.

A continuous (low-cost) monitoring method has to be adapted to the specific CNT properties.

M12. Number vs. surface vs. mass metrics

Some chemical reactions (in biological systems or elsewhere) occur on the surface of CNT. In this particular case, pertinent process parameters will be governed by the available surface area, rather than mass or number of particles. The total surface area of an aerosol can be determined quantitatively by applying a saturated surface charge to the particles, followed by a measurement of the total charge. A recognized approach to ensure useful data is obtained for special cases needs to be defined.

These topics have been judged individually by the workshop participants using importance and urgency as criteria. Results of this evaluation are summarized in the following map. For reasons of clarity the error bars have been left out of the map. Tables providing the detailed results, including mean value and standard deviation according to the feedback provided by participants, are documented in chapter 6.



2.2 Release and potential exposure during the production of CNT and processing of CNT-containing products

R1. Sampling and online instruments (Analysis vs. Background, automated+statistics, sampling+online in parallel, total + distribution, efficient/representative sampling, non-spherical aerosols)

The production and processing of CNT-containing products is inherently a multi-component system. Hence all issues of CNT-detection that are discussed in 2.1 are even more demanding: selectivity against background (such as non-CNT-containing pure polymer debris) and selectivity for different CNT-polymer hybrids (with CNTs embedded, CNT protrusions, CNT decorated particles, pure CNT particles). These aerosols, generated during the production of CNT and processing of CNT-containing products, are always non-spherical, very polydisperse, hence hard to sample and detect in a representative way. Instruments to quantify these aerosols are needed.

R2. Release tests with agreed methods (various stress conditions, recommended instruments, test protocols)

Agreed methods for measuring particle release are needed in order to provide consistent and predictable results, to provide a basis for confidence across stakeholders that true zero counts are reported and that any released CNT-related materials are sufficiently characterized with regard to risk evaluation. Among other considerations, such methods may need to consider protocols for relevant stress conditions and release scenarios (for example, imitating fabrication processes, wear in consumers' hands, disposal practices, environmental degradation of composites), media and conditions into which releases would occur, positive and negative controls with respect to presence and release likelihood of CNTs, sampling procedures in consideration of the specific qualities of the CNT-related particles that are released, recommended instrumentation, what data to report to allow benchmarking and statistical evaluations.

R3. Quality of release (differentiate ENP vs hybrids vs recondensed matrix) with respect to hazard principles

The materials released from CNT composites may include free CNT, CNT associated materials (such as catalysts and production by-products), CNT fully embedded in matrix material, CNT attached to the matrix, and matrix material on its own. With respect to problem formulation for risk analysis of the added CNT, these qualitative aspects of the released material will set the scope for considerations concerning subsequent environmental transport and fate, exposure, and risk evaluations. For this reason, widely agreed methods for measuring and characterizing the released material are needed to ensure that the effect of the added CNT on nanoscale particle release can be evaluated with respect to its hazard principles.

R4. Standard materials for release measurement (pos/neg control)

Standard materials (reference materials) are needed to calibrate instruments and methods and to enable a consistent identification of the effects that added CNT invoke on the qualitative and quantitative aspects of the materials released from CNT composites. Materials available should be suitable for use as positive or negative controls in measurement methods applicable to the most likely release scenarios. In this context a negative control would be a sample of the matrix used in a CNT composite that does not contain CNT. A positive control would be a sample of a composite consisting of CNT and matrix material that is known to release CNT-related materials under the simulated fabrication, use or disposal conditions in the context of anticipated applications for CNT composites, closely linked to topics R3 and R7.

This topic had been evaluated initially to a mid-term time scale. Further discussion during the session led to an altered judgment that the existence of evaluated standard materials is a prerequisite for many of the other topics and should therefore be shifted to an earlier time in the map of topics.

R5. Quantity from weathering (Combined action weathering + low-mid stress, detection limits)

Apparatus and methods for weathering tests of coatings, plastics etc. are commercially available and ISO-standardized. But these methods focus on the optical and mechanical properties of the bulk material that remains after weathering, whereas no methods are validated to investigate the fragments that may be released. Both, the material released during the weathering test and the release from a combined action of normal-use mechanical stress after weathering deserve novel methods of assessment. The first goal is the identification of released fragments, the second their quantification.

R6. Classification of processing steps with probability of release

To predict the release of CNT-related materials it is necessary to consider properties of the CNT composite from initial production, compositing (through master batches, pre-preg, final compositing), fabrication involving the composite, coated composite products in consumer hands, and disposal. For example, coated CNT composite materials during use in an undisturbed environment may be less likely to release CNT than fabrication processes that involve milling or abrasion of the composite. The systematic evaluation and development of heuristic or classification principles for these likelihoods across ranges of material uses (for example the type of polymer or CNT as well as the product use of the composite) would facilitate an identification of measurement and risk management priorities. Such principles would also facilitate the development of composite-use combinations that consider the benefits of release minimization at selected stages of CNT composite production, use, and disposal.

R7. Classification of nanomaterials with probability of release (Correlation between quality of nanocomposite and release probability)

To enable a more efficient assessment of exposure probability, even before R&D is conducted on a certain novel nanocomposite material, a classification by 'indicators of release probability' will be required. Some obvious indicators will be extrapolated from the known life cycle behavior of the matrix material (e.g. photostability, softness/hardness). Others may include the quality of dispersion of the nanofillers within the matrix, the degree of compatibilization between the nanofiller surface and the matrix, or known catalytic action of the nanofillers. This structure-activity relationship can be derived from a multidimensional nanofiller/compatibilizer/matrix series, which will include some non-commercial materials, closely linked to topic R4.

R8. Long-term stability of CNT in air

A few references in the literature are reporting that CNT can be decomposed under the influence of enzymes. Therefore it is of interest to determine the time scale for such processes under normal ambient conditions. Another topic which could be of interest is the stability of the surface functionalization and associated chemistry on CNTs over the time in the environment to answer the question if a "fresh CNT" under environmental conditions has the same interaction potential as a CNT after month or years of exposure.

R9. Validate release lab results with industrial scale field tests

Some nanocomposite materials are produced commercially, albeit not in scenarios that are known to enable the release of chemicals (including nanocomposite fragments). Using adapted lab methods to simulate e.g. agglomeration in conventionally ventilated production, a direct link between lab simulation and industrial reality can be established. Further validation concerns the machining of nanocomposite materials in workshops. Generic lab methods that determine shear stress need to be adapted to the circumstances of very specific machining tools in order to reproduce all relevant mechanical, chemical, and temperature dependencies.

R10. Focus on release from end-of-life (shredder, recycle, landfill, incineration, weathering)

Preliminary investigations have indicated that there is a low probability of individual, free CNTs to be released by in-use-scenarios. However, equally preliminary investigations confirmed that individual CNTs can appear under end-of-life scenarios, where the matrix is chemically changing, especially in the case of organic matrices. These scenarios vary strongly in the time scale involved: Some take years (landfill, weathering), some only seconds (incineration). They are less easy to simulate on lab scale than mechanical in-use-scenarios. A detailed exploration of the end-of-life-scenarios has to be initiated.

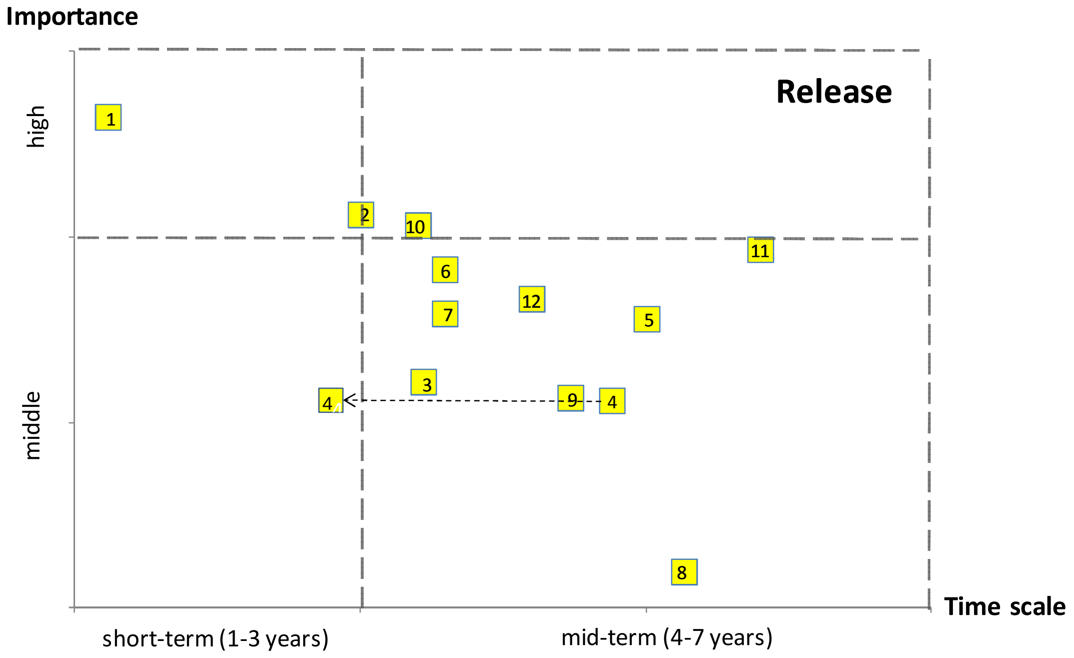
R11. Extrapolate hazard assessments from pristine to released

In a normal Tox-Test the hazard potential of the material as produced or used in the production is tested. The hazard potential of the released material from a product can vary because of differences in surface chemistry or morphology. But the amount of material getting out from release experiments is in most cases not sufficient for conducting a Tox-Test. Therefore it would be advantageous to have a tool that allows extrapolating the results from the pristine material to that being released.

R12. Build database of existing data

A number of projects create data that characterize the release of CNT under different scenarios, but there are up to now no database in existence where this information is collected in well-structured material categories and release scenarios. Such a database would be a useful tool for assessing release and also for identification of research gaps. Under ideal conditions an extrapolation from the structure of a material to the release potential is possible.

The identified topics of this session have also been judged individually by the workshop participants using importance and urgency as criteria. Results of this evaluation are summarized in the map below. Tables providing the detailed results are documented in chapter 6.



Remark: Topic R4 has been evaluated first to a mid-term time scale. The discussion to this session provides the judgment, that the existence of evaluated standard materials is a prerequisite for many of the other topics. Therefore it was decided to shift this topic to an earlier time in the map of topics.

2.3 Life Cycle Analysis of CNT-containing products

L1. Adapt LCA: scrutinize inputs / assumptions, consider most relevant scenarios, include release data, consider typical duration of use-phase until disposal

Emerging technologies are not conductive to a full-spectrum LCA due to insufficient detail knowledge about the inputs and outputs of the system. Applying LCA to nanomaterials and nanoproducts requires special consideration of certain aspects of data collection and impact modelling, such as the need to fully understand the toxicity potential of nanomaterials in human health and in the environment. The main barriers for conducting full LCAs in the nanotechnology field are: 1) the need to apply the life cycle concept consistently in all the studies; 2) the lack of reliable inventory data (inputs and outputs) as well as of data on impact relationships; 3) information gaps due to proprietary information on manufacturing processes; 4) the lack of toxicological test results; 5) wide process-to-process variability. Some of these barriers are slowly being solved by generating data at all life cycle stages. Nevertheless, it is essential to have release data at one's disposal, especially in the use and end of life stages of the life cycle.

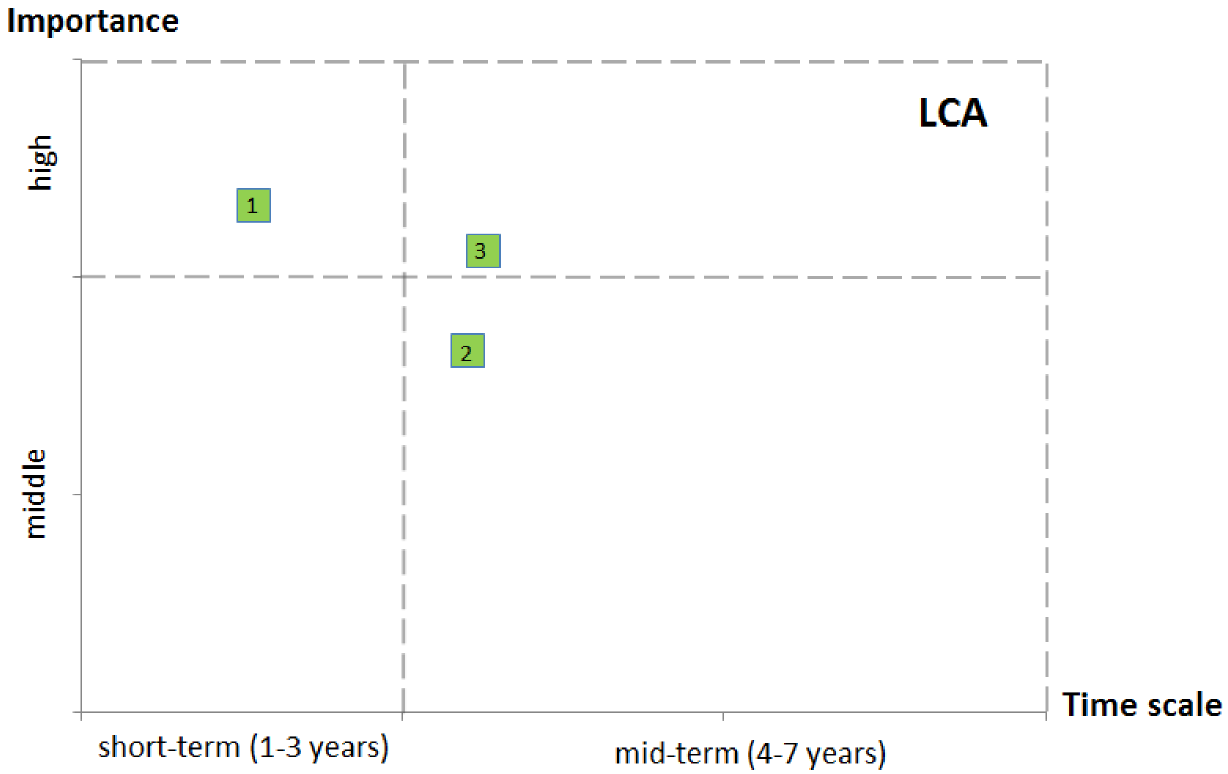
L2. Integrate NM-specific risk assessment into LCA

It is important to recall the broader context of life cycle impact assessment (LCIA) over other types of impact analysis, such as risk assessments (RA), which focus on specific materials under defined exposures for specific target organs. The data generated in risk assessment studies should be included in the LCA analysis because the combination of LCA with toxicity data and RA will enable the assessment of the overall impact and allow an identification of trade-offs.

L3. Perform LCA for high volume CNT-applications now / in 5y (with turnover)

Processes may be influenced significantly by the effect of large-scale diffusion. To this end, using a scaling-up scenario analysis to assess the traceability of nanomaterials in time and space and to evaluate the sustainability of different trajectories is recommended. This analysis will be affected by a high degree of uncertainty, but nevertheless contributes important complementary information for ongoing studies and is particularly relevant to policy makers.

The procedure for this session was the same as before. The map of topics is given in the following map, detailed results of the evaluation in chapter 6.



3. Programme

Metrology	**Chair: Heinz Fissan**
B. Stahlmecke[1], M. Hildebrandt[1], C. Asbach[1], N. Dziurowitz[1], S. Plitzko[2], H.J. Kiesling[3], M. Voetz[3], T.A.J. Kuhlbusch[1] *[1]Institut für Energie- und Umwelttechnik e.V., [2]Federal Institute for Occupational Safety and Health (BAuA), [3]Bayer Technology Services GmbH*	Comparison of different methods for generation and sampling of airborne CNTs
Jurg Schutz *CSIRO Materials Science and Engineering*	Detection of Carbon Nanotubes in Air
Shuji Tsuruoka[1], Endo Morinobu[1], Bunshi Fugetsu[2], Naoto Saito[3], Yuki Usui[3], Toshihiko Fujimori[1], Kestumi Kaneko[1] *[1]Shinshu University, Research Center for Exotic Nanocarbons, [2]Hokkaido University, Laboratory of Environmental Medical Chemistry, Graduate School of Environmental Science, [3]Shinshu University, School of Medicine*	Novel technique to detect nanocarbon distribution using CNT peapod
Mareile Renker, Astrid John, T.A.J. Kuhlbusch *Institut für Energie- und Umwelttechnik e.V.*	Characterisation of CNT using a thermo-optical elemental carbon / organic carbon analyser
David Y.H. Pui[1], Jing Wang[2] *[1]University of Minnesota, [2]ETH Zurich and EMPA*	Dispersion, Measurement, Filtration, and Exposure Assessment of CNTs

Release and potential exposure during the production of CNT and processing of CNT-containing products	**Chair: Richard Canady**
Heinz Fissan *Institut für Energie- und Umwelttechnik e.V.*	Strategies for Nanoparticle Release Assessment from Powders, Liquid and Solid Materials into the Environment
Carsten Möhlmann *Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA)*	Exposure to carbon nanotubes in research and industry
Gwi-Nam Bae *Korea Institute of Science and Technology*	24-hr monitoring of nanoaerosols in a CNT manufacturing workplace
Elisabet Fernández-Rosas[1], Gemma Janer[1], Martí Busquets[2], Víctor Puntes[2], Socorro Vázquez-Campos[1] *[1]LEITAT Technological Center, Terrassa (Barcelona), Spain; [2]Institut Català de Nanotecnologia, Campus UAB, Bellaterra (Barcelona), Spain*	Ageing/weathering of MWCNT and MWCNT nanocomposites
M.Ono-Ogasawara[1], M.Takaya[1], H.Kubota[1], Y.Shinohara[1], E.Akiba[2], S.Tsuruoka[3] , S.Koda[1] *[1] JNIOSH, [2]KURARAY LIVING Co., Ltd, [3]Shinshu University*	Exposure Assessment of a weaving process of CNT-coated yarn by applying carbon analysis

Life Cycle Analysis of CNT-containing products	**Chair: Mariko Ono-Ogasawara**
Martin Möller *Öko-Institut*	Nano Sustainability Check
Richard Canady *ILSI Research Foundation*	NanoRelease Project
Wendel Wohlleben *BASF SE*	Characterization of fragments released from CNT-composites under use-phase-scenarios, benchmarked on CNT-formulations
Matthias Voetz *Bayer Technology Services GmbH*	Exposure in the Lifecycle of CNT – Measurements from Production to Weathering

4. List of participants

First Name	**Family Name**	**Affiliation**	**Country**
Eiji	Akiba	Kuraray Living Co., Ltd.	Japan
Gwi-Nam	Bae	Korea Institute of Science and Technology	Korea
Markus	Berges	IFA - Institute for Occupational Safety of the DGUV	Germany
Richard	Canady	ILSI Research Foundation	USA
Heinz	Fissan	Institute of Energy and Environmental Technology - IUTA e.V.	Germany
Wouter	Fransman	TNO	Netherlands
Rebecca	Goldscher	NES Consortium	Israel
Holger	Hoffschulz	Bayer Technology Services GmbH	Germany
Astrid	John	Institute of Energy and Environmental Technology - IUTA e.V.	Germany
Péter	Krüger	Bayer MaterialScience AG	Germany
Hefetz	Meir	Plasan Sasa	Israel
Carsten	Möhlmann	Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA)	Germany
Martin	Möller	Öko-Institut e.V.	Germany
Eiichi	Niino	Mitsui Bussan Techno Products Co., Ltd.	Japan
Atsushi	Ogawa	JFE Techno-Research Corporation	Japan
Mariko	Ono-Ogasawara	Japan National Institute of Occupational Safety and Health (JNIOSH)	Japan
Martin	Pick	Q-Flo Limited	UK
Jürg	Schütz	CSIRO Materials Science and Engineering	Australia
Burkhard	Stahlmecke	Institute of Energy and Environmental Technology - IUTA e.V.	Germany
Eheline	Süßmann	Mitsui & Co. Deutschland GmbH	Germany
Shuji	Tsuruoka	Shinshu University	Japan
Socorro	Vázquez-Campos	LEITAT Technological Center	Spain
Matthias	Voetz	Bayer Technology Services GmbH	Germany
Jing	Wang	ETH Zurich/EMPA	Switzerland
Wendel	Wohlleben	BASF SE	Germany

5. Abstracts

Session Metrology

Comparison of different methods for generation and sampling of airborne CNTs

B. Stahlmecke[1], M. Hildebrandt[1], C. Asbach[1], N. Dziurowitz[1], S. Plitzko[2], H.J. Kiesling[3], M. Voetz[3], T.A.J. Kuhlbusch[1]
[1]Institut für Energie- und Umwelttechnik e.V., [2]Federal Institute for Occupational Safety and Health (BAuA), [3]Bayer Technology Services GmbH

Particle sampling is an integral part of exposure measurement. This is especially true for airborne fibres like carbon nanotubes (CNT) or carbon nanofibres (CNF), since online specific measurement techniques for fibrous particles are still under development. In the present study we investigated the generation of airborne CNT and CNF either by wet dispersion of an aqueous suspension using an atomizer followed by a Nafion dryer or by dry dispersion of the CNT or CNF powder respectively. Two commercial Nanoaerosol Samplers (NAS, TSI model 3089) with different polarity and the prototype of a thermal precipitator (TP prototype of personal sampler; Federal Institute for Occupational Safety and Health, BAuA) were utilised to sample the airborne particles on suitable substrates. Also, the influence of a charger and preseparator on sampling efficiency of one of the NAS was studied in detail. We will present the setup and discuss results of the statistical investigation based on a scanning electron microscopic analysis of the different test samples.

Detection of Carbon Nanotubes in Air

Jurg Schutz
CSIRO Materials Science and Engineering

Detecting Carbon Nanotubes (CNT) as an aerosol poses a number of challenges compared to more conventional aerosols such as smoke or fog. Whereas latter are comprised of relatively dense spherical particles with aspect ratios (length to diameter) of 1, CNTs are highly flexible fibres with aspect ratios of 10^3 to 10^7. Although the fibres are only 1 to 100 nm (or more typically 2 to 20 nm) in diameter they mainly present themselves as objects of extremely low density and large, more sphere-like cross section. The propagation behaviour is not only governed by its shape, a cylinder, but is in fact generally dominated by its secondary morphology: the way in which the CNT fibre is formed into a pill, a tangle or into a bundle in conjunction with other CNT fibres. These secondary structures are very stable in aerosols due to the relative strength of the van der Waals forces binding them and inter-molecular forces of the surrounding gas. Because CNTs consist entirely of carbon, it is generally not possible to detect these structures by their composition within background contaminants and in the view of their nanometre dimensions it is necessary to use high resolution Scanning or Transmission Electron Microscopy.

Novel technique to detect nanocarbon distribution using CNT peapod

Shuji Tsuruoka[1], Endo Morinobu[1], Bunshi Fugetsu[2], Naoto Saito[3], Yuki Usui[3], Toshihiko Fujimori[1], Kestumi Kaneko[1]
[1]Shinshu University, Research Center for Exotic Nanocarbons, [2]Hokkaido University, Laboratory of Environmental Medical Chemistry, Graduate School of Environmental Science, [3]Shinshu University, School of Medicine

We are developing a novel technique to determine CNT existence using a simple method that is applicable to evaluate environmental concentration of CNTs. It has been an issue to detect CNTs in a mixture because it is not easy separate CNTs from the other carbons without chemical and/or physical procedures. We propose a solution to distinguish CNTs from the other carbons in situ in environment. CNTs including heavy atoms or their salts can be detected by X-ray equipment such as XRD, XAFS, etc., even though those concentrations are quite low. In addition, they do not bring any characteristic changes of the CNTs surface, which does not affect biological responses in nature and physicochemical reactions in soil and surface water. Those atoms and salts give their unique spectra that determine CNTs in environment. In this presentation, the fundamental characteristics of CNTs including those heavy atoms will be presented.

Characterisation of CNT using a thermo-optical elemental carbon / organic carbon analyser

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Institut für Energie- und Umwelttechnik e.V.

A method for the detection and quantification of carbon nanotubes in ambient and workplace air is needed in view of exposure assessment during CNT production and the processing of CNT-containing products. Thermo-optical carbon analysis is a standard to determine exposure to soot at workplaces (NIOSH method 5040). This method uses a specific thermal protocol to fractionate different types of "organic carbon" (OC) during a first analysis step in pure helium. Similarly, "elemental carbon" (EC) is analysed in a second step in a helium/oxygen atmosphere. An optical correction is applied to account for artefact formation during analysis. In our study, different CNT are analysed to determine similarities and differences in their thermal behaviour. In addition to the above mentioned NIOSH protocol, other generally applied methods for ambient air analyses (EUSAAR 2, IMPROVE, quartz.par) are tested to determine the reaction of CNT to different temperature protocols. Finally, CNT are compared to other types of elemental and organic carbon (e.g. ambient samples, diesel soot, thermal soot) to determine if CNT can be specifically detected in workplace or ambient samples.

Dispersion, Measurement, Filtration, and Exposure Assessment of CNTs

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Dispersion plays a significant role in CNT studies as CNTs often form large agglomerates of the order of microns when provided by manufacturers. We developed an electrospray system to disperse and aerosolize CNT colloidal suspensions with controlled degree of agglomeration. Results of dispersion of CNTs and relation between the geometrical length and electrical mobility size of airborne CNTs will be presented. Results from exposure measurement in an industrial production facility for CNT-imbedded nanocomposites will be shown. We investigated particle release from CNT-imbedded composites during a mechanical abrasion process and observed free CNTs.

Session Release and potential exposure during the production of CNT and processing of CNT-containing products

Strategies for Nanoparticle Release Assessment from Powders, Liquid and Solid Materials into the Environment

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There is an increasing interest in making use of nanoobjects to take advantage of their properties to improve the functionality of powders and composite materials. Those nanoobjects can occur in form of nanoparticles and fibers (e.g. CNT) (NP) as well as their agglomerates and are used either as powders or dispersed in liquids or solids. A discussion about the possibility of negative health effects of NPs and their agglomerates/ aggregates in air has started. However, negative effects in human beings and nature can only occur, if NPs and their agglomerates/aggregates are emitted, e.g. during synthesis, from products during their lifetime and recycling or after littering in the environment. The latter case is not considered here. To reduce the chances for NP emission, the following topic areas have to be addressed: control of emission and exposure including adequate measurement techniques, abatement strategies and standardized procedures to assess the probability of nanoparticle-release from nanomaterials into the environment.

To form nanostructured materials, NPs are produced in form of powders and suspended into liquid and most often in solid materials. Different methods under different conditions trying to simulate the real world activities like in case of handling of composite material, sawing and drilling have been used thus far. The approach thus far taken to investigate the NP-release from all kinds of materials containing NPs and the different handling processes, however, is extremely time consuming. An understanding of the underlying basic processes and their representation by a limited number of test methods is needed. It should be based on determining the release probabilities of NPs for different materials. This is depending in a first step on the easiness to separate the matrix material from the NPs, which may become airborne in a second step.

Besides the complex environmental stress, two types of stress can be differentiated for the NP containing materials: mechanical and thermal stress. Almost all treatment processes (like drilling, sawing and so on) start with mechanical stress forming chunks of matrix materials containing NPs. Except in cases where the particles are loosely bound to surfaces with direct access to the environment – actually they are already matrix material free – there is no real chance to liberate the NPs, because the achievable smallest chunk size is still too big. To get to smaller and smaller dimensions of these blocks, one has to locally introduce more and more mechanical energy into the material, which becomes increasingly difficult. In case of

powders existing dustiness tests may be modified to especially concentrate on NP-release. For liquids very small droplets are produced with electrospray containing just one particle each.
In case of composites the mechanical energy input causes a (local) heating of the material.
The thermal energy input leads to evaporation and oxidation processes, which transfer material into the gas phase. In cases where the needed evaporation and /or oxidation energy for the matrix material is lower than for the NPs, there will be free NPs without matrix material. The knowledge of the basic physics and chemistry already allows for setting up a list of separation probabilities for different nanostructured materials, based on the thermal properties of the matrix material.
Since thermal energy input is the most likely relevant process to separate matrix material and NPs in case of composites, which is the first, but needed step to release NPs into air, the determination of the separation probability should be based on a thermal process, which finally can be standardized. The Thermo-Gravimetric Analysis (TGA) is a well defined and representative process, which allows the determination of the release of the matrix material into the air in comparison to nanoparticle combustion or sintering as a function of temperature.
Starting with a matrix containing a systematic order of the different forms of nanostructured materials and the list of different handling procedures, the handling procedures will be sorted according to different stress situations. Possible standard processes for different stress situations will be identified and described. Available first results for different stress situations will be discussed. It will be demonstrated how the tremendous work needed for investigating all possible handling procedures for all existing and expected nanostructured materials can be reduced by concentrating on representative processes for different stress situations, which may become standards in the future.

Exposure to carbon nanotubes in research and industry

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During the NANOSH project potential exposures from the production and/or handling of carbon nanotubes (CNTs) were measured in 26 measurement sets/handling processes and 109 measurements were made. 12 sets were achieved in production, and 14 in downstream use, both sets involving mainly research activities. As measurement strategy sequential measurement periods of similar length for nano-activities and non nano-activities were taken. Several direct-reading instruments were used to determine the number concentrations, particle size distributions, surface area concentrations and additional mass concentrations. The results were collected in a database and the differences between nano-activity and non nano-activity periods assessed to determine whether there were any significant changes in concentration. Additional aerosol sampling using TEM grids was performed to obtain an additional assessment criterion for the occurrence of nanoparticles. For the specific case of CNTs, exposure was found to be “likely” for 4 of the 18 measurement sets obtained, in 7 cases “not likely”, and for 7 cases “possible/not excluded”. The ratios for the number and surface area concentrations between nano- and non nano-activity ranged between 0.65 and 30, the highest values coming from an extrusion process. A change in particle size could only be observed in 4 measurement sets: dry sawing of composites with CNTs, extrusion and cutting of plastics containing multiwalled carbon nanotubes (MWCNTs), production of MWCNTs, and weighing and pouring MWCNTs. When handling agglomerates of CNTs, a change in the size range of 1 to 10 µm was detected. For reliable exposure estimation it is very important to have the collected aerosol samples analysed. In 5 cases the TEM analysis revealed the occurrence of CNTs, confirming the likelihood of exposure to CNTs.

24-hr monitoring of nanoaerosols in a CNT manufacturing workplace

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Area monitoring of nanoaerosols was carried out in the workplace where the CNT was manufactured through CVD (chemcial vapor deposition) process using catalyst. SMPS (scanning mobility particle sizer), dust monitor, and NAM (nanoparticle aerosol monitor) were used to monitor particle number size distribution and particle surface area. In addition, aethalometer was utilized to detect selectively elemental carbon contained in the CNT. Also, filter sampling was conducted to analyze elemental carbon using an OC/EC analyzer. In this work, time-series data plot shows some events related with the process. Background level obtained on weekends was compared with working days.

Ageing/weathering of MWCNT and MWCNT nano composites

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The incorporation of only small amounts of nanoadditives in polymeric compounds can change the nature of the original matrix due to the large surface area to volume ratio of nanomaterials. Particularly, multi-walled carbon nanotubes (MWCNT) in polymeric composites offer some interesting added properties. They can be processed easily, strengthening and stiffening amorphous materials as well as semicrystalline polymers. MWCNT are found to disperse and distribute appropriately and in a highly oriented way in polymeric matrices. Therefore, increasing the yield strength, the Young’s modulus, ultimate tensile strength, increasing the photo-oxidative durability, and the toughness in matrices such as PP and nylon6 (PA6) [1]. With PA6 it has also been demonstrated that nanocomposites with a hybrid composition of nanofillers (CNT-clays) increase the tensile modulus and the tensile strength by about 290% and 150% respectively [2]. In other polymeric compounds like ethylene vinyl-acetate (EVA), carbon nanotubes act as inner filters and antioxidants, which contribute to reduction in the rate of photooxidation of the polymer [3]. These additional properties can be used to produce advanced materials with new applications in the most of the industrial sectors, with a particularly high incidence in electronics, automotive and textile.

Morphological changes are the subject of discussion for semicrystalline polymers, but over the last years, it has become increasingly apparent the need to know how nanofillers modify, not only the final product, but its behaviour during aging. With this aim, the present work has focused in two main objectives: i) Manufacturing of MWCNT nanocomposites (included in thermoplastic polymer nylon6 (PA6)) and accelerated aging in weathering chambers, and ii) evaluation of the migration and/or release of nanoadditives during aging. To better understand the importance of compatibilization between the matrix and the nanomaterial, two nanocomposites containing pristine MWCNT (incompatible with the polar polymeric matrix) and a MWCNT-PA6 masterbatch (well dispersed MWCNT in the polymeric matrix) have been generated. The work presented here will include the results obtained on the migration evaluation of nanoadditives into the polymeric matrix and the role of dispersibility when nanocomposites are submitted to accelerate aging conditions. Furthermore, toxicological evaluation of potential released MWCNT in different stages of their life cycle will be shown. Finally, this data will be used to perform an exhaustive life cycle assessment analysis for nanotechnology-based products.

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[2] Liu, T. X., Phang, I. Y., Shen, L., Chow, S. Y., Zhang, W. D. *Macromolecules* **2004**, 37, 7214.
[3] Morlat-Therias, S., Fanton, E., Gardette, J-L., Peeterbroeck, S., Alexandre, M., Dubois, P. *Polymer Degradation and Stability*, **2007**.92(10), 1873-1882.

Exposure Assessment of a weaving process of CNT-coated yarn by applying carbon analysis

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Japan NIOSH has conducted exposure assessment mainly for the workplace where nanomaterials including multi-walled carbon nanotubes (MWCNT) are handled because higher exposure was expected. Downstream users, who handle small amount of MWCNT and/or MWCNT containing products, also need exposure assessment. One of the applications of MWCNT is an sheet heating element1) woven from MWCNT-coated yarn, CNTEC®, which was developed by Kuraray Living Co., Ltd. and Mitsui Co. Ltd., We visited the factory, Matsubun Textile Co. Ltd., to assess the probability of exposure to MWCNT or MWCNT containing particles during the weaving process of MWCNT-coated yarn. This assessment was conducted by measuring particle concentrations, microscopic observation, and carbon analysis with the modified protocol.

In the weaving process, neither the increase in the number of particles nor the difference in particle-size distribution was observed. From the scanning electron micrographic observation, there were micron-size particles containing MWCNT as fragments of the MWCNT-coated yarn. We could not detected MWCNT fibers by this field monitoring. In the workplace, there are large amount of polyester fragments from polyester yarn and small amount of fragments from MWCNT-coated yarn. In order to distinguish between particles containing MWCNT and polyester particles, we sophisticated the method of carbon analysis. Transmission electron microscopic observation supported the separation between both particles by the carbon analysis. The concentration of MWCNT contained in micron-size particles did not exceed 0.0053 mg-C/m^3 for both area sampling and personal sampling (conducted by one of the authors) around the loom. This value was much lower than the respirable dust mass concentration.

1) http://www.baytubes.com/news_and_services/pr_100223_heater.html

Session Life Cycle Analysis of CNT-containing products

Nano Sustainability Check

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Öko-Institut

As part of the current debate on the opportunities and risks of nanotechnological applications, the debate on possible contributions to sustainable development is becoming increasingly controversial. It should rather be conducted on a more objective level. This objectification, however, can only be achieved on a case-specific basis, performing – as quantitatively as possible – a risk-and-benefit assessment targeted towards the total life cycle. The methodological basis for such a systemic view, however, is still largely lacking.

Against this background, the Öko-Institut, with the Nano Sustainability Check, provides an instrument offering a systematic grid for an integrated approach relative to sustainability aspects of nanotechnological applications. The approach chosen allows the Nano Sustainability Check to serve as a strategic radar system for the management of opportunities and risks, in order to be able, for example, to anticipate beneficial effects for the environment and to identify new markets on the one hand, and on the other to strive to avoid bad investments and dangers to the society.

With the help of the Nano Sustainability Check, companies that develop or produce nanotechnological products and applications can carry out themselves an evaluation of their own business activities.

The aim of the Nano Sustainability Check is to examine the sustainability of products and applications containing nano-materials in terms of their practical advantages. The most important feature in this context is an evaluation grid by means of which nano-products (i.e. products that are produced with nano-materials) can be analyzed by comparison with an existing reference product that has been manufactured without the use of nano-materials. In addition, the evaluation grid is able to address any possible risks.

In terms of methodology, the Nano Sustainability Check is based on PROSA (Product Sustainability Assessment), a tool for strategic analysis and assessment of product portfolios, products and services which has been developed by the Öko-Institut. PROSA takes into account the entire life cycle and analyzes and assesses the environmental, economic and social opportunities and risks of future development paths. With its underlying integrated view, PROSA helps to identify system innovations and options for action in line with a sustainable development and structures the decision-making processes necessary to this end.

The aspects investigated within the Nano Sustainability Check are represented in the form of a total of 14 key performance indicators. The focus is on aspects of environmental and climate protection, which are – as far as possible – considered from a quantitative point of view. In addition, questions relating to the fields of occupational safety and health are examined, as well as benefit and socio-economic aspects. Due to the complexity of the issue, in many cases only a qualitative assessment is possible with view to these aspects. Even in such cases, however, the use of specifically formulated criteria and key questions enables a transformation of the qualitative approach into a semi-quantitative, comparative assessment between nano and reference products.

The results of the individual key performance indicators are combined into a single representation. To this purpose, the "SWOT analysis" originally derived from business administration is taken up and adapted for the purposes of the Nano Sustainability Check. The established tool of strategic management combines an inward-looking strength / weakness analysis with an opportunity / threats analysis which is related to environmental factors.

In the framework of the Nano Sustainability Check, the strength / weakness analysis refers to the intrinsic properties and potentials of the product, for example in terms of CO_2 footprint, usability and life cycle costs. Complementarily, the opportunity / threat analysis takes into account external conditions such as impact on employment, social benefits and risk perception. When comparing nano and reference product, each individual key indicator is assigned to one of these two levels. If, for example, the nano-product as compared to the reference product performs better in terms of the CO_2 footprint, this key performance indicator may be regarded as a strength. If, however, the employment effect is lower than that of the reference product, there is a threat in this key performance indicator. If the indicator is on par with both products, it is regarded to be indifferent and is reported separately. In this way, a "SWOT matrix" is created as a central tool in the communication of results. A more extensive aggregation of the results, as through a one-point assessment, will not take place, as this would involve an excessive loss of information.

Based on the SWOT matrix, recommendations for a strategic optimization of the investigated application can finally be developed. Their goal is to maximize the positive potential of strengths and opportunities with regard to sustainability while minimizing potential negative effects of weaknesses and risks.

Besides the description of the methodical approach, this report contains the results of two case studies in which the Nano Sustainability Check was first applied as part of a pilot survey. These cases concerned a surface coating of glass with high UV protection (pro.Glass® Barrier 401 by Nanogate Industrial Solutions GmbH) and a concrete catalyst (X-SEED® by BASF SE).

Based on these case studies, it could be shown that the Nano Sustainably Check allows for a differentiated consideration of sustainability aspects when comparing a nano-product to a reference product. Although in both cases the products under consideration were still in the phase of market introduction, the data required for the key indicators could be determined. The case studies also show that nano-products with significant leverage effects in the CO_2 savings potential are currently under development. Both large companies such as BASF as well as small and medium businesses like Nanogate are thus provided with a development-accompanying tool that enables them to quantify and systematically harness the existing potentials of nanotechnological applications. Moreover, knowledge gaps that still exist and possible risks can be identified at an early stage. This can help to develop appropriate problem solving strategies. The Nano Sustainability Check offers users the facility of an early warning system and thus provides an important indication as to what direction should be taken in the innovation process of nano-products.

NanoRelease Project

Richard Canady

ILSI Research Foundation

The NanoRelease project (www.ilsi.org/ResearchFoundation/Pages/NanoRelease1.aspx) is a multi-stakeholder consortium across government agencies, civil society organizations, leading industry, and academics. The goals of the project are to:

- Compile laboratory analysis methods for and understanding of release of engineered nanomaterials (ENM) over the life cycle of solid product fabrication, use, and disposal,
- Identify gaps where additional methods development is needed, and
- Design and carryout methods-development plans to fill gaps so that generally accepted and useful methods are available.

Through these actions the project will translate developing science of nanotechnology into best practice, infrastructure, experience, and confidence in methods to measure ENM source terms for estimating exposure and risk relevant to commercial products. This will aid development of guidance for risk assessment and management, facilitate safe development of products, and generate confidence in the safety of certain uses of the technology.

To make the methods most directly applicable, the project will select and then focus on a particular type of material in commercial applications. The first material type chosen by the project is multiwalled carbon nanotubes (MWCNT) in a polymer matrix. Other specific material types may be selected in future evaluations by the project. Outputs of the project will include:

- A state of the science report regarding the methods to measure release of specific ENMs from a specific kind of matrix, relevant to a material with broad application in commerce.
- Laboratory testing results for the methods, where the intention of the testing will be to build confidence in the utility and robustness, among other attributes, of the methods.
- Referral of measurement methods to a Standards Development Organization for development of standard methods.

The Steering Committee of the project is currently recruiting and convening three expert groups to develop white papers on 1) MWCNT "release" measurement methods, 2) material characteristics that influence MWCNT release, and 3) release scenarios across the life cycle of typical commercial MWCNT-polymer products. A workshop is planned for mid 2012 to close out the white paper development. Inter-laboratory testing and development of methods is intended to begin in late 2012.

Characterization of fragments released from CNT-composites under use-phase-scenarios, benchmarked on CNT-formulations

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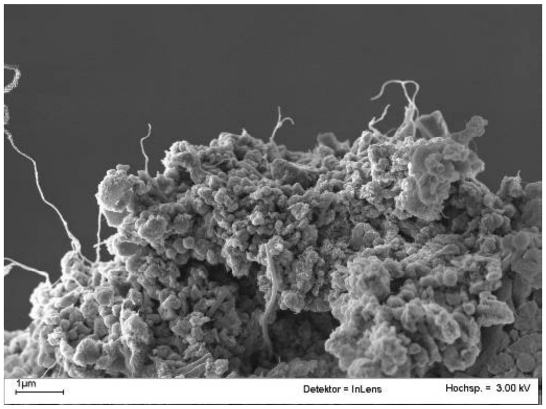
BASF SE

Risk assessment of nanomaterials takes into account their changing properties e.g. by compounding in a matrix, by consumer use or release scenarios and during hazard testing. Typical consumer products are nanocomposite materials, where a matrix contains some wt% of nanoparticles or -fibers. We report on the pertinent questions 'what kind of fragments are released from nanocomposites?' and 'how many free nanofillers are released?'.



We characterized the degradation products from thermoplastic and cementitious nanocomposites after weathering vs. sanding vs. normal use, up to the in vivo effects of the released fragments (ref 1). Novel results support our preliminary, risk assessment of nanocomposites. The figure shows fragments from a cement / CNT composite after do-it-yourself sanding.

Although ISO standards exist, many particle methods need validation before one can quantify for CNTs their degree of individualization and dispersed concentration and their designed or spontaneous adsorbates. Such metrology issues were adressed for formulations (ref 2) but help also to identify CNTs in the debris from lifecycle studies.

1) W. Wohlleben et al., 'On the lifecycle of nanocomposites: Comparing released fragments and their vivo hazard from three release mechanisms and four nanocomposites.', *Small*, in print (**2011**). DOI: 10.1002/smll.201002054
2) E. Karabudak, C. Backes et al., 'A universal ultracentrifuge spectrometer identifies CNT-intercalant-surfactant complexes from movies of fractionation', ChemPhysChem 11, 2010, 3224-3227 & Chem. Eur. J. 16, 2010, 13176-13184

Exposure in the Lifecycle of CNT – Measurements from Production to Weathering

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Over the whole lifecycle from CNT is the possibility of an emission in the environmental given. Therefore we investigate in the projects CarboSafe and CarboLifecycle as a part of Inno.CNT the possible emission/exposure of air borne single MWCNT or small agglomerates of MWCNT, starting at the production site of MWCNT and ends at a simulation of the shredding process for recycling or incineration at the end of the life of a CNT/Polymer Compound.
In the talk we present the results and/or the design of these Experiments and measurements.

6. Tables

The subsequent tables provide detailed results, including mean value and standard deviation according to the feedback provided by participants.

Metrology

No.	Topic	Time scale [1)]	Deviat-ion	Impor-tance [2)]	Deviat-ion
1	Couple classification + online spectroscopy	1,89	0,62	2,26	0,66
2	Collector + automated image analysis	1,55	0,60	2,50	0,61
3	Labeling vs. natural / non-CNT background (not only aerosol)	1,55	0,68	2,25	0,55
4	Distinguish HARN vs WHO fibers	1,53	0,62	2,16	0,66
5	To generate predefined CNT aerosols	1,58	0,70	1,95	0,67
6	Calibration for elemental carbon	1,56	0,60	1,78	0,62
7	By length / MMAD / shape	1,85	0,45	2,10	0,43
8	By chemistry/surface funct., → persistence, fate	1,90	0,60	2,50	0,54
9	→ (tox)	2,27	0,64	2,40	0,68
10	Precursor particles as tracer for CNTs	2,11	0,50	1,68	0,57
11	Continous monitoring (low-cost)(not always HARN)	1,80	0,49	2,65	0,64
12	Number vs surface vs mass metrics	1,79	0,66	2,21	0,58

Release and potential exposure during the production of CNT and processing of CNT-containing products

No.	Topic	Time scale [1]	Deviat-ion	Impor-tance [2]	Deviat-ion
1	Sampling and online instruments	1,06	0,11	2,82	0,29
2	Release tests with agreed methods	1,50	0,50	2,56	0,49
3	Quality of release	1,61	0,54	2,11	0,59
4	Standard materials for release measurement	1,94	0,44	2,06	0,55
5	Quantity from Weathering	2,00	0,33	2,28	0,64
6	Classification of processing steps with probability of release	1,65	0,61	2,41	0,62
7	Classification of nanomaterials with probability of release	1,65	0,53	2,29	0,58
8	Long-term stability of CNT in air	2,07	0,25	1,60	0,72
9	Validate release lab results with industrial scale field tests	1,87	0,46	2,07	0,37
10	Focus on release from end-of-lif	1,60	0,64	2,53	0,62
11	Extrapolate hazard assessments from pristine to released	2,20	0,43	2,47	0,50
12	Build database of existing data	1,80	0,64	2,33	0,71

Life Cycle Analysis of CNT-containing products

No.	Topic	Time scale [1]	Deviat-ion	Impor-tance [2]	Deviat-ion
1	Adapt LCA	1,27	0,39	2,67	0,44
2	Integrate NM-specific risk assessment into LCA	1,60	0,56	2,33	0,44
3	Perform LCA for high volume CNT-applications now / in 5y (with turnover)	1,63	0,70	2,56	0,49

[1] 1: Short-term (1-3 years), 2: Mid-term (4-7 years), 3: long-term (> 8 years)
[2] 1: low, 2: middle, 3: high