



Consumer Products Monograph Series

Multi-Walled Carbon Nanotubes in Polymer Matrices

Phase 2.5 Report—Comparison of Existing
Studies of Release Measurement for
MWCNT-Polymer Composites



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Comparison of Existing Studies of Release Measurement for MWCNT-Polymer Composites

Phase 2.5 Report

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Comparison of Existing Studies of Release Measurement for MWCNT-Polymer Composites

Phase 2.5 Report

1. Introduction: Study Aims

Currently there are no broadly accepted methods for evaluating release of multi-walled carbon nanotubes (MWCNTs) from polymer matrices, which is a crucial component of conducting exposure assessments for nanomaterials in consumer products. The objective of Phase 2.5 of the NanoRelease project is to provide a clear path forward for methods development through the review of the specific strengths and limitations of existing test methodologies for measuring release of MWCNTs from polymer matrices. For Phase 2.5, we:

1. Reviewed all published studies of MWCNT release from polymer composites,
2. Interviewed experts in laboratories that had conducted such studies regarding unpublished analyses and details of the studies relevant to selecting materials and methods best suited for further methods development,
3. Compared the results to the draft white papers prepared by the NanoRelease project, and
4. Compiled this report to support NanoRelease Consumer Products Steering Committee (Steering Committee) deliberations for selecting material(s) and method(s) to be carried forth for Phase 3 Interlaboratory Studies.

Although we believe we have identified and included the most relevant studies and laboratories for the decision needs of the Steering Committee, this report is being continually updated (as of May 2013) as studies are added to the open literature and as unpublished studies are made available. It is anticipated that there are unpublished studies that could be added through the methods development process undertaken by the NanoRelease Consumer Products Interlaboratory Testing Group (ITG). Over 35 studies were reviewed that investigated a variety of MWCNT-polymer combinations in release scenarios relevant to different product life stages such as manufacturing, consumer use, and end-of-life cycle. Additional studies were reviewed where analytical methods were thought to be informative for CNT and polymer release measurements. Eleven laboratories have been interviewed to include information from ongoing and unpublished studies, to clarify the details of materials and methods used in publications, and to gain insight into the choices made by leading researchers who are addressing this information and methods gaps. The aim of this report was not to have conducted a full review of all possible standard methods but of those with the highest relevance.

This report is provided as “information only” for the use of the Steering Committee and should not be taken as binding conclusions of the NanoRelease project. It is recognized that there are multiple paths for methods development that could be undertaken by the Steering Committee, and any one selection will be taken to reduce scope to manageable levels rather than to make a statement of risk or absolute priority. The selection of a path forward in methods development must consider a balance between the utility of the methods developed toward addressing a risk management need and the feasibility of developing methods with current understanding, technology, and accepted practice.

2. Summary of the Information from the Literature Review and Interviews

Information regarding MWCNT-polymer release scenarios, mechanisms, and methods was reviewed from existing publications on MWCNT-polymer release and interviewed experts from relevant organizations (see [Phase 2.5 Question Matrix](#)). Note that studies on non-CNT and non-polymer systems that were considered informative for analytical methods were also included in the report.

In summary, the studies on nanomaterial release from solid matrices reviewed for this report either simulated a specific release mechanism in a laboratory setting, modeled release through recreation of real-world conditions, or sampled the environment in actual release settings. Table 2.1 summarizes the potential release scenarios and simulated release mechanisms from past and current studies; references not specific to MWCNTs and polymers are noted in bold type.

2.1. Note Regarding Definitions of Release Mechanisms or Processes Studied for MWCNT Release

Depending on materials and use patterns, release of MWCNTs may occur to varying degrees of magnitude throughout the life cycle of commercial products and may be caused by a wide variety of processes. In reviewing the literature, it became clear that the use of terms for the release processes differed widely between the different publications and in some cases, the terms are used inconsistently (for example, abrasion in one study may refer to a process similar to sanding in another study). Therefore, it is useful to list the kinds of release processes reviewed. Our understanding of the terms used in this report is as follows.

2.1.1. Mainly Mechanical Processes

Mixing and sonication is a mechanical process where the nanomaterial is brought into or already in a liquid phase. This process is required to create different formulations of MWCNT-polymers using raw or functionalized MWCNTs. Workplace conditions are typically conducted with local exhaust ventilation along with a glove box to minimize exposure (Dahm et al., 2012).

Table 2.1 Potential release scenarios and simulated release mechanisms used in existing studies

Potential Release Scenario	Release Mechanism	Simulated Release Scenarios (Number of studies and interviews)	Actual Real-Time Scenarios (Number of studies and interviews)	References
Manufacturing (Machining)	Mixing/Sonication	0	2	Dahm et al., 2012; Fleury et al., 2011
	Sanding	16	1	Cena and Peters, 2011; Gohler et al., 2010; Gohler et al., 2012; Gupta, 2013*; Hellmann et al., 2012; Hirth et al., 2013; Huang et al., 2012; Koponen et al., 2009; Koponen et al., 2011 ; Methner et al., 2012; Nanocyl, 2013*; Saber et al., 2012 ; Schlagenhauf et al., 2012; Stintz, 2013*; Voetz, 2013*; Wohlleben et al., 2011; Wohlleben et al., 2013
	Grinding	3	1	Bello, 2013*; Fleury et al., 2011; Methner et al., 2012; Ogura et al., 2012
	Drilling	2	1	Bello et al., 2010; Dahm et al., 2012; Voetz, 2013*
	Cutting/Sawing	3	1	Bello et al., 2009; Methner et al., 2012; Scott et al., 2012; Voetz, 2013*
Consumer Use (e.g., sports equipment, electronics, windmill blades/fuel system parts, tires, textiles)	UV Weathering	9	1	Bello, 2013*; Golanski, 2013*; Hirth et al., 2013; Nanocyl, 2013*; NanoPolyTox, 2013*; Nguyen et al., 2011; Nguyen et al., 2012; Voetz, 2013*; Wohlleben et al., 2011; Wohlleben et al., 2013
	UV + Wet Weathering	5	1	Bello, 2013*; Hirth et al., 2013; Nanocyl, 2013*; NanoPolyTox, 2013*; Voetz, 2013*; Wohlleben et al., 2013
	Abrasion	13	0	Golanski et al., 2010; Golanski et al., 2011 ; Golanski et al., 2012; Golanski, 2013*; Guiot et al., 2009; Meng et al., 2009; Nanocyl, 2013*; Schlagenhauf et al., 2012; Scott et al., 2012; Stintz, 2013*; Vorbau et al., 2009 ; Wohlleben et al., 2011; Wohlleben et al., 2013
Thermal degradation		2	0	Bouillard et al., 2013; Orhan et al., 2012
Landfill	See Abrasion and Weathering	--	--	--

Extracted from TG3 White Paper and [Phase 2.5 Question Matrix](#)

BOLD text denotes studies that are **not** specific to MWCNTs and polymers, but that were included to provide further information on some release mechanisms and particle measurement approaches.

*Information gathered from an interview.

Sanding is a higher-energy type of mechanical stress where shear forces of a rough surface act on the matrix. Cracks can be propagated through the polymer and pull the MWCNTs only partially out of the matrix due to sheer strength between the CNT and the matrix. In this case, the CNTs typically form micron-sized protrusions on the polymer surface (Cena and Peters, 2011; Hirth et al., 2013; Huang et al., 2012). As with all high-speed processes, sanding may also produce some heat, influencing a possible release.

Abrasion is a mechanical process describing the dynamic friction between two surfaces, one of which sometimes has a rough surface. It is supposed to simulate, for example, use of consumer products like cleaning, sliding, walking, and scratching. Hence, it is low-energy type of mechanical stress with a lower likeliness of heat production. One of the most commonly used methods for simulating abrasive damage is the Taber Abraser test, which is described in many national and international standards (e.g., DIN 53754:1977, DIN 68861-2:1981, ISO 5470-1:1999, and ASTM D 4060-95:2007). Briefly, the Taber Abraser rotates the sample against the abrasion wheels and wear rate is measured as a function of mass loss by the sample.

Grinding is understood as a mixed process of milling and cutting of materials. It can occur upstream or downstream of the manufacturing process for MWCNT-polymers. MWCNT-polymers can be ground or cut to form pellets for injection molding machines (Hellmann et al., 2012). At the end-of-life recycling stage, composite waste can be ground or cut to generate new pellets for recycling. MWCNTs released during the grinding process can generate significant airborne MWCNTs still embedded in particles of the polymer matrix (Fleury et al., 2011). Release may occur during the act of opening the grinder lid and product removal. In addition, micron-sized particles with protruding fibers released via grinding may be volatile particles released by the friction heat produced by the grinding process (Ogura et al., 2012).

Drilling is understood as a mechanical process where high-speed mechanical shear forces are used often to produce a hole. Release rates and particle characteristics from drilling are affected by composite type, drilling rate (rpm), sample thickness, and dry versus wet conditions (Bello et al., 2010). Wet drilling can be accomplished by continuously spraying the sample composite with distilled water, leading to reduced heat.

Cutting/Sawing is a relatively low-speed mechanical process with a limited contact area to the material. It is used to derive specific forms and pieces from composite materials. Wet cutting and sawing is sometimes used to reduce heat.

Scratching is a special case of a low-speed mechanical process with a limited contact area to the material. This process can be simulated by using, for example, a metallic comb being pushed over a surface with a specific weight (Golanski et al., 2012).

Mechanical shock is another special case of low-energy mechanical process. This process is seen to simulate short hits as they may occur when the product falls down

to the ground or experiences sudden mechanical hits by accident. This process can be simulated by a vibrating plate/engraver as was tested by Golanski et al. (2012).

2.1.2. Chemical and Physical Processes

UV Weathering is a process of degradation and release that can be simulated using UV radiation leading to the oxidation of an organic matrix, for example. Hence, exposure to UV radiation (e.g., under dry conditions) can degrade the CNT-polymer matrix, leaving behind an entangled collapsed CNT network (Hirth et al., 2013). Most studies employed ISO 3892-2:2006 with the SunTest™ XLS weathering chamber apparatus at standard-black temperature 65 °C, with UV irradiation (111 W/m² at 300–400 nm). Another study (Nguyen et al., 2011) used exposure to UV radiation using a 2-m integrating sphere-based weathering chamber, referred to as SPHERE (Simulated Photodegradation via High Energy Radiant Exposure).

Wet Weathering extends on the dry weathering method by adding simulated rain. The latter may lead to leaching and erosion from surfaces as well as enhanced degradation mechanisms by radicals formed in the liquid film on a CNT containing polymer matrix, for example. This simulation may also mimic to a limited degree the incorporation into a landfill at disposal, which could include other solvents that can degrade CNT-polymer matrix. Studies used ISO 4892/06: Humidity cycle (102 min dry, 18 min rain), at average relative humidity of 50 ± 10% (Hirth et al., 2013; Interview with NanoPolyTox, 2013; Wohlleben et al., 2013). Time of studies varied from 1000 to 1243 h to simulate a 9-month treatment, at the same standard-black temperature of 65 °C in the Atlas SunTest™ XXL weathering chamber. One study analyzed lyophilized rainwater as well as aged MWCNT powders dissolved in water (Interview with NanoPolyTox, 2013).

2.1.3. Thermal Processes (Special Case of Chemical and Physical Processes)

Thermal Degradation is another mechanism of selectively removing the matrix from a CNT containing polymer. The mechanisms involved here are evaporation of matrix components as well as changes in the chemical composition by elimination and cracking as well as some oxidation reactions. Only few studies on thermal degradation are currently available. For instance, Orhan et al. (2012) examined thermal stability as a function of carbonaceous char formation using direct-pyrolysis mass with a thermogravimetric analyzer (TGA). Another study was conducted by Voetz et al. (see Interview in Question Matrix for Phase 2.5) within the German InnoCNT initiative.

Combustion is an exothermal process not entirely different from thermal degradation (see above). The main difference is the high energy release in the form of heat during explosion or fire leading to mainly oxidized compounds as the final product. This also means that differently from thermal degradation, combustion may lead to the total oxidation and hence partial or total degradation of CNT. This was investigated and shown in, for example, studies by Bouillard et al. (2013). Some work on CNT-composite materials in fires began recently within the European Union's Project Decora.

Incineration differs from thermal degradation and combustion in that it aims at high temperatures in an oxygen sufficient system with a minimum of residence time of the compounds in the incineration zone. Asbach et al. (to be published) conducted such a study within the German Innovation Alliance CNT initiative and showed the complete degradation of the CNT in the systems investigated.

Table 2.2 summarizes the various methodologies that have been utilized to generate release samples, the different types of instrumentation used for measurement of particles released, and the data analysis method. These data were compiled from a series of existing publications and interviews from past, current, and ongoing studies.

2.2. Summary of Information Received for Each Question

Questions were selected to allow identification of the most common approaches used to investigate MWCNT release from polymers (e.g., material, scenario modeled, technique, instrumentation, etc.), allow comparison across laboratories, and match laboratories with similar approaches for the Interlaboratory Study in Phase 3. The responses to the [Phase 2.5 Question Matrix](#), along with the evaluation, and comments on the appropriateness of the approaches will build the basis for recommending which methods to pursue in the Interlaboratory Study in Phase 3.

The question matrix developed for this investigation is divided into six major sections:

- A. CNT, polymer, and CNT-polymer systems used
- B. Release scenario modeled
- C. Sample generation
- D. Analytic method used to measure release
- E. Instrumentation used to measure release
- F. Existing collaboration and networks (interview only)

Question sections A-E were used for the evaluation of the literature as well as for the interviews. The last section is applicable only to the interviews.

A. Questions regarding CNT, polymer, and CNT-polymer systems used

1. What was the source for the CNT?

Sources for CNTs included commercial CNTs (Baytubes[®], Nanocyl[™] NC 7000, Glonatech, Arkema GRAPHISTRENGTH[®], Chengdu Institute of Organic Chemistry) or CNTs that were generated in house by the laboratory.

2. What type of CNT was used (descriptive)?

Most CNTs used were multi-walled and had a carbon purity of 90% or greater. CNTs varied in width and length. For example, Baytubes C150P were 5–20 nm in width and 1–20 μm in length. Nanocyl NC 7000 MWCNTs had an average diameter of 10 nm and length between 0.1 and 10 mm. In-house-generated MWCNTs varied greatly from 10–50 nm in diameter and 1–150 μm in length.

Table 2.2 Methods simulating possible MWCNT release mechanisms

Release Mechanism	Release Mechanisms Simulated and Usable Standards	Standards Used for Sampling or Analysis of Samples	Quantification of Release	Instrumentation for Release Measurement	References
Mixing/Sonication	Not specified, no standard simulation machines	NIOSH MAM (2006a); NIOSH Method 5040; NIOSH Method 7402	Particle Concentration	ELPI, SMPS, TEM	Dahm et al., 2012; Fleury et al., 2011
Abrasion	Taber Abraser degradation; sandpaper; rotating metallic brush and a vibrating engraver tool with a round tip; pin-on-disc wear tester	ISO 15900 (DMA), ISO/CD 27891 (CPC), ISO 21501-1 (Light scattering aerosol spectrometer)	Particle Amount, Suspension Analysis	APS, AUC, CPC, ELPI, FMPS, LDPSA, NAS, SEM, SMPS, TA, TEM, TOF-SIMS, UNPA	Golanski et al., 2010; Golanski et al., 2012; Guiot et al., 2009; Meng et al., 2009; Schlagenhauf et al., 2012; Stintz, 2013*; Vorbau et al., 2009; Wohlleben et al., 2011; Wohlleben et al., 2013
Sanding	Hand sanding, orbital sanding, belt sanding, disc sanding, automated sanding simulation system, no standard simulation machines	NIOSH Method 5040	Particle Size, Diameter and Count of Fraction with High Atomic Number, Particle Count, Particle Concentration, Suspension Analysis	AUC, APS, CPC, ESP, FMPS, LDPSA, NSAM, OPC, SEM, SMPS STEM, TEM, TOF-SIMS, UNPA, XPS	Cena and Peters, 2011; Gohler et al., 2010; Gohler et al., 2012; Gupta et al., 2006; Hellmann et al., 2012; Hirth et al., 2013; Koponen et al., 2009; Koponen et al., 2011; Methner et al., 2012; Saber et al., 2012; Schlagenhauf et al., 2012; Stintz, 2013*; Voetz, 2013*; Wohlleben et al., 2011; Wohlleben et al., 2013
Grinding	Milling and cutting of composites, no standard simulation machines	N/A			Bello, 2013*; Fleury et al., 2011; Methner et al., 2012; Ogura et al., 2012

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Drilling	Drilling of composite with air sampling; automated drill press, no standard simulation machines	NIOSH 7400; NIOSH Method 5040; NIOSH Method 7402 (modified); NIOSH MAM (2006a)	Particle Size and Count	APS, ESP, FMPS, PAS TEM, TP, WRASS	Bello et al., 2010; Dahm et al., 2012; Voetz, 2013*
Cutting/ Sawing	Band-saw, rotary cutting wheel, wet saw cutting, no standard simulation machines	NIOSH 7400; NIOSH Method 5040	Particle Size and Count, Concentration	APS, CPC, Dust Trak™, ESP, FMPS, TP, TSI	Bello et al., 2009; Methner et al., 2012; Voetz, 2013*
UV Weathering	UV irradiation; Weathering apparatus, Suntest™ XLS+, ISO 4892-2:2006; SPHERE (Simulated Photodegradation via High Energy Radiant Exposure)	N/A	Particle Size and Mass, Suspension Analysis	AUC, CPC, FTIR, LDPSA, SEM, SMPS, TA, XPS	Bello, 2013*; Hirth et al., 2013; NanoPolyTox, 2013*; Nguyen et al., 2011; Voetz, 2013*; Wohlleben et al., 2011; Wohlleben et al., 2013;
UV + Wet Weathering	Weathering apparatus, SunTest XLS+ or XXL, ISO 4892-2:2006; real-time precipitation; lyophilized rainwater	N/A	Particle Size and Mass, Suspension Analysis	AUC, CPC, LDPSA, SEM, SMPS, TA, XPS	Bello, 2013*; Hirth et al., 2013; NanoPolyTox, 2013*; Voetz, 2013*; Wohlleben et al., 2013
Thermal Degradation and Combustion	Combustion of polymer used in automotive industry; Thermal degradation of flame-retardant polymer	N/A		TGA, ELPI, TEM	Bouillard et al., 2013; Orhan et al., 2012

Aerodynamic Particle Sizer (APS); Analytical Ultracentrifugation (AUC); Condensation Particle Counter (CPC); Energy Dispersive X-Ray Analysis (EDX); *Electrical Low Pressure Impactor (ELPI)*; Electrostatic Precipitator (ESP); Fast Mobility Particle Sizer (FMPS); Field Emission Scanning Electron Microscope (FE-SEM); Fourier transform infrared spectroscopy (FTIR); Inductively coupled plasma mass spectrometry (ICP-MS); Laser Diffraction Particle Size Analyzer (LDPSA); Laser-Induced Breakdown Spectroscopy (LIBS); Nano-Aerosol Sampler (NAS); Optical Particle Counter (OPC); Photoelectric aerosol sensor (PAS); Scanning electron microscopy (SEM); Scanning Mobility Particle Sizer (SMPS); Surface Sensitive Device (NSAM); Taber Abraser (TA); Thermogravimetric Analyzer (TGA); Thermophoretic Precipitator (TP); Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS); Transmission electron microscopy (TEM); Universal Nano Particle Analyzer (UNPA); Wide-Range Aerosol Particle Sampling System (WRASS); X-Ray Photoemission Spectroscopy (XPS).

Extracted from [Phase 2.5 Question Matrix](#).

BOLD text denotes studies that are not specific to MWCNTs and polymers, but that were included to provide further information on some release mechanisms and particle measurement approaches.

* Information gathered from interviews.

3. Was the CNT functionalized or modified? If yes, how?

Very few studies used functionalized CNTs and generally did not specify the type of functionalization used. Only two studies specified how MWCNTs were functionalized (e.g., with amine, hydroxyl groups) (Meng et al., 2009; Interview with NanoPolyTox, 2013).
4. What was the source for the polymer?

If a polymer was used in a study, it was most commonly commercially purchased from vendors such as BASF, Lati Thermoplastic Industries (Italy), Altuglas, Hexicon, or ZIG Sheng Industrial Co. For studies examining surface coatings (e.g., paint, lacquer), no polymer was used. The majority of studies did not report the polymer source.
5. What was the type of the polymer?

The most common polymer type was epoxy (12 studies). All polymer types used included the following:

 - a. Acrylonitrile-Butadiene-Styrene (ABS)
 - b. Epoxy
 - c. Ethylene Vinyl Acetate (EVA)
 - d. Polyamide 6 (PA6)
 - e. Polyamine
 - f. Polycarbonate
 - g. Polyethylene
 - h. Polyoxymethylene (POM)
 - i. Polypropylene
 - j. Polystyrene
 - k. Polyvinyl Chloride-Based Resin
 - l. Thermoplastic Polyurethane (TPU)
 - m. Cross-linked Thermoplastic Polyurethane (XPU)

Additionally, testing of rubbers containing CNT was mentioned in several interviews as being of relevance for possible future use.
6. Can you provide specific formulation details?

In most cases, the specific formulation of the polymer was not stated due to manufacturer confidentiality. For epoxy resins, in most cases the MWCNTs were mixed with the polymer using a magnetic stirrer, twin-screw extruder, or three-roll mill. Then, the MWCNT-polymer composite was either: 1) poured into a mold of desired shape and allowed to cure at room temperature or high heat for 12–24 hours, or 2) first cured, then extruded into a mold or pelletized.
7. What MWCNT load was used?

The concentration of MWCNTs in composites varied up to 7% by weight, most averaging 2–3% MWCNT.
8. Were other additives/compounds used in CNT-polymer ‘mixture’ (i.e., for stability, etc.)?

Additives and compounds added to the CNT-polymer formulation included the following: aromatic diamine curing agents, polyoxypropylenetriamine curing agent, carbon fiber, and organophosphorus flame retardants.

9. Can you make any predictions for how the other additives/compounds (if any) may have influenced the measured release?
No detailed information received.

B. Questions regarding release scenario modeled

1. What type of release processes did you test in what way?
Most release scenarios modeled occupational situations, with a focus on various aspects of the machining process (drilling, cutting/sawing, sanding, grinding, etc.) and abrasion. A few studies evaluated weathering (UV and wet). The majority of studies were simulation, although a few involved actual workplace measurement.
2. What is the medium into which initial release occurs (air, water, soil, dust, food)?
The majority of studies investigated particle release into air; only four studies examined release into water and one examined release into dust. No studies examined particle release into soil or food.
3. How was the release simulated (brief overall description)? (What method was used to induce release?)
Methods to generate particle release varied greatly using low and high energy tools (manual, hand-held devices, or automated systems). There was no uniform method to initiate particle release with the exception of abrasion (Taber abrasion test). Briefly:
 - a. Sanding was accomplished manually, mechanically or through an automated system, typically with sandpaper of 1–3 grit sizes affixed to a disc at 1–3 sander speeds in a closed compartment with air monitoring.
 - b. Grinding was performed by a “grinder,” double grinder, or mill to generate granules from injection molded bars.
 - c. Abrasion most commonly used Taber equipment, with the material abraded against a steel brush, sandpaper, or wheel to generate a dynamic friction.
 - d. UV and wet weathering was conducted in a weathering chamber (e.g., Atlas SunTest XXL) or under real-time outdoor conditions.
4. Is the release that the project modeled intended to represent “real-world” release?
In most cases, release was conducted in controlled laboratory settings modeled after real-world situations. Several studies evaluated samples from actual workplace scenarios.
5. If not, what is the purpose of the approach to generate released material?
The purpose of controlled settings was to identify sources of particle release, the potential release mechanism, and “proof of principle”

for characterizing releases.

6. If not, in what aspects is the release different from a similar “real-world” release scenario?

Differences were not specified in any study or interview. However, in a few cases, a comparison to simulated versus real/outdoor weathering condition was done.

7. Can you make any predictions for how these aspects may have differed the results from “real-world” release?

Simulated release may have differed due to less controlled experimental conditions in the workplace.

C. Questions regarding sample generation

1. What process was used to generate sample material from the polymer composite?

This was dependent on the release scenario modeled and varied greatly with each study:

- Wet/dry machining (sanding, grinding, drilling, cutting, etc.)
- Abrasion: Taber Abraser
- Wet/UV weathering: SunTest XXL or XLS+ (Atlas) weathering chamber

2. Were standard release methods used for any part of the measurement? The majority of studies did not employ a standardized release method. Those employed were:

a. Mechanical processes:

- i. DIN 53754:1977: Testing of plastics; determination of abrasion, abrasive disk method
- ii. DIN 68861-2:1981: for abrasion of furniture surfaces
- iii. ISO 5470-1:1999 Standard Test Method for Abrasion Resistance of Organic Coatings
- iv. ASTM G99 - Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus
- v. Taber Abraser™ test

b. Wet/UV weathering:

- i. ISO 4892/06, ISO 4892-2 (Verf. A) Methods of exposure to laboratory light sources for plastics

It was noted by several investigators that no such standard methods exist.

3. Were standard sampling methods used for any part of the measurement?

Most studies did not use standardized methods for sampling. For a few studies, (Bello et al., 2009; Bello et al., 2010; Dahm et al., 2012), the NIOSH Method 5040 for diesel particulate matter (as elemental carbon), and NIOSH Method 7400 for Asbestos and other fibers were adapted as sampling methods, as well as analytical methods. If yes, can you provide citations and brief descriptions?

See [Phase 2.5 Question Matrix](#).

D. Questions regarding analytic method used to measure release

1. Was more than one analytic method used to measure released material?
In all studies, more than one analytic method was used.
2. Was the method designed to quantify the released amount?
Methods for quantifying generally focused on particle count and respirable mass in air and in some cases the quantification included representative electron microscopic samples of the morphologies of particles released.
Few CNT specific release amounts were reported to be quantitative (e.g., AUC for Hirth et al., 2013; FTIR for NanoPolyTox, 2013).
3. If method was only for detection, what was the set detection limit?
No detection limits were specified.
4. If released amount was quantified, how was the released material defined compared to a control blank? Was the quantification in terms of a detection limit or an exposure amount?
In many cases overall particle mass, mass distribution, diameter, and count were compared to negative control with no CNTs present. Morphology of particles from select representative images were verified by SEM/TEM; however, quantitative estimates of CNT or CNT-particle composites were not provided.
5. Were standard methods used for simulating release, sampling, or analyzing release used for the measurements?
Most studies did not use standardized methods with the exceptions below. Also see Table 2.1 for additional information.
 - NIOSH Method 7400 for Asbestos and other fibers
 - NIOSH Method 7402 for Asbestos by TEM (modified)
 - NIOSH Method 5040 for diesel particulate matter (as elemental carbon)
6. If yes, can you provide citations and brief descriptions? See Question D5.
7. How many cycles of release and measurement have been done using this method by your project (approximately)? If the number is difficult to estimate, then how long has the overall method been in use by the project? Few weeks?
Cycles of release and time interval of measurement varied greatly. In many studies, tests and measurements were completed in triplicate under different conditions (e.g., machining scenario, CNT loading, machining rate, etc.)

E. Instrumentation used to measure release

Please list the primary instrumentation for this project that allow release of CNT to be measured from polymer composites.

A wide range of instrumentation was used. However, most instruments were only used to describe particle counts that did not distinguish CNT from other particles. The relative mass of CNT in particle counts (e.g., in respirable fraction) or elemental analysis of

mass fractions (e.g., FTIR) was inferred in a few studies, compared to release from polymer without CNT.

Aerosol analysis

- a. Aerodynamic Particle Sizer (APS)
- b. Condensation Particle Counter (CPC)
- c. Electrostatic Precipitator (ESP)
- d. Electrical Low Pressure Impactor (ELPI)
- e. Fast Mobility Particle Sizer (FMPS)
- f. Nano-Aerosol Sampler (NAS)
- g. Optical Particle Counter (OPC)
- h. Particle Surface Sensitive Device (e.g., NSAM, DiscMini, Nanocheck)
- i. Scanning Mobility Particle Sizer (SMPS)
- j. Thermophoretic Precipitator (TP)
- k. Universal Nano Particle Analyzer (UNPA)
- l. Wide-Range Aerosol Particle Sampling System (WRASS)

Suspension analysis

- m. Analytical Ultracentrifugation (AUC)
- n. Dynamic Light Scattering (DLS)
- o. Laser Diffraction Particle Size Analyzer (LDPSA)

Chemical and morphological analysis

- p. Energy Dispersive X-Ray Analysis (EDX)
- q. Field Emission Scanning Electron Microscope (FE-SEM)
- r. Fourier Transform Infrared Spectroscopy (FTIR)
- s. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
- t. Laser-Induced Breakdown Spectroscopy (LIBS)
- u. Photoelectric Aerosol Sensor (PAS)
- v. Scanning Electron Microscopy (SEM)
- w. Thermogravimetric Analyzer (TGA)
- x. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)
- y. Transmission Electron Microscopy (TEM)
- z. X-Ray Photoemission Spectroscopy (XPS)

F. Existing collaboration and networks (interview only)

1. Have you participated in an interlaboratory study for any part of the CNT-composite release measuring?
Generally the answer is no; however, some interlaboratory studies are in the planning phase.
2. Are you part of a consortium or collective with regard to measurement of nanoparticle release?
Yes, some are participating in collaborations with other groups.
3. Did you use shared facilities or collaborate with other laboratories in these measurements or the modeling?

Although difficult to determine from publications, this varied from laboratory to laboratory.

4. If so, please identify:
XPS, automated microscopy, and AUC.
5. Would you be willing to participate in an interlaboratory study?
Interviewed laboratories replied that they would be willing to participate, contingent on funding.
6. Would you be willing to serve as a pilot project with one or two other laboratories in further developing standard methods for measuring release?
Interviewed laboratories replied that they would be willing to participate, contingent on funding.

3. Summary of Findings in the Task Group White Papers in Comparison to the Phase 2.5 Literature Review and Interviews

Chapter 3 describes the materials, release scenarios, and nanomaterial measurement methods that were reviewed by the NanoRelease Consumer Products Task Groups (TGs) in the context of the studies reviewed and experts interviewed in Chapter 2. The purpose of this comparison is to present a clearer background for consideration of what would be most useful to develop (for example with regard to a particular release scenario) versus what is most feasible to further develop to best or standard practice (for example, with regard to methods that are understood and have a general level of practice in the community). Note that, for example, the NanoRelease project Steering Committee could choose to select a release process that results in a relatively large released amount where quantification is needed (but that is in a well controlled environment) or could select a release process that is expected to be very low where *de minimus* detection is needed (but that is in an uncontrolled environment where many could be exposed).

The *method* and *release* are terms that have overlapping meaning and so for the purpose of this discussion, we propose the following conventions as contained in the project glossary.

- **MWCNT-polymer composite** – multi-walled carbon nanotubes (MWCNTs) embedded in a polymer matrix
- **Fragment** – a piece of polymer matrix that may or may not contain MWCNTs
- **Product** – a finished good fabricated from a MWCNT-polymer composite
- **Release** – detachment of a fragment from a larger whole. Specifically, when a fragment that contains MWCNTs detaches from a MWCNT-polymer composite and is *nano-sized* or possesses *nano-characteristics*, the release is considered to be a nanorelease; both fragments and discrete MWCNTs may be released

- **Release mechanism** – a process, such as abrasion or degradation, which results in the release of fragments and discrete MWCNTs from a MWCNT-polymer composite
- **Measurement** – detection, quantification, and characterization of fragments or discrete MWCNTs released from a MWCNT-polymer composite or product; results may be qualitative or quantitative
- **Method** – an experimental or analytical technique for various processes and measurements, including generation, collection, detection, quantification, and characterization of fragments or discrete MWCNTs released from a MWCNT-polymer composite or product
- **Lifecycle** – a time sequence depicting the life of a MWCNT-polymer composite or product, the phases of which include MWCNT-polymer composite production, product manufacture and use, and end of life of the composite and product, *e.g.*, disposal, recycling, or re-purposing
- **Release scenario** – an event or chain of events resulting in a release during a lifecycle phase of a MWCNT-polymer composite or product as described by the release mechanism, setting (*e.g.*, workplace, dwelling, and environment), relevant media (*e.g.*, air, water, mixed solids, and biological matrices), and form and amount of released material
- **Lifecycle simulation** – a release scenario replicated in a laboratory setting or by modeling and computation
- **Probability of release** – the likelihood of release, as determined by a quantitative or qualitative measurement or prediction of the total number or mass concentration of released material, for a specified release scenario and time interval
- **Release evaluation** – a total assessment of release, including the release mechanism, form of the released entity, release scenario, probability of release, and lifecycle simulation, if relevant
- **Standard** – documentary standards—consensus-based, well-defined methods, such as for sample preparation and property measurement, and reference material standards—artifacts with well-defined property reference values and uncertainty analysis that may be used for instrument calibration, interlaboratory studies, and the development of documentary standards

Also note that when speaking of standardized methods or standard practice that there are different meanings and levels of application of the terms. There are also best practices and standard operating procedures that occur for some aspects of the measurements and modeling approaches considered. However, the project has not found any standardized method or best practice or standard operating procedure that provides a way to measure the nanomaterial-relevant release from any release process. A particular goal of the project is to develop or facilitate the development of such standard methods so that critical release processes can be understood and, where warranted, used to evaluate risks in support of sustainable design and other risk management approaches.

3.1. Materials

3.1.1. Materials Covered by TG2

Task Group 2 (Material Characteristics) (TG2) of the NanoRelease Consumer Products project described and evaluated the physicochemical characteristics, likelihood for degradation, and likelihood of release of MWCNTs (if data available) for a selection of polymer matrices (Kingston et al submitted 2013).

The polymer systems evaluated were chosen based on expert input regarding the polymers (as relevant to MWCNT-polymer matrices) representing a range of physicochemical characteristics (and thus a range of releases), likelihood of direct exposure to consumers and potential degree of consumer exposure, commercial/industrial production volume, MWCNT-polymer data availability, likelihood of modifications (additives, coatings, stabilizers, etc.) in production or manufacture, and general expert opinion of the polymer's importance or relevance to the issue at hand (Table 3.1).

Based on the expert input, the following polymers were chosen for evaluation:

- Epoxy
- Polyamide (PA)
- Polyurethane (PU)
- Polyethylene (PE)
- Polycarbonate (PC)

The following polymers were also considered for inclusion in the TG2 report but were ultimately not selected for detailed evaluation: polypropylene (PP), polyvinyl chloride (PVC), elastomer (cis-polyisoprene), polyethylene terephthalate (PET), and polyether ether ketone (PEEK).

TG2 considered information on characteristics relevant to degradation (and thus release likelihood) of both the polymer alone and the polymer-CNT nanocomposite (with emphasis on available information relevant to MWCNT). TG2 recognizes that the existing market for MWCNT-polymer matrices likely features modification of the CNTs (such as amine and hydroxyl group functionalization) and additives to the nanocomposite (such as stabilizers), and that these changes may affect degradation and release likelihood.

In summary, the materials covered by TG2 include the polymers epoxy, PA, PU, PE, and PC, as used in nanocomposites with MWCNTs (as well as SWCNTs if relevant for methods development). Typical surface modifications of the CNTs in the reviewed literature were carboxylation and amino functionalization. CNT modification was almost always used in order to have a useful and stable nanocomposite; thus, it should be expected that the market products will most likely contain MWCNTs with surface modifications. Additives/stabilizers were almost always used in order to have a useful and stable nanocomposite; thus, it should be expected that products on the market will most likely have additives in the MWCNT-polymer nanocomposite.

Table 3.1 Summary of polymer nanocomposite information evaluated by TG2 relevant to MWCNT-polymer matrices for methods development (Kingston et al submitted 2013)

	Epoxy		PA	PU	PE	PC
Characteristics	Hard, brittle	Soft, ductile (less brittle than epoxy), crystalline	Most common: PA-6 and PA-66	Soft, ductile, elastomer	Soft, ductile Can exist as HDPE (50%), LDPE, and LLDPE	Hard, ductile (increasing brittleness with higher CNT load)
CNTs						
Type	Other than MWCNT, SW and DW also have been studied.			SW and MWCNT used.	SW and MWCNT used, specific MWCNT unspecified in current studies.	CNT-PC composites are being manufactured, but unclear if currently used in market (MWCNTs used, potentially SWCNTs as well).
Load/dispersion	Load affects stability; 2-5% ideal for temperature.	Higher load increases agglomeration and thus decreases stability (0.5% ideal for temperature, and above 1% already decreasing in stability)		Typical CNT loading > 0.1%, < 5%. Higher load (but increased dispersion and alignment) increases tensile strength and modulus, thermal stability, electrical conductivity.	Degree of dispersion and strength of interfacial interaction influences property of composite.	Higher load increases compressive strength, Young's modulus, ductility, viscosity, conductivity. Better dispersion and higher load (5-20%) most likely to have better storage modulus (less release) for MWCNT-PC.
Modification	Carboxylation (increases dispersion, thus stability). Amino functionalization (reduces UV degradation).	Amino functionalization (aromatic amine for superior dispersion and adhesion with matrix) using grafting technique		Acid treatment with nitric and sulfuric acid to improve interfacial bonding between CNTs and PU.	Surface functionalizations possible, but not specified.	

continued

Table 3.1 (Continued)

<p>Potential Additives or Coatings</p>	<p>Reinforcement with glass fiber, less often with aramid or boron</p>	<p>Reinforcement with glass fiber or mineral/clay common, less often with carbon black/carbon fiber.</p>	<p>Various additives for desired properties (ex: blowing or gelling catalysts, blowing agents, antioxidants, fire retardants, pigments, surfactants, and various fillers), melt modification</p>	<p>UV stabilizers and free radical scavengers (antioxidants) are often added to retard UV degradation.</p>	<p>Since PC is susceptible to photooxidation, antioxidants are used to maintain low color and high transparency for end-use applications (additives such as phosphites).</p>
		<p>5-20% sulfonamides as heat stability plasticizer.</p>	<p>Additives are common for TPU in particular, including: antistatic, flame-retardant (halogen free), hard phase modifier, surface matting, UV stabilizer, plasticizer, lubricant.</p>		
		<p>For fishing lines (flexibility), 30% plasticizer (more impact resistant, less abrasion resistant).</p>			
		<p>For flame retardancy, halogenated or phosphorous additives (such as brominated polystyrene, red phosphorus, organic phosphinate).</p>			
		<p>UV stabilizers: HALS, amine light stabilizers added in low levels</p>			

Additives used depended on the intended use of the material. For example, typical additives used in these nanocomposites can serve the following purposes: increased reinforcement, heat stability, flame retardancy, UV stability, impact modification, melt modification, antistatic, lubricant, and color/texture modifiers. For the first pilot study for methods development in this project, it is recommended that both the MWCNT surface modifications and the additives in the nanocomposite should be decided according to the chosen polymer (and then further specified by considering the table above and the materials findings from Phase 2.5).

3.1.2. Materials Covered by Literature Review and Interviews in Phase 2.5

Studies reviewed in the Phase 2.5 evaluation included epoxy, PA, PU, PE, PC, polyoxymethylene (POM), polypropylene (PP), ABS (Acrylonitrile-Butadiene-Styrene), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and poly(methyl methacrylate) (PMMA). The majority of existing studies selected epoxy polymer nanocomposites (13) for various release scenarios, followed by PA (4) and PU (4) (Table 3.2). The type of MWCNTs used in nanocomposites varied greatly and were acquired commercially or produced in the laboratory by the individual research group. Of the polymers deemed relevant by TG2, most studies and interviews did not specify if polymers contained additives or if MWCNTs were functionalized, with the exceptions listed in Table 3.2.

Briefly, the exceptions are that in the study by Methner et al. (2012), the cleaning process for MWCNTs increased the degree of carbonyl groups. NanoPolyTox (2013) functionalized MWCNTs using amine terminal and hydroxyl groups. One study by Meng et al. (2009) treated MWCNTs with acid and further modified them with amines for purposes of purification.

Other studies that used additives in polymer composites are listed in Table 3.2 and are described below:

- Orhan et al. (2012) also added organophosphorus flame-retardant additive (Clariant Exolit OP1312) to a poly(methyl methacrylate) composite.
- Wohlleben (2013, interview) added an organic additive for dispersion facilitator in the cement but not polymer matrix.
- Stintz (2013, interview) added an amine-based hardener (Aradur 5021) for epoxy resin.
- Nguyen et al. (2011) added a polyoxypropylenetriamine curing agent to amine-cured epoxy resin.
- Fleury et al. (2011) and Bouillard et al. (2013) added PA 6 (15 wt%) to “high heat” ABS (Acrylonitrile-Butadiene-Styrene) polymer matrix from the masterbatch, a special grade with high temperature stability.

3.1.3. Summary/Comparison of Materials Covered by TG2 versus the Phase 2.5 Literature Review

Generally there is no preponderance of studies that examined a material that was not covered by TG2. The polymers POM, PP, ABS, PET, PVC, and PMMA were used in

Table 3.2 Summary of polymer nanocomposite information from published studies evaluated and interviews conducted for Phase 2.5

Type of Polymer	Number of Studies/ Interviews	Functionalization	Other Additives	All References for Polymer Type
Epoxy	13	Higher degree of carbonyl groups (Methner, 2012)	Carbon fiber (Huang, 2013) Amine-based hardener (Aradur 5021) (Stintz, 2013*) Aromatic diamine curing agent Epikure 3402 (Hexion) (Schlagenhauf, 2012) Polyoxypropylenetriamine curing agent (Nguyen, 2010)	Bello, 2009; Bello 2010; Cena and Peters, 2011; Golanski, 2012; Gupta, 2013*; Hellman, 2012; Hirth, 2013; Huang, 2012; Methner, 2012; Nguyen, 2010; Peters, 2013*; Schlagenhauf, 2012; Stintz, 2013*
Polyamide (PA)	4	Amine terminal group, hydroxyl group (NanoPolyTox, 2013) CNTs were treated by acid and further modified with amines (Meng, 2009)	None or not specified	Golanski, 2012; Meng, 2009; NanoPolyTox, 2013; Voetz, 2013*
Polyurethane (PU)	4	None or not specified	None or not specified	Hirth, 2013; Peters, 2013*; Stintz, 2013*; Wohlleben, 2013
Polyethylene (PE)	1	None or not specified	None or not specified	Voetz, 2013*
Polycarbonate (PC)	3	None or not specified	None or not specified	Bello, 2013*; Golanski, 2010; Golanski, 2012

* Information acquired via interview

a few studies; however, the rationale for choosing these polymers (e.g., in relation to commercial use) is not clear. Furthermore, when choosing polymers to focus on in the white paper, TG2 included PP, PET, PVC, and PMMA in their consideration and made an expert decision that these were of likely less importance at that time to discuss for methods development for the release of MWCNTs from polymer matrices (as compared to epoxy, PA, PU, PE, and PC). During the interviews, rubber was mentioned several times as a possibly relevant polymer material (Nanocyl, 2013*; Wohlleben, 2013*). This has not been studied thus far to our knowledge. We may recommend a mixture of polymers to be used in Phase 3 since any possible release

will depend on the polymer matrix as well as the stress exercised to the material. Variations of polymer properties taken into consideration could be brittleness, softness, and combustibility, for example.

Modification of MWCNTs was similar in both the TG evaluation and the Phase 2.5 literature review (use of amine, hydroxyl, and carbonyl functionalization in a few cases in the published literature). Additives were not specified in the studies evaluated in Phase 2.5 except for epoxy, for which the additives used were (not simultaneously) carbon fiber, amine-based hardener, aromatic diamine curing agent, and polyoxypropylenetriamine curing agent. On the other hand, additives considered relevant for MWCNT-epoxy nanocomposites in the TG2 evaluation were reinforcement with glass fiber, aramid, or boron. Therefore, the variety and purposes of additives are issues that need to be resolved if such additives would affect method development or utility (with the goal of being as relevant as possible to market or near-market products).

3.2. Release Scenarios, Release Modeling Approaches, and General Nanoparticle Characterization Approaches

(For relevant materials addressed by existing studies as compared to the needs identified by Task Groups)

3.2.1. Research Needs Identified by Task Groups (for Combinations of Materials, Scenarios, and Release Methods)

Task Group 3 (TG3) identified two main scenario types in which release of MWCNTs from polymer matrices could occur, and three main life cycle stages during which release may occur, with several specific examples of release scenarios for each.

3.2.2. Scenario Types

- **TYPE 1 SCENARIOS:** Release due to **high-energy processes** during post manufacturing of master batch (occupational, consumer, environmental exposures)
 - **RELEASE METHODS:** Wet and dry machining: band-saw, rotary cutting wheel, wet and dry solid core drilling
 - **ANALYTICAL METHODS** (for laboratory simulations): High-energy processes are likely to release mainly into the airborne phase, which enables the use of state-of-the-art aerosol and particle sampling and analysis techniques, of which the following metrics are seen as relevant: particle size distribution, number, mass and active surface area concentrations along with particle morphology analysis (e.g., via TEM and SEM).
- **TYPE 2 SCENARIOS:** Release due to **low-energy processes** during consumer use or environmental degradation (UV exposure, weathering)
 - **RELEASE METHODS:** Low-speed wet and dry solid core drilling, lower energy sanding and abrasion (manual), accelerated weathering under UV radiation.

- ANALYTICAL METHODS (for laboratory simulations): The same measurement techniques as given for the type 1 scenario can be used for the airborne phase. Release of MWCNTs in the liquid phase becomes important in the type 2 scenarios. It has to be noted that the measurement, sampling, and analysis techniques available for the liquid phase are not as advanced as for aerosols, especially with regard to size resolved measurements. Still, the same metrics as for the airborne phase are seen as important to be determined in the liquid phase: particle size distribution, number, mass and active surface area concentrations, along with particle morphology analysis (e.g., via TEM and SEM).

3.2.3. Life Cycle Stages and Examples of Release Scenarios

- MANUFACTURING
 - Example 1: Manufacturing of products or articles via injection molding
 - Example 2: Processing of nanocomposites (cutting, sawing, drilling, and sanding of raw nanocomposites)
- NORMAL/CONSUMER/COMMERCIAL USE
 - Example 1: CNT-composites used in sports equipment
 - Example 2: CNT-composites used in electronics
 - Example 3: CNT-composites used in larger non-consumer use applications, i.e. non-abrasive outdoor applications (e.g., windmill blades) and small CNT-composite parts within larger structures (e.g., fuel systems components in cars)
 - Example 4: CNT-rubber composites used in tires
 - Example 5: Release from textiles
- POST-CONSUMER/END OF LIFE/DISPOSAL
 - Example 1: Incineration or combustion of CNT-composites
 - Example 2: Chemical aging and weathering of CNT-composites in landfills

Task Group 2 (TG2) identified the following release scenarios for their discussion of the five chosen polymers (epoxy, PA, PU, PE, PC):

- Weathering/outdoor exposure
- UV degradation
- Mechanical stress (abrasion/deformation)
- Leaching
- Temperature and flammability
- Chemical treatment
- End of life

Using the TG-identified factors for release scenarios, Phase 2.5 and TG2's identified materials, Phase 2.5 and TG2's findings on material applications, TG2's identified relevant media into which release occurs, Phase 2.5 and TG2's key findings and research needs, and relevant methods discussed by all, one can deduce the likely most useful combinations of materials, release scenarios, and methods for Phase 3.

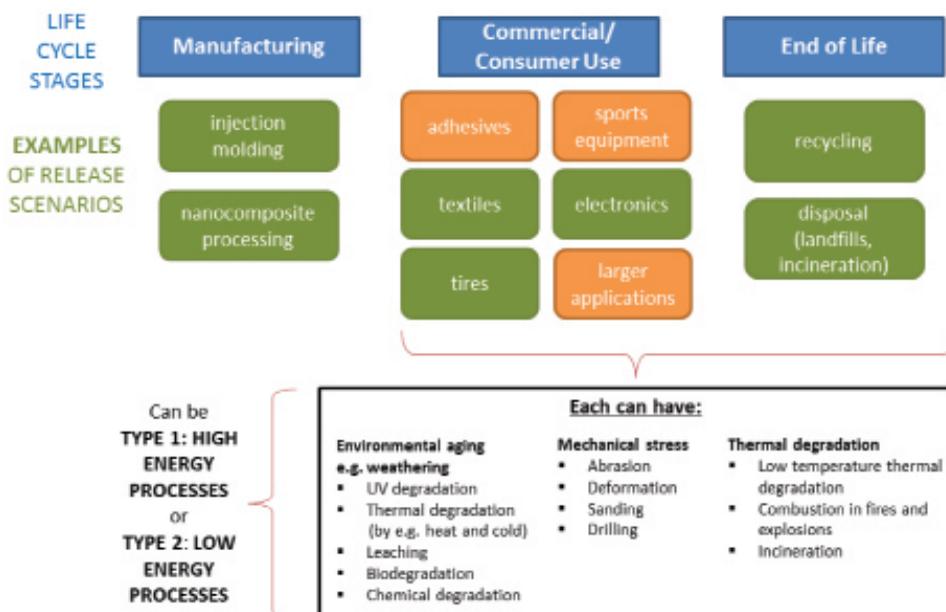


Figure 3.1 Types of release scenarios for MWCNT-Polymer nanocomposites as identified by TG2 and TG3. Orange boxes are specific to MWCNT-epoxy applications as an example of all epoxy applications. “Larger applications” refers to automobile parts, aircraft parts, and other examples typically employed for the increased durability/mechanical strength and decreased weight when MWCNTs are incorporated into the polymer.

In Figure 3.1, the types and examples of identified release scenarios are organized into a diagram in which the orange boxes are most relevant to MWCNT-epoxy nanocomposites, as indicated by TG2 (see Table 3.3 in epoxy section).

3.3. Detection and Quantification of “MWCNT-Relevant” Released Nanoparticle Characteristics

A particular challenge of the NanoRelease project is the identification and measurement of the characteristics of released materials that are relevant to understanding 1) what is *different* about the particles *because of* the addition of engineered nanomaterials to a composite and commercial product and 2) what should be quantified with respect to conveying that difference in a way that would inform exposure assessment or safety assessment for any needed nano-specific change in risk management. With regard to quantification, there is also a further distinction between a detection level (at what quantity and for what characteristics can you say that you would have seen something if it was there) and a quantification level (at what quantity can you begin estimating an exposure level with sufficient precision). There are accepted practices in exposure assessment for level of detection and level of quantification; however, the first issues are what characteristics to measure and whether there are instruments and methods to measure the characteristics.

Table 3.3 Release scenarios, methods, and research needs identified for MWCNT-polymer nanocomposites evaluated by TG2

Polymer (& Potential Uses)	Media	Considered Release Scenarios	Methods Used (if any) for Simulating and Measuring Release	Key Findings and Research Needs
Epoxy Aerospace/aircraft, wind turbines, consumer use of sporting goods, adhesives	Air/wind, water/moisture/humidity	Weathering/outdoor exposure	<u>Sookay et al., 2003</u> : Outdoor exposure to various climates in South Africa, compression test to test strength.	Studies have been done with outdoor exposure/ weathering; humidity and UV combined causes surface cracking. Release rate needs to be studied for outdoor and simulated weathering scenarios.
	Air	UV degradation	<u>Nguyen et al., 2009</u> : Amine-cured epoxy polymer with 0.72% load MWCNT. UV exposure was done using 2 m integrating sphere-based weathering chamber "SPHERE" that has a mercury arc lamp system producing 480 W/m ² in 290-450 nm UV flux at 75% relative humidity and 50°C. Mass loss determined with analytical balance, surface morphology examined by AFM and FE-SEM, chemical change measured with FTIR spectroscopy in ATR mode, ZnSe prism used for ATR measurement.	MWCNT-epoxy undergoes rapid photodegradation. What is the release rate of MWCNT?
	Air	Mechanical stress (abrasion/ deformation)	<u>Gojny et al., 2003</u> : MWCNTs were oxidized via sulphuric and nitric acid and then triethylenetetramine, then amino-functionalized, added to epoxy with hardener (Ruetadur Teta). <u>Gojny et al., 2005</u> : Epoxy with anime hardener with SWCNT, DWCNT, MWCNT. MWCNTs were thin, purified, amino-functionalized with 15 nm diameter and up to 50 µm length. Mechanical characterization — tensile tests DIN EN 527.1/2, Zwick universal tensile tester, fracture toughness investigated by ASTM D 5045-99, deformation measured by detecting crack opening displacement using extensometer MTS, crack was introduced using razor blade and hammer. Electron microscopy — SEM (Leo FE-SEM 1530), TEM (Philips EM 400).	Carboxyl and amino functionalization improve stability; however, agglomeration and high loading can reduce stability. Release rate should be studied. Sanding produced released nanocomposite particles with protruding CNTs, but no free CNTs were observed. Consider if larger-than-nano polymer particles with protruding CNTs is considered "release".

Cena, 2011: Hand sanding of MWCNT-epoxy nanocomposite. Airborne particle # and respirable mass conc. measured with condensation particle counter (CPC) and optical particle counter (OPC).

Cena, 2010: Hand sanding of epoxy-2%MWCNT nanocomposite. Airborne particles characterized. Sample prep — material in acetone, images collected using STEM and elemental information using energy dispersive x-ray spectroscopy (EDX).

Cena and Peters, 2011: MWCNT 10-50 nm diameter and 1-20 μm length mixed with epoxy, specific details/formulation unknown. Measurement/characterization — airborne particle # and respirable mass conc. measured with CPC and OPC. Morphology of airborne particles — TEM. Samples collected with copper TEM mesh grid sampler with PC membrane filter. Sanding — manual sanding of epoxy nanocomposite sticks (2% MWCNT by weight) with sandpaper, aerosol concentrations measured for 15-30min adjacent to sanding process (with CPC and OPC) and in operator's breathing zone (with flexible tubes to CPC and OPC). Fume hood was used.

Schlagenhauf et al., 2012: MWCNT (1-10 μm length, 13 nm diameter) in epoxy resin, cured with aromatic diamine curing agent, MWCNT load was 0%, 0.1%, and 1% in different samples. Abrasion by Taber Abraser 5135 with enclosure chamber and particle collection tube directly behind abrasion area and manipulated air flow/suction. Particles characterized in aerosol form by particle size distribution measurement (APS, FMPS, SMPS, CPC) and in collected particle form by SEM, TEM, and EDX. Imaging by SEM and TEM.

	Air	Leaching	n/a	Leaching has not yet been studied for MWCNT-epoxy.
	Air	Temperature & flammability	Bikiaris, 2011 : TGA analysis and treatment with high temperature to test temperature stability and flame retardancy.	Neat CNTs reduce thermal stability. 2-5% load CNTs with amine or carboxyl functionalization is best thermal stability and flame retardance.
	Solvents, acids, bases	Chemical treatment	The Dow Chemical Company (Epoxy Curing Agents product overview guide) : no methods indicated	Effect of solvents, acids, and bases on MWCNT-epoxy has not been studied; however, epoxy is generally resistant to bases and non-polar solvents, but is susceptible to acids and polar solvents. What is the release rate of MWCNTs when nano-composite is treated with acids or polar solvents?
	Air, solvents, acids, fire, soil	End of life: Incineration, landfilling, recycling (grinding/pulverizing or chemical degradation)	n/a	Release rate needs to be studied for end-of-life scenarios of MWCNT-epoxy (only carbon fiber-epoxy studied for end-of-life release).
PA Automotive parts, electronics, appliances, carpeting, textiles, brushes, fishing lines	Air, water	Weathering	Pillay et al., 2009 : Moisture exposure on carbon-nylon 6 processed using VARTM. Bao and Yee dual diffusivity model used to evaluate moisture uptake, SEM used to show surface morphology.	Moisture is absorbed over time by PA, eventually affecting shear and impact resistance. Need outdoor studies for various products of MWCNT-PA.
	Air	UV degradation	Pillay et al., 2009 : UV exposure on carbon-nylon 6 for up to 600 hours, looked at color (yellowing) of samples and crystallinity increase.	UV studies were done on carbon fiber reinforced PA6 showing low degradation. Further studies are necessary for MWCNT-PA and UV degradation, particularly in combination with humidity/rain.
	Air, water	Mechanical stress (abrasion/deformation)	Giraldo et al., 2008 : MWCNT-PA6 at loads 0.2, 0.5, 1.0% by weight using melt mixing, characterized by SEM, TEM, TGA, scratching, sliding wear, and tensile testing.	MWCNT increase scratch hardness and stiffness and reduce friction of PA6, low probability of release but need studies to quantify any low level of release, particularly for abrasion since additives are used to increase elongation ability and thus increase likelihood of CNT protrusions and release in sanding/abrasion.

	Air, water	Leaching	<p><u>Meng et al., 2009</u>: MWCNT 50-80 nm diameter, 5-20 μm length treated with acid and amine modified, composited with PA6 in 1.0% load (using extruder). Tensile test via Instron 8871 via ASTM D638M, tensile strain measured via extensometer. Water absorption evaluated by immersing in water at room temp for 24 h and calculated % increase in weight. Microhardness measured using FUTURE TECH FM 700e Vickers microhardness tester. Differential scanning calorimetry analysis on TA DSC Q20. Friction and wear tests via pin-on-disc wear tester via ASTM G99 under dry sliding and water lubricated conditions. Mass loss weighed with electrical balance to calculate wear rate. Worn surfaces observed by SEM.</p>	<p>Need to study mechanical stress in water for MWCNT-PA (such as for fishing lines). Moisture is absorbed over time by PA, eventually affecting shear and impact resistance, not yet studied for MWCNT. Also for fishing lines, there is more plasticizer so more impact resistant but less abrasion resistant.</p>
	Air, nitrogen	Temperature & flammability	<p><u>Li et al., 2006</u>: thermal degradation of MWCNT/PA6 under air and nitrogen atmosphere using TGA. Amino-functionalized MWCNTs. FTIR spectroscopy, FE-SEM imaging, TGA, DTG analyses.</p> <p><u>Giraldo et al., 2008</u>: see above.</p> <p><u>Ribeiro et al., 2012</u>: text unavailable.</p>	<p>Leaching has not yet been studied for MWCNT-PA. MWCNT increase thermal stability of PA6 in air, but no stabilizing effect occurs in nitrogen atmosphere. 0.5% ideal MWCNT load, above 1% decreases thermal stability.</p>
	Solvents, acids, bases	Chemical treatment	<p>colparmer.com, k-mac-plastics.net</p>	<p>Stable/resistant to bases and inorganic chemicals such as ammonia and sulfurous acid. Susceptible to: oxidants, concentrated inorganic acids, chlorine-based decolorants, weak organic acids (acetic acid), some alcohols (isopropyl alcohol). Need to do release studies with these treatments as they could increase release of MWCNT.</p>
	Air, soil	End of life: landfilling, (unlikely to be incinerated or recycled)	n/a	<p>Release rate needs to be studied for landfilling end of life for MWCNT-PA.</p>

<p>PU Wind turbine blades, cable sheathing, plugs and terminations, spiral tubing, films, ski-boot shells, technical moldings, strain sensors intended for smart textiles, flame retardants in various applications</p>	Air, water (humidity)	Weathering	<p><u>Bernard et al., 2011</u>: PU was one component water borne anionic dispersion of poly-ester urethane resin in water and in NMP. Surfactants and additives unknown. UV radiation was a 2m integrating sphere-based environmental chamber called SPHERE UV. Characterization – chemical degradation studied via Fourier transform IR spectroscopy (t-FTIR and FTIR-ATR modes), surface morphology studied via FE-SEM, AFM, and LSCM (laser scanning confocal microscopy), and mass loss measured with analytical balance. Presence of naked CNTs by photoelectron spectroscopy (XPS).</p>	<p>MWCNT increase fatigue life of PU composite by 2.5x. MWCNT increase coefficient of friction and wear resistance of PU composite. Mechanical degradation is affected by presence of phase modifiers, plasticizers, and lubricants (all often used with TPU). Weathering tests caused PU matrix to recede, exposing entangled CNT matrix on surface. No methods/studies validated to assess release of free CNTs from this top layer of degraded nanocomposite. Wet weathering + UV is 3x more progressive than UV only. Hydrolysis of PU is a potential major degradation pathway.</p>
	Air, water (humidity)	UV degradation	<p><u>Wohlleben et al., 2013</u>: volume resistivity of CNT-TPU measured according to ISO 3915 (4-point method), hardness measured according to DIN 53505, elongation at break according to DIN 53504. Sanding with air tight housing flushed with filtered air as sample rotates against sanding paper at 2000rpm, airborne fragments aspirated onto membrane filter and fallen fragments collected. Scanning Mobility Particle Sizer (SMPS) used to measure conc. and size distribution. Taber Abraser test (352G) used to quantify wear resistance. UV radiation via ISO 4892-2:2006 with Sunset XLS+. Wet weathering performed using ISO 4892-2 Verf A. XPS, SEM, EDX, analytical ultracentrifugation (AUC) used to characterize/ evaluate the samples.</p>	<p>Presence of CNT may slow down photooxidation. UV degradation is affected by presence of UV stabilizers and antioxidants (often used with TPU). UV irradiation is a potential route of release and needs to be studied, particularly when in humid environment.</p>

	Air	Mechanical stress (abrasion/deformation)	<p><u>Koerner et al., 2005</u>: MWCNT in TPU, in situ x-ray scattering evaluation during deformation, SEM.</p> <p><u>Wohlleben et al., 2013</u>: see above</p> <p>Sanding (high shear, machining simulation) and Taber Abraser (normal use simulation) aerosols monitored and the release assessed by battery SMPS, CPC, XPS, SEM, AUC, LLD</p> <p>Free CNTs analysis done by SEM for morphology and XPS for surface chemistry, as well as size selective detection.</p>	<p>Polyether or polyester-based PU have similar mechanical properties. MWCNT increase coefficient of friction and wear resistance of PU composite.</p> <p>On a large scale, deformation is much more influenced by the PU matrix (since MWCNT-PU deformation is similar to PU deformation).</p> <p>With sanding and Taber Abraser, nanocomposite vs. neat TPU had similar aerosol number conc., no evidence of free CNTs, and no tubular protrusions. No significant probability of release.</p>
	Air	Leaching	n/a	Leaching has not yet been studied for MWCNT-PU.
	Air	Temperature & flammability	<p><u>Deka et al., 2009</u>: MWCNT with hyperbranched seed oil-based PU matrix. SEM, TEM, XRD, TGA thermograms, RBC protection assay, and FTIR analyses.</p> <p>Tensile strength test and elongation at break, thermal stability tests (melting temperature, melting enthalpy, shape recovery, thermal degradation onset and peak temperatures), bacterial degradation with <i>Pseudomonas aeruginosa</i>.</p>	<p>CNT increase thermal stability of PU composite. PU alone degrades above 240C with various steps to degradation. MWCNT –PU likely only has one degradation temperature and is higher than neat PU. Higher load (but increased dispersion and alignment) increases thermal stability.</p>
	Acids, bases, various solvents	Chemical treatment	n/a	<p>TPU is degraded by concentrated acids and alkaline solutions even at room temp. Ketones are partial solvents and highly polar organic solvents dissolve TPU.</p> <p>Thus, there is higher potential for CNT release from TPU nanocomposites in such chemical environments.</p>

	Air, water, micro-organisms	End of life	<u>Deka et al., 2009</u> : see above	<p>BIODEGRADATION: PU is known to be susceptible to breakdown by microorganisms, depending on various mods to the polymer. Polyether or polyester-based PU may have different lysis degradation mechanisms. Long term aging may be important to look at since this is may be used as a soft matrix, which mayb e more likely to release free CNTs in comparison to hard applications of PU. Not addressed by TG2.</p>
<p>PE Use with CNTs: Automotive external body components, electrostatic dissipation materials, hot melt adhesives, materials/yarns surface resistivity HDPE uses (may eventually be applied with CNTs): milk jugs, detergent bottles, margarine tubs, garbage containers, paint "cans," toys/ housewares, automotive gas tanks, chemical storage containers, water pipes, fencing, decking, playground equipment LDPE uses (may eventually be applied with CNTs): plastic bags, stretch-and shrink-wrap film, adhesives, paperboard coating, trays, general purpose containers, corrosion-resistant work surfaces</p>	n/a	Weathering	n/a	
	Air	UV degradation	<u>Zepp, Okungbowa et al. 2011</u> (need full document)	<p>Degradation via autooxidation is accelerated by UV radiation and increase in temperature. Light and free radicals causes build up of carbonyls in PE, which can react further with light to increase degradation. MWCNTs could reduce UV degradation. MWCNT-PE release due to UV exposure should be studied further. However the use of UV stabilizers and the effect of MWCNTs themselves should be considered.</p>
	Air	Mechanical stress (abrasion/ deformation)	n/a	<p>PE is generally resistant to abrasion and impact due to flexibility and likely applications will not have much abrasion exposure, thus release is unlikely for this scenario. Of all the PE's, HDPE is the hardest and thus most likely to be susceptible to abrasion release, if at all.</p>

LLDPE uses (may eventually be applied with CNTs): plastic bags, sheets, plastic wrap, stretch wrap, pouches, toys, covers, lids, pipes, buckets and containers, covering of cables, geomembranes, flexible tubing including squeeze bottles	Air/water	Leaching	n/a	Leaching of MWCNTs not likely to be significant release for undegraded PE, but once degraded the potential would be greater.
	Air	Temperature & flammability	CNT-PE composites are typically characterized by SEM	CNT-PE is exceptionally electrically and thermally conductive. Degradation via autooxidation is accelerated by UV radiation and increase in temperature.
	Acids, bases, microbials	Chemical treatment	n/a	PE is resistant to chemicals (generally resistant to degradation by acids, bases and microbial activity).
		End of life	n/a	Not addressed by TG2. "PE is so stable under landfill conditions that it has often been chosen as the liner system for the landfills" (TG3).
PC Potential use with CNTs in electronics/ technical, medical/ healthcare, automotive applications (headlamp, interior instrument panels, bumpers) Current uses of CNT-PC in electrical equipment, high strength impact resistant materials, mechanical processing of soft material surfaces, lightning strike protection for aircraft, cars, wind turbines	n/a	Weathering:	n/a	Not addressed by TG2.
	Air, water	UV degradation	<u>Diepens, 2007</u> : simulated weathering of bisphenol A PC showing photooxidation as most dominant degradation reaction. FTIR spectroscopy and various other analyzing techniques.	Sunlight, humidity, and oxygen cause PC to degrade, thus it is possible that photooxidation is a major degradation pathway (thus release pathway) for MWCNT-PC.
	Air, hydrogen peroxide	Mechanical stress (abrasion/ deformation)	<u>Singh et al., 2003</u> : SWCNT in PC matrix produced as films with 0.06-0.25%wt CNTs. SEM analysis shows CNTs form entangled network throughout the film, increase in young's modulus.	Higher CNT load increases compressive strength, young's modulus, viscosity. Lower molecular weight PC (rather than higher molecular weight PC) has higher compressive strength with MWCNT.

Eitan et al., 2006: MWCNT produced by thermal chemical vapor deposition, 31nm mean diameter, broad distribution of length. Lexan 121 polymer matrix. MWCNTs were surface modified with epoxide (EP), then oxidized and reacted with hydroxyl terminated epoxide molecule. Load into PC was 2-10% by wt. Differential scanning calorimetry (DSC) used to verify lack of stress crystallization. MWCNTs removed from matrix via filtration PTFE using THF solvent. Tensile tests of dog-bone shaped samples via Instron 3042 with extensometer. Temperature and frequency tests via Rheometrics DMTA-V in tensile mode. Viscoelasticity characterized through loss modulus and relaxation spectra. Electron microscopy and probing of fracture surface with nanomanipulator within SEM. Raman spectroscopy used to monitor efficiency of load transfer, polarized Raman spec to measure degree of MWCNT alignment.

King et al., 2010: Tensile modulus, ultimate tensile strength, flexural modulus, ultimate flexural strength, and strain were measured for CNT-PC 2-8% by weight.

Oliver et al. 2008: see below

Han et al., 2009: PC 201 15 supplied by LG Chemical Ltd with MWCNT diameters 9-12nm and lengths 10-15um. MWCNT treated with H₂O₂ and acid treated. Dynamic measurements of rheological properties via Advanced Rheometric Expansion System ARES. Morphology via TEM using unstained samples embedded in epoxy and cut with microtome. Also, AFM at room temp.

Wang et al., 2007: SWCNT in PC thermoplastic composites. SEM and AFM characterization, dynamic mechanical property tests for storage modulus measurement.

HOWEVER, MWCNT load can affect ductility, depending on amount, can act as impurity or increase rigidity and brittleness. **This can potentially increase release, needs to be studied further.**

n/a	Leaching	n/a	Not addressed by TG2.
Air	Temperature & flammability	<u>Oliver et al., 2008</u> : non-functionalized MWCNT in PC studied at room temp and 77K, ranging from 0% to 10% by weight CNT. Mechanical testing for strength, young's modulus, ductility, analyzed via Weibull distributions. SEM of fracture surfaces to support measurement results.	LOW temperatures studied for cryogenic applications of CNT-PC composites, finding that interfacial debonding increases with lower temperatures, particularly with higher CNT load.
Acids, bases, water	Chemical treatment	<u>Pinero, 2005</u> : alkali-catalyzed depolymerization of PC wastes via alcoholysis in supercritical or near critical conditions to study decomposition of PC using methanol and NaOH.	PC is susceptible to degradation under basic conditions, incorporation of MWCNT will likely not change degradation tendency of PC matrix under basic conditions, thus this is a potential release pathway for MWCNT-PC and needs to be studied. PC can be unstable in humidity induced hydrolysis catalyzed by acid.
Air/soil	End of life: landfilling	<u>Romero et al., 2007</u> : Geotrichum-like fungus degrades PC in vitro, examination by SEM showing destruction of PC layer.	PC can undergo biodegradation during landfilling end of life, therefore MWCNT-PC needs to be tested for release in this pathway.

Task Group 1 (TG1) of the project undertook the challenge of describing the methods that are available and relevant to these issues. TG1 reviewed the existing measurement methods relevant to hazard identification, and human and environmental exposure assessment for releases from MWCNT-polymer matrices. Four major areas were considered sequentially: Materials and Products, Release Processes, Measurement of Released Material, and Gaps and Needs. Two release scenarios were considered:

- (1) Release due to mechanical driving forces resulting in released polymer fragments that may or may not contain MWCNTs, and, less frequently observed, unbound MWCNTs.
- (2) Release or potential release due to photolytic, hydrolytic, chemical, biological, and thermal driving forces resulting in polymer degradation and released unbound MWCNTs, or entangled networks of MWCNTs at the composite surface that may subsequently be released due to agitation, wear, or fluid flow.

The majority of the effort focused on existing measurement methods for detection, quantification, and characterization of release material, including sample preparation for various types of media into which material may be released, depending on the release scenario.

Detection of MWCNTs: TG1 considers detection as part of identification, and currently, there are no detectability limits published for any measurement method. TG1 noted that the detectability limit (e.g., MWCNT number or mass concentration) will vary from method-to-method and will need to be determined for each method.

Quantification of MWCNTs: TG1 stated that quantification of released MWCNTs by number or mass concentration is not feasible for many of the reported measurement methods, namely microscopy-based methods that analyze surface and not embedded MWCNTs.

Characterization of MWCNTs: TG1 reported that there are few studies characterizing MWCNT release from MWCNT-polymer composites. The authors identified five major physicochemical characteristics of MWCNTs released material important to exposure assessment:

- Size (*i.e.*, MWCNT length and diameter)
- Size distribution of MWCNTs
- Shape of MWCNTs, including free MWCNTs and those in polymer fragments
- Surface chemistry of MWCNTs
- Spatial distribution of MWCNTs in polymer fragments

Instrumentation: TG1 classified instruments into three major categories, based on availability and practicality, of instrumentation for measuring MWCNT release. Commercial instruments that are widely available and easily used such as:

- scanning electron microscopes (SEM)
- atomic force microscopes (AFM)

Expensive commercial instruments that are frequently not available and often require expert users such as:

- transmission electron microscope (TEM)

Non-commercial and often world-class instruments available at one or a few organizations such as:

- synchrotron spectroscopy

Measurement Challenges: TG1 identified the following major issues related to measurement:

- Release media; environmental media (e.g., air, water, solids) and biological media (e.g., saliva, blood, tissues)
- Form of the MWCNT (e.g., MWCNT is encased in the polymer matrix or protruding from the polymer surface)
- Large diversity of length scale of various material (e.g., nanometer-scale MWCNTs vs. fragments up to hundreds of micrometers)
- Properties of the polymer matrix (e.g., instabilities due to inherent polymer properties at varying lifecycle stages or impurities in the polymer itself)
- Availability of suitable instruments

In summary, measurement methods for each of the three stages of measurement—detection, quantification, and characterization of MWCNTs in polymer fragments released from MWCNT-polymer composites—were assessed by TG1. Factors that are relevant for each method for each stage of measurement were analyzed. These factors include spatial resolution, detection limit, relevant media, availability, practicality, and potential for quantification. TG1 also considered potential methods for pilot or interlaboratory test methods.

TG1 concluded that there are currently few practical methods quantifying characteristics of MWCNT-polymer fragments relevant to measuring release. The methods that may be used are either impractical from a resource standpoint (e.g., electron microscopic analysis and counting of morphologic or compositional traits of released particles in samples taken from release process modeling) or are experimental and require a high level of expertise. Methods related to quantitative detection of MWCNTs released from some scenarios and some media may be feasible, if the characteristics of interest are clearly defined.

4. Expert Comments and Points to Consider (Recommendations from the Oversight Sub-Committee)

This discussion is intended to develop a basis for selecting which method(s) and material(s) to be further developed in pilot methods development and interlaboratory approach. Furthermore, we offer recommendations for specific method-material-scenario combinations to be carried forth for such interlaboratory studies. The primary aim is to identify the material-method-scenario conditions that are the most feasible and offer the greatest utility to improving measurements needed today,

based on findings of existing research and interviews with experts, focusing on the following considerations:

- which method(s) are most advanced and effective in detecting MWCNT releases from matrices of interest;
- which material(s) (e.g., carbon nanotubes and polymers) are most commercially relevant;
- which scenario(s) are most relevant to anticipated commercial applications; and
- which methods have the greatest potential for having broad applicability to other materials and scenarios not included in this project.

As noted in the introduction of this report, these recommendations are those of the experts drafting the report and are not intended to be taken as conclusions of the Steering Committee.

The tables in sections 2 and 3 summarize the currently reviewed information on release processes of CNTs containing composite materials and sort this information according to processes that may lead to a release via three main mechanisms: 1) mechanical stress, 2) thermal stress, and 3) complex stress (e.g., weathering). The number and depth of existing studies for these three primary mechanisms differ significantly. Most studies published to date are related to mechanical stress such as sanding, abrasion, drilling, sawing, and grinding. Of these, the majority of studies are related to the prior two mechanical stress situations, sanding and abrasion. Furthermore, sanding and abrasion are relevant sources for personal exposure to workers and consumers.

4.1. Mechanisms of MWCNT Release on the Basis of Existing Expertise and Practice

A number of different criteria have been considered for selecting release mechanisms to include in this study. Among them, relevance to commercial applications and feasibility of establishing standardized, validated techniques have been identified by the Steering Committee as particularly important. In evaluating the full range of mechanisms discussed in this report (Table 3.3), existing evidence would suggest that sanding, abrasion, and weathering qualify among the most practical to pursue on the basis of published work and expertise in academic, industry, and government laboratories. These release mechanisms are relevant to commercial practice and, depending on the specifics of the release scenario, may be relevant to exposure conditions of greatest interest to the Steering Committee.

While the mechanical forces introduced to the composite material are relatively high during sanding, forces acting on the composite material during abrasion were viewed by the experts we consulted as gentler and possibly more representative for normal use by consumers. Hence, both processes are relevant and can be viewed as complementary.

4.1.1. Sanding

- Frequently studied by research groups all over the world
- Viewed as a relevant source of personal exposure
- Housed facilities have been developed allowing easier identification and quantification of the emission and ensure safety for the worker
- First interlaboratory test will start soon
- No standard testing conditions have been applied yet
- Some basic information is missing such as influence of grit size and weight of sanding paper
- Information on heat production during sanding is limited

4.1.2. Abrasion

- Frequently studied by research groups all over the world
- Viewed as relevant source of personal exposure
- Housed facilities have been developed allowing easier identification and quantification of the emission and ensure safety for the worker
- Standards for this testing procedure exist and were employed in quite a few studies
- Relevant process parameters have yet to be harmonized

Evaluation of sanding and abrasion may have the further advantage of allowing development of analytic measurement methods, such as particle morphology or MWCNT content of specific fractions of the released material, that may be relevant to understanding other release scenarios. For this reason, and in consideration of the established expertise for these release mechanisms, we recommend pilot work using sanding and abrasion.

⇒ **Recommendation: Start with testing of sanding and abrasion.** With regard to complex release situations, weathering has been studied in at least 11 laboratory studies. This release mechanism is less likely to directly lead to human exposure but is an important process for environmental release; important points to consider are listed below.

4.1.3. Weathering

- Frequently studied from research groups all over the world
- Viewed as a relevant source of environmental release and exposure
- Housed facilities are available and exposure to test personnel can be limited
- Particle release can be discriminated from background by using enclosures
- Standards for artificial weathering exist and were employed in most weathering studies
- Standardization is seen as a straight-forward approach but specific analytical methods for the liquid phase may require development

⇒ **Recommendation: Weathering is viewed as important, following abrasion and sanding.**

4.1.4. Thermal Degradation

Thermal degradation, such as from heat stress, combustion, and incineration processes, is a different mechanism possibly leading to release of MWCNTs from polymer composites. To date, they have been studied in a limited context using TGA techniques, simulation of combustion conditions in incinerators, or general combustion conditions. The number of researchers involved is limited to two groups, (Bouillard, 2013; Orhan, 2012). These initial studies show full combustion of tested CNTs when temperatures exceed 700°C for an adequate time period. Consequently, combustion is viewed as of minor importance in this evaluation.

However, MWCNTs may be more stable at high temperatures, especially in polymers formulated with metals and metal-oxides, which may make thermal degradation a more important pathway for this project.

Studies of mechanical stress processes like drilling and sawing are seen of higher relevance compared to combustion due to their potential to generate direct, acute exposures but lower relative to the other aforementioned processes. In addition, less information (e.g., little research) has been published for inclusion in the first standardization testing cycle.

4.1.5. Detection Methods

Electron microscopy, sometimes coupled with other compositional techniques such as X-Ray Photoemission Spectroscopy, is the only specific method identified to characterize MWCNTs and MWCNT-polymer fragments. Some methods have been used to estimate upper limits of what amount of exposure-relevant MWCNTs could be present in released material such as those measuring particle number, surface area, or mass concentrations in particular fractions or sampling locations. In special cases, the concentration of catalysts (e.g., Ni, Co) used for the production of the specific MWCNTs (Interview with Voetz, 2013*) and /or thermal – optical measurements of the samples (Ono-Ogasawara and Myojo, 2011; Ono-Ogasawara and Myojo, 2013; Ono-Ogasawara et al., 2013; Renker et al.; 2013) have been proposed to estimate MWCNT concentrations.

4.1.6. Polymer Material

Commercial relevance and relevance to release scenarios were primary criteria proposed by the TGs and Steering Committee for selecting polymers and MWCNTs to study in methods development. MWCNT-fortified polymers in widespread use in applications with potentially high consumer and/or occupational contact are of greatest interest. A wide variety of polymer composite materials were used in existing studies and included various types of epoxy resins, polyurethane, polycarbonate, polyamide, polyethylene, and so forth. Based on the criteria of interest and existing research examined, however, no specific recommendation on material selection can be derived from the studies in the literature. At times, information on the polymer type was provided in the studies since it was of product-specific relevance, whereas

in other cases, different polymer types were used to determine the influence of matrix material on the test results. The latter argument (choosing materials based on range of the methods that are being developed) is one of relevance to be considered in first standardization tests to define realistic test conditions. The choice of the matrix material is relevant since soft materials like polyethylene are not appropriate for certain release scenarios (e.g., sanding due to material softness). Furthermore, the interaction of the matrix material with the CNT maybe of relevance, especially if functionalized CNTs will be tested. Then, chemical properties in addition to mechanical forces could enhance or limit the binding of MWCNTs in the matrix.

⇒ ***Recommendation: A mix of different polymer materials with specific varying properties should be chosen (e.g., brittle and soft material, hard combustible to easy inflammable), depending on the specific release scenario of greatest interest to the Steering Committee.***

⇒ *Also consider additives: glass fiber or carbon fiber (for reinforcement), amine-based hardeners/curing agents based on findings of the TG2 experts.*

4.1.7. CNT-Material

The review of the literature shows that nearly all release-related studies were conducted for non-functionalized MWCNTs, most frequently CNTs from Bayer and Nanocyl. It is clearly seen that the type of CNT (e.g., long straight, bent, multi-walled, and single-walled) can lead to significant differences in the way CNTs are embedded into the polymer. However, information on this is very limited in the published reports. Therefore, in consideration of the TG2 findings, **MWCNT functionalization** should be considered. Of the modifications, carboxyl, amine, and hydroxyl functionalization seem most common. However, no specific source or type of CNT can be recommended based on the studies reviewed or the TG findings.

5. Appendix

5.1. List of Researchers/Organizations Contacted and Interviewed

Interviewed

- Dhimiter Bello, University of Massachusetts Lowell (USA)
- Luana Golanski, CEA-Grenoble (France)
- Amit Gupta, Battelle Laboratories (USA)
- Keld Alstrup Jensen, National Research Centre for The Working Environment (NRCWE) (Denmark)
- Carsten Möhlmann, M Berges German Insurance Institute (Germany)
- Julie Muller-Bondue, Nanocyl SA (Belgium)
- Thomas Peters, University of Iowa (USA)
- Michael Stintz, TU Dresden (Germany)
- Socorro Vázquez-Campos and Gemma Janer for NanoPolyTox/Leitat Technical University (Spain)
- Matthias Voetz, Bayer Material Science (Germany)
- Wendel Wohlleben, BASF (Germany)

5.2. List of Web Pages Related to CNT Release

Organization/Project	Contact Name	Website
BASF	Wendel Wohlleben	http://www.basf.com/group/corporate/nanotechnology/en/microsites/nanotechnology/safety/safety-research
Bayer Material Science	Matthias Voetz	http://www.productsafetyfirst.bayer.com/
Center for the Environmental Implications of NanoTechnology (CEINT)	Mark Weisner	http://www.ceint.duke.edu , http://www.ceint.duke.edu/news/est-special-issue
Innovations Consortium for Carbon Nanotubes (INNO:CNT)	Peter Krueger	http://www.inno-cnt.de/en/ , http://www.inno-cnt.de/en/projekte_carbosafe.php , http://www.inno-cnt.de/en/projekte_carbolifecycle.php
Nano GEM	Thomas Kuhlbusch	http://www.nanopartikel.info/cms/lang/en/Projekte/nanogem
Nano-Engineered Composite aerospace Structures Consortium	Brian Wardle	http://web.mit.edu/dept/aerastro/labs/necstlab/consortium.shtml
NanoPolyTox	Socorro Vázquez-Campos NanoHealth & Safety Group Leader	http://www.nanopolytox.eu/?page_id=21
National Research Centre for Working Environment (U.Vogel)	Ulla Vogel/Keld Alstrup Jensen	www.nrcwe.dk
National Research Council, Canada	Chris Kingston	http://www.nrc-cnrc.gc.ca/eng/solutions/nano.html
NEPHH - Nanomaterials related Environmental Pollution and Health Hazards throughout their lifecycle	John Njuguna	http://www.nephh-fp7.eu
NIST polymers division	Jan Obrzut	http://www.nist.gov/mml/msed/complex_fluids/jan-obrzut.cfm
Stony Brook University (Consortium for Inter-Disciplinary Environmental Research)	Alexander Orlov	http://mysbfiles.stonybrook.edu/~aorlov/
University of California Center for the Environmental Impact of Nanotechnology	Andre Nel	http://www.cein.ucla.edu/research/3-FT/UC_CEIN_research_FT-7.html

US Consumer Product Safety Commission (CPSC) and National Institute on Standards and Technology (NIST) on CNT releases from products	Keana Scott, Tinh Nguyen (NIST), Treye Thomas (CPSC)	http://www.nist.gov/mml/mmsd/nanotube_041508.cfm , http://www.nist.gov/el/building_materials/
US National Institute of Occupational Safety and Health	Chuck Geraci	http://www.cdc.gov/niosh/topics/nanotech/
<u>Other laboratories/efforts to provide input:</u>		
CSIRO and Safe Work Australia evaluation of machining studies	Jurg Shutz CSIRO, Howard Morris, Safe Work Australia	http://www.csiro.au
International Council on Nanotechnology publications database		http://icon.rice.edu/
NEDO nanomaterial characterization methods project	see web link - also see emails for Isamu Ogura and Atsuo Kishimoto	http://www.aist-riss.jp/projects/nedo-nanorisk/index_e.html

5.3. List of Publications and Meeting Presentations Reviewed

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- Bernard, C., Nguyen, T., Pellegrin, B., Holbrook, R.D., Zhao, M., Chin, J. Fate of graphene in polymer nanocomposite exposed to UV radiation. *J Phys Conf Ser* 2011;304:012063.
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- Dahm, M., Evans, D., Schubauer-Berigan, M., Birch, M., Fernback, J. Occupational exposure assessment in carbon nanotube and nanofiber primary and secondary manufacturers. *Ann. Occup. Hyg.* 2012;56:542-556.
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