

SIRENA 



LIFE 11 ENV/ES 596

**SIRENA - SIMULATION OF THE RELEASE OF NANOMATERIALS FROM
CONSUMER PRODUCTS FOR ENVIRONMENTAL EXPOSURE ASSESSMENT**

**BEST PRACTICE MANUAL FOR THE SIMULATION
OF THE RELEASE OF NANOMATERIALS FROM
POLYMER NANOCOMPOSITE PRODUCTS**

DECEMBER 2015



Inspiring
Business



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Table of contents

1.	Introduction.....	5
2.	Basic information	6
3.	Lessons learnt.....	13
3.1.	Do evaluate the release	13
3.2.	Use a reference material.....	15
3.3.	Do not start from scratch... Adapt existing standards whenever available	16
3.4.	Correlate the specific nano-release process to the specific stages the sample will undergo throughout its life cycle and also to the nature of the sample that is being tested	18
3.5.	Monitor (and isolate) background and/or alternative emissions not specifically related to the process that is being simulated	20
3.6.	Use calibrated and sensitive measurement equipment	22
3.7.	Evaluate both aerosols generated and deposited particles, as both materials are relevant to estimate the release.....	23
3.8.	Correlate the emission or release taking place with the actual simulation process under assessment	24
3.9.	Collection step.....	25
3.10.	Protect personnel carrying out the research	26
4.	Outlook and steps to standardisation	27
5.	References List	28



List of Abbreviations

- CNT – Carbon Nanotube
- DMA - Differential Mobility Analyser
- EAPNC – Emitted Aerosol Particle Number Concentration
- ELPI - Electrical Low Pressure Impactor
- ENMs – Engineered Nanomaterials
- ESD - ElectroStatic Discharge
- ESPs - Electrostatic precipitators
- NEPs - Nanotechnology Enabled Products
- PSD- Particle Size Distribution
- PNC –Particle Number Concentration
- POSS – Polyhedral Oligomeric Sisesquioxane
- SIMS - Secondary Ion Mass Spectrometry
- TRL - Technology Readiness Levels
- XPS - X-Ray Photoelectron Spectroscopy



1. Introduction

One of the main applications of nanotechnology is the manufacturing of polymer nanocomposites, reinforced polymers with low quantities of nanosized ingredients dispersed into a thermoplastic or thermoset matrix. The use of engineered nanomaterials in composites production offers enormous advantages over traditional macro- or microsized fillers and applications across a wide range of industrial sectors are currently on the market.

In absence of an international consensus in relation to the (eco)toxicological impact of ENMs, industry must evaluate and, if feasible, quantify the risk of ENMs embedded into composite matrixes release to the environment throughout their life cycle as an integral part of its design processes. This information should be made available to the relevant regulatory authorities and consumers.

The main goal of the SIRENA LIFE Project is to demonstrate and validate a methodology to simulate the unintended release of ENMs from consumer products by replicating different life cycle scenarios to be adopted by a wide number of industrial sectors in order to get the necessary information for exposure assessment. To this aim, nanocomposite samples of different nature representing applications in the Automotive, Aerospace and Renewable Energy sectors have been mechanically degraded –via drilling and crashing- under controlled conditions in order to verify if embedded ENMs are released in these processes.

The present guidelines have been developed on the basis of the experience gained within SIRENA. The document compiles a series of practices that have been found to be successful for the evaluation of the release of ENMs from the plastic matrixes where those are embedded under mechanical stress.

Alternatively, nano-release can take place via chemical decomposition of the host matrix (including UV-assisted, thermal, hydrolytic and biological degradation) which could lead to direct release of ENMs either by exposing embedded particles to the material surface or by indirect release via attenuated diffusion properties. Many of the principles described in the next pages for experimental design are also applicable to this type of release.



2. Basic information

Relevant definitions to understand the information presented on this document are hereby provided:

Item	Definition
Emission	The act of producing or sending out something from a source
Release	To set free from physical restraint or binding
Aerosol	A system of colloidal particles dispersed in a gas, as smoke or fog
Dusts	Solid aerosols generated by the handling, grinding, abrasion, or cutting of a bulk material
Mists	Liquid aerosols generated by condensation from a gaseous state or by the breaking up of a bulk liquid into a dispersed state
Smoke	Solid aerosols resulting from the incomplete combustion of carbonaceous materials
Fumes	Solid aerosols generated by the condensation of vapors or gases from combustion or other high temperature processes
Bioaerosols	Solid or liquid aerosols from biological sources
Fibers	A special (based on toxicological properties) kind of dust that is fibrous in nature (i.e., longer than it is width). Aspect ratio (L:W) defined as 3:1 or 5:1

Additional definitions of relevance to the present document include:

Item	Definition
Nanomaterial	With the aim of ensuring that a nanomaterial is defined consistently in all pieces of EU Regulation, the Commission adopted a Recommendation on the definition on 18 October 2011: "Nanomaterial" means: <i>A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the</i>



Item	Definition
	<p><i>number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm</i>". Nevertheless, this definition has generated a great controversy due to, fundamentally, the size range and percentage of particles it defines and, the selection of the particle number as the main measurement unit.</p> <p>The SCENIHR (Scientific Committee on Emerging and Newly Identified Health Risks), for example, considers that a material might be considered as a nanomaterial when >0.15% of the material has a size below the designated upper size limit and the Nanotechnology Industries Association (NIA), considers that the 50% threshold should be increased. The Commission is currently waiting on a third part of the report "Towards a review of the EC Recommendation for a definition of the term nanomaterial" from the Joint Research Centre (JRC). The first part (Part 1: Compilation of information concerning the experience with the definition) was published in July 2014 and the second one (Part 2: Assessment of collected information concerning the experience with the definition) in September 2014.</p> <p>The term "nanomaterial" is also defined in ISO/TS 80004-1:2010: "<i>material with any external dimension in the nanoscale or having internal or surface structure in the nanoscale</i>". This definition is generic, as it covers both nano-object (any external dimension in the nanoscale) and nanostructured material (internal or surface structure in the nanoscale). Among nanostructured, they define five different subcategories:</p> <ul style="list-style-type: none">• Nanostructured powder (including nanostructured aggregate, agglomerate, core-shell particle and capsule)• Nanocomposite (comprising polymer matrix, metal matrix, and ceramic matrix nanocomposite)• Solid nanofoam• Nanoporous material• Fluid nanodispersions (including nanosuspension, nanoemulsion, liquid nanofoam, nano aerosol). <p>WIESNER et al. (2009) refer that NMs may include individual nanoparticles (NPs), NP composites, macroscopic objects composed of NPs such as thin films, and many other objects composed of materials with the requisite characteristics of having at least one dimension of 1-100nm and displaying novel properties.</p> <p>Engineered nanomaterials (ENM) or engineered nanoparticles (ENPs) are materials intentionally created with specific properties related to shape, size, surface properties and chemistry.</p>
Composite	Combination of two or more different materials mixed in an effort to blend the



Item	Definition
	best properties of both
Nanocomposite	<p>Composite material in which one or more phases of the components has at least one dimension that is nanoscopic in sizeEngineers ().</p> <p>Nanocomposites display enhanced physical, thermal and other unique properties when compared to conventional microscale composites. Nanocomposites based on the nature of matrix phase can be divided into polymeric, ceramic and metallic composites.</p> <p>Nanocomposites can also be classified according to their types of filler material (such as clay nanocomposites, ceramic nanocomposites, carbon nanotube composites, metal and metal oxide nanocomposites and nanobiocomposites).</p> <p>According to the IUPAC, a nanocomposite is a <i>Composite</i> in which at least <i>one</i> of the phases has at least <i>one dimension</i> of the order of nanometers (WORK et al., 2004).</p>

The transition from microparticles to nanoparticles yields dramatic changes in physical properties. Nanoscale materials have a large surface area for a given volume. Since many important chemical and physical interactions are governed by surfaces and surface properties, a nanostructured material can have substantially different properties from a larger-dimensional material of the same composition.

In polymer science, the most relevant classification of ENMs is that related to their geometry, since, depending on the application of interest, high aspect-ratio particles are used for nanocomposites manufacturing. Attending to their geometry, ENMs are classified into three classes: particle, layered and fibrous materials. Examples of particulate materials include metallic and ceramic nanoparticles and POSS; fibrous materials are exemplified by carbon nanotubes and silicates such as sepiolite and wollastonite; finally, graphene and montmorillonite are layered materials.

Nevertheless, some authors (Nowack et al., 2012) argue that when trying to carry out their hazard identification they should be categorized based on the location of the nanoscale structure in the system/ material. In this sense, Hansen (2007) developed a categorization framework depending on where the nanoscaled structure is located.

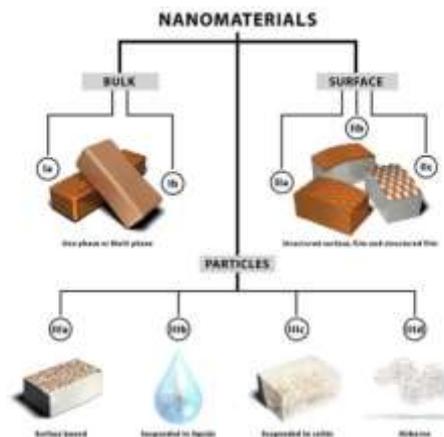


Figure 1: Categorization framework to aid hazard identification of nanomaterials. S. Foss Hansen, B.H. Larsen, S.I. Olsen, A. Baun. *Nanotoxicology*, 2007, 1-8. According to this categorization, nanocomposites belong to class III, subcategory c “Nanoparticles suspended in solids”.

2.1. Commercial relevance of Nanocomposites

The development of polymer nanocomposites is one of the most active areas of production of nanomaterials and the polymers and nanofillers used to these applications are continuously increasing in the last years.

According to BCC Research (Global Markets for Nanocomposites, Nanoparticles, Nanoclays, and Nanotubes. NANO21F, May 2014) the Global consumption of nanocomposites will reach by 2019 584.984 metric tons/\$4.2 billion (a CAGR of 21.1% in unit terms and 24% in value terms between 2014 and 2019).

Although the Asia- Pacific region was the largest geographical market for nanocomposites in 2013, consuming about 36% of the market, it is expected that in 2019, Europe (with the 33.2% of the market) will be the first consuming region as can be seen in the next table:

Market	2013	2014	2019	CAGR% 2014-2019
Asia-Pacific	443.6	502.1	1,356.0	22.0
Europe	409.5	486.7	1,405.8	23.6
U.S.	265.7	325.2	1,163.0	29.0
Rest of World (ROW)	112.5	129.6	303.0	18.5
Total	1,231.3	1,443.6	4,227.8	24.0

Table 1: Consumption of nanocomposites by country/region through 2019 (\$ Millions). Source BCC Research

However, as can also see in the table, the US market for nanocomposites has the highest projected growth rate of any major market (29%), followed by Europe and Asia.

Relating the consumption by type, in 2013, clay nanocomposites accounted for 59% of total nanocomposite consumption by value in 2013, followed by carbon nanotube composites (17.7%) and metal/metal oxide nanocomposites (12.8%). For 2019, authors expect that clay nanocomposites’

market share will increase and carbon nanotube composites and metal/metal oxide nanocomposites' share will drop.

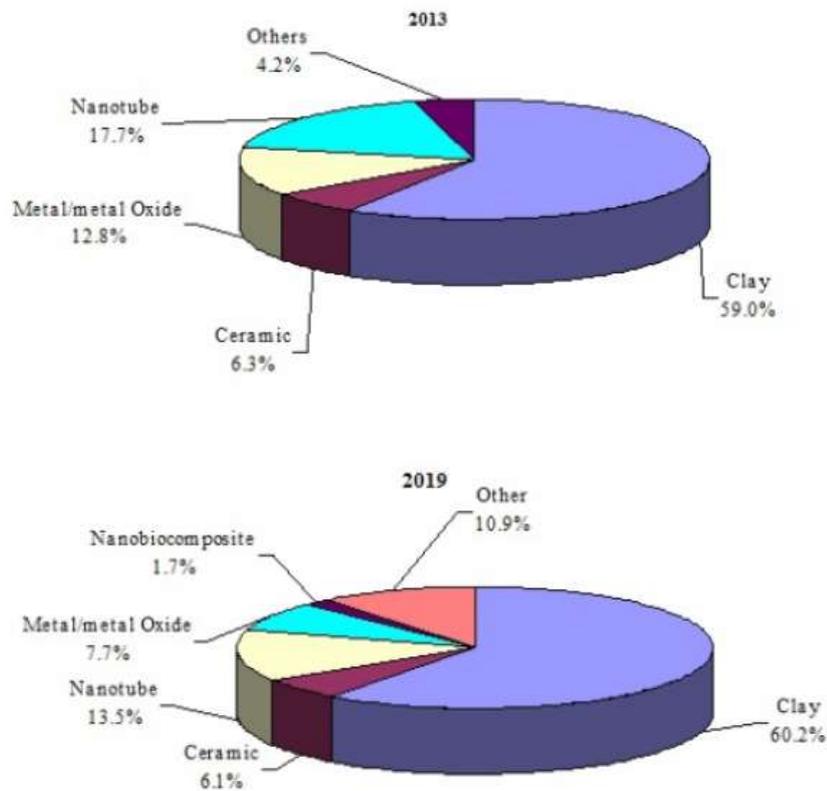


Figure 2: Global nanocomposite consumption by type, 2013 VS 2019 (% of total value) Source: BCC research

Regarding nanocomposite consumption by application, in 2013, automotive area was the main nanocomposite application area with 51.4% of the worldwide market, continued by packaging (22.5%) and electronics/ESD (13.85). In authors' opinion, automotive and electronics/ESD share will drop and packaging while increase slightly. Textiles are going to emerge as the fourth largest nanocomposite application area in 2019.

Polymers used as matrices of nanocomposites, include Nylon, Polyolefin, Polyethylene, Polypropylene, Polyvinyl chloride, Polystyrene, Ethylene- vinyl acetate copolymer, epoxy resins, polyurethanes, polyamides and polyethylene terephthalate.

Nanofillers used in order to improve the properties of the different polymers are applied at rates 1-10% (in mass) and the most common ones are nanoclays, nano oxides, carbon nanotubes and metallic nanoparticles.

Some applications of polymer matrix nanocomposites include:

- Mechanical Reinforcement: By adding nanofillers to polymers an improvement in mechanical properties can be achieved (mechanical stability, stiffness, strength, toughness ...).
- Barrier and membrane separation properties



- Flammability resistance: The addition of some nanofillers to polymers lead to an increased flammability resistance
- Polymer blend compatibilization: It has been demonstrated that the addition of nanoparticles can prevent the coalescence retaining improved dispersion after shear mixing.
- Biomedical applications
- Fuel cell applications
- Electrical/electronics, optoelectronics and sensors

2.2. Who should read this manual

Within the actual regulatory framework, companies do not need to declare the nanoparticles or ENMs used within their consumer products and processes with several exceptions. The EU Cosmetics Regulation and the EU Biocides Regulation contain both specific provisions for nanomaterials according to which the materials used in the nanometric scale need to be identified as such on the product labels. The proposal for a Regulation on medical devices refers that, where applicable, an indication that the device incorporates or consists of nanomaterial is to be included on the label unless the nanomaterial is encapsulated or bound in such a manner that it cannot be released into the patient's or user's body when the device is used within its intended purpose.

It is therefore expected that the regulatory framework affecting the integration of ENMs within a number of fields changes in the next years, integrating specific provisions for nanomaterials.

In accordance with the *Study to Assess the Impact of Possible Legislation to Increase Transparency on Nanomaterials on the Market* (June 2014), there appears to be a widespread (but not universal) view that available information on nanomaterials is insufficient for informed decision-making. This was reflected in the call by the European Parliament¹ in 2009 for the European Commission to compile: "*an inventory of the different types and uses of nanomaterials on the European market, while respecting justified commercial secrets such as recipes, and to make this inventory publicly available*".

Since then, several Member States (most notably France) have launched initiatives for national registries for nanomaterials. Furthermore, Austria, Belgium, the Czech Republic, Denmark, France, Italy, Luxemburg, the Netherlands, Spain, Sweden and Croatia have asked the Commission² to "*propose legislation on registration or market surveillance of nanomaterials or products containing nanomaterials*". Various stakeholders and non-governmental organisations have also called for a registry for nanomaterials.

There exists a significant controversy in relation to the present approach and an international consensus has not yet been reached. In case of approval, there exist several options to accomplish with the registry. One of such options is the EU Nanomaterial Registry by Application. This would require manufacturers/importers/downstream users/distributors to submit a new declaration for each new

¹ European Parliament resolution of 24 April 2009 on regulatory aspects of nanomaterials (2008/2208(INI))

² As indicated in the Commission's Working Document:
<http://ec.europa.eu/DocsRoom/documents/5282/attachments/1/translations/en/renditions/native>

Best practice manual for the simulation of the release of nanomaterials from polymer nanocomposite products



nanomaterial-containing mixture or article that they put on the market. This would allow for full traceability of an ENM across the supply chain.

The nano-release assessment serves **the safer-by-design principle**, allowing the reformulation of NEPs (Nanotechnology Enabled Products) with a reduced ENMs content or with different configurations so that release is decreased or eliminated until the associated (eco)toxicological impact of ENMs is cleared out. The most logical step following the registry, would be the evaluation of the potential ENM release of these products, in order to evaluate consumer and environmental exposure beyond manufacturing stages of the so called NEPs (Nanotechnology Enabled Products).

Furthermore, the Article 13 of REACH refers that testing (human toxicity...) may be omitted where justified by information on exposure and implemented risk management measures. On the basis of the present article, if it can be demonstrated that there is no exposure to ENMs throughout their life cycle; ie, no release takes place, no testing is to be carried out.

The present guidelines are addressed to research centres and universities, having conducted the majority of the nano-release assessment studies to date but also to a wide number of industrial sectors. The efforts by BASF in the present area represent an example of industrial leadership in the present area of development.



3. Lessons learnt

The present section describes several ideas that could be taken into account when designing an investigation to evaluate the release of ENMs from polymer nanocomposites. These ideas come from the experimental work conducted within SIRENA and also from the thorough assessment of additional research studies and initiatives at this regard that has been carried out by means of the Technological Surveillance during the implementation of the project.

3.1. Do evaluate the release

The first and fundamental step in the control of hazards is their **recognition**.

ENMs released from products may exhibit a different toxicity than pristine ENM (Nowack et al., 2012) which are used for toxicity tests. Once released in the environment, physical and chemical transformations and biotic metabolism can change the properties of ENM and thus influence their toxicity. Examples of abiotic influences on ENM are; thermal treatment (incineration, heating), dissolution, transportation, agglomeration, aggregation, absorption, sorption, sedimentation, etc. Moreover, chemical changes to released ENM and their functionalized surface can occur (for example by oxidation). Such modifications in natural media influence surface-chemistry-related factors such as mobility, persistence, reactivity, bioavailability and biocompatibility of ENMs ((CIEL) et al., 2015). As a consequence, the associated hazard profile of the released materials will be affected.

Predicting exposure to ENMs and the relevant exposure concentration begins with an assessment of the environmental availability of ENMs throughout their life-cycle. This will largely be determined by the engineered matrices in which these materials are found, such as composites in intermediate or finished consumer goods. ENM could be released during primary production processes (synthesis), formulation and application of intermediate products, waste treatment as well as accidents that may occur at each stage of a product's life cycle.

However, the unintentional release of ENM from products is often not anticipated or taken into account prior to their commercialization, amongst other because no standardized methods and protocols are available to evaluate the release.

A relevant consideration to be made refers to the actual target of the assessment to be carried out. Nano-release evaluation can serve two different purposes:

- Exposure assessment to released nanosized particles: worker, consumer or environmental exposure to articles or processes in which Nanotechnology is present in either way under normal or accidental conditions. We can refer to this part of the assessment as nanosized EMISSION or DUST.
- Nano-release assessment: in present assessment the main target is to verify if Nanotechnology incorporating products actually release these ENMs throughout their life cycle (be it Nanosilver incorporating t-shirts or plastic food containers integrating ENMs). This evaluation can be referred to as RELEASE (and more specifically as NANO-RELEASE).

Different questions are therefore to be answered particularly for the materials of interest of SIRENA:

Best practice manual for the simulation of the release of nanomaterials from polymer nanocomposite products



- What is the physico-chemical nature of the particles released by nano-additivated composites under mechanical stress (in comparison with the traditional formulations –including micro-additivated samples-)? Particle size distribution...
- Do embedded ENMs actually release from nanocomposite samples under mechanically stressing conditions? The answer to this question is challenging, because freely released ENMs may constitute too small a portion of the total released mass that instruments are not sensitive enough to detect them and released ENMs could adhere to the surfaces of larger abraded particles and thus remain hidden from conventional particle sizing experiments.
- If affirmative, what are the specific characteristics of the released materials? Chemical composition of mixed nature, variety of shapes, number distribution...

The World Health Organization published in 1999 (WHO, 1999) that "*Dusts usually originate from larger masses of the same material, through a mechanical breakdown process such as grinding, cutting, drilling, crushing, explosion, or strong friction between certain materials (e.g., rocks). Dust thus generated is often called "primary airborne dust."* The generation of dust from materials under mechanical stressing conditions is therefore a well-known phenomenon. It is also acknowledged that dust particle size is related to the amount of energy involved in creation; the higher the energy, the smaller the particle created; the lower the energy, the larger the particle created.

We can expect dust to be generated in the mechanical degradation processes that are considered within SIRENA, and such dust will convey an environmental and/or human exposure. What we do not know is neither if the exposure associated to these mechanisms on nanocomposite materials is different to the exposure associated to the traditional materials (with microparticles or no particles embedded) nor if ENMs do release from the embedding matrix as isolated or hybrid particles (matrix-ENM).

In most of the studies conducted to date, no free nanofillers have been observed; rather, released particles were agglomerates of the nanofillers and the host matrix. Considering the samples and mechanical processes tested within SIRENA no free nano-fillers have been observed either. However, this conclusion cannot be extrapolated to any polymer nanocomposite material, since nano-release is specific to the type of sample and degradation process investigated and it must therefore be evaluated on a case by case basis.



3.2. Use a reference material

From a life cycle perspective, **samples with the same functionality** should be selected as a reference which sometimes means using samples with traditional macro or microsized fillers and not necessarily with the non-reinforced matrix, which would enable a fair comparison (taking into account functionality issues). This would be especially relevant for assessments related to the changes in particle size distribution and aerosol generation in the samples of interest. If nano-release is the very specific target, the selection would necessarily be nano VS non-nano containing specimens.

The selection of the test materials is crucial. Within SIRENA pre-market materials have been selected considering that the nano-release assessment needs to be performed on materials that are likely to reach the market in their actual configuration. As a matter of fact, within SIRENA we have verified that the performance of the reinforced specimens is increased in contrast with the reference materials and thus, have a real potential to replace the traditional formulations in specific applications.

Bello et al. (2012) refer as sample materials to two types of advanced CNT-hybrid composites. In detail: (1) "fuzzy fiber" reinforced plastic laminate composite containing woven alumina fibers in each lamina with aligned CNTs grown on the surface of the alumina fibers (referred to here as CNT-alumina [CNT-A]), and (2) a graphite-epoxy prepreg system (aligned and collimated carbon fibers with an epoxy resin arranged in a layered laminate configuration) with aligned CNTs placed at the centre (termed here CNT-carbon [CNTC] composites). No practical examples of the type of applications containing these materials are provided; the reader cannot tell from the information on the article whether the selected materials are of commercial relevance or if those have been manufactured for RTD purposes only.

In a different study, Cena and Peters (2012) have not used a reference sample, but, instead, airborne concentrations were measured during two processes: weighing bulk CNTs and sanding epoxy nanocomposite test sticks (2% wt CNT). Though this study can provide data on the emissions associated to the use of CNTs in the referred scenarios, it provides no information on the emissions associated to alternative traditionally used fillers for a relative perception of the associated risk.



3.3. Do not start from scratch... Adapt existing standards whenever available

No specific standard is available to date for nano-release assessment from nanocomposite samples. For instance, the ISO/TS 12025:2012 – *Nanomaterials. Quantification of nano-object release from powders by generation of aerosols* describes how to choose the measurement device and the sampling procedure to follow. However, it only concerns release of nanoobjects from powders and not from actual nanoproducts as solid parts undergone mechanical stress situations.

However, standard tests exist simulating accelerated ageing, mechanical or chemical stress; as most of these protocols serve the purpose of verifying if a certain material or product can perform well under certain use conditions. These standards only cover the equipment to use and procedure to follow in order to carry out the mechanical tests but do not mention the measurement of nanoparticles released or their collection. Notwithstanding with the above mentioned, such standards can be adapted to the purposes of the assessment we are conducting. In fact, in literature, standard methods that have been adapted for nano-release assessment have been reported as hereby exemplified:

- Golanski et al. (2011) refer the use of the ISO 11998 for nano-release assessment in a wet abrasion study on TiO₂ nano-additivated paints.
- Wohlleben et al. (2011) & Wohlleben et al. (2013) refer the Taber Abraser test as an established method of the coatings industry to quantify wear resistance which is described in several national and international standards (e.g. DIN53754:1977, DIN 68861-2:1981, ISO 5470-1:1999 and ASTM D4060-95:2007).
- On a pilot interlaboratory comparison of protocols that simulate aging of nanocomposites and detect released fragments, Wohlleben et al. (2014) have simulated the year-long outdoor use by consumers on the basis of ISO-standardised weathering tests established for plastics and coatings, in particular ISO 4892-2 (2013).
- On a different context, the international standard ISO 105-Co6:1994, for determining colour fastness in commercial and industrial laundering has been reported for nano-release assessment from textiles incorporating ENMs (Windler et al., 2012).

Simulation of the release of nano-sized particles during experimental processes in several studies have used existing standardized procedures. However, to the best of our knowledge, no standard methods exist to test drilling resistance; due to this fact the typical drilling conditions in an industrial setting have been selected and uniformly applied to all sample materials within SIRENA. However, in the case of the cashing/impact approach, the test conditions described in the Euro NCAP regulation for 'Impact Testing' (<http://www.euroncap.com/en/for-engineers/protocols/general/>) have been selected.

Automatic processes are preferred over manual process since those can be easily controlled enabling repeatable and reproducible tests. Note that the purpose of the research is to evaluate and quantify the release of ENMs, not the assessment of the consumer exposure in manual DIY operations. Depending on the focus of the assessment, industrial or domestic processes could also be simulated.

In relation to the generation of controlled conditions for nano-aerosol measurement and characterization, to the best of our knowledge, no specific standard exists. Groso et al. (2010) have developed a procedure for managing the occupational safety and health risks relevant to research laboratories producing and using nanomaterials. *The procedure consists of two parts. Using a decision*



tree authors sort the "nano-laboratories" into three hazard classes (Nano 3 = highest hazard to Nano 1 =lowest hazard), which corresponds to analogue approaches applied to other hazard types (biohazard, radioprotection or chemistry). For each hazard level authors then provide a list of required risk mitigation measures (technical, organizational and personal).

Alternative standards to be used as a starting point are the emission chambers used to measuring the discharge of volatile organic compounds in indoor air.

Within SIRENA, the developed prototype by Cranfield University underwent a Local Exhaust Ventilation (LEV) test in order to evaluate if the system is safe towards the operator.

Finally, the chamber should have implemented temperature and relative humidity monitoring/control systems, since these two parameters might affect the agglomeration status of the airborne materials. These two have not been monitored within SIRENA but could be observed in future optimizations of the developed prototypes. Other parameters such as air exchange rate, loading rate, air velocity and clean air supply should be known as they might have an effect on the emitted particles.

3.4. Correlate the specific nano-release process to the specific stages the sample will undergo throughout its life cycle and also to the nature of the sample that is being tested

This tip is especially relevant if the (eco)toxicological potential of the released particles or nanofillers is to be evaluated. It has been written on the basis that the nano-release simulation study should be planned in agreement with the ulterior scenarios the material will go during its life time, for instance a piece of polyamide to be placed inside the car will not undergo hydrolysis or chemical degradation processes in contrast to pieces exposed to environmental stress.

The key issue is to define what type of exposure is to be evaluated: depending on the exposure -worker exposure, consumer exposure, environmental exposure- the forms of the nano-objects will vary. The assessment should focus **the most relevant forms of the released particles when the exposure takes place.**

An additional relevant consideration to be made is related with the **nature of the samples** that is being evaluated. In fact, according to Duncan (2015) the available literature on release of ENMs from nanocomposites as a result of mechanical degradation suggests that the physical properties of the host material (and the types of forces applied) are integral to determining the number and size of particles released.

In agreement with the above statement, within SIRENA, in the drilling experiments noticeable differences were observed when comparing emissions of thermoplastic and thermoset materials, the first ones with a lower release which is attributed to the fact that Polypropylene melts and nanosized particles are retained in this process.

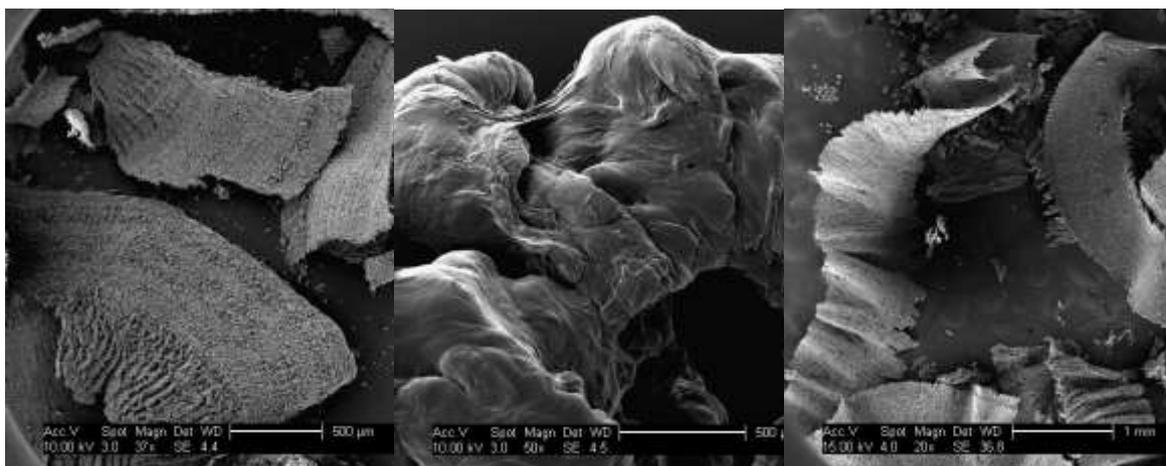


Figure 3: SEM image of the turns collected from a Polyester/ Al_2O_3 sample Thermoset

Figure 4: SEM image of the turns collected from a Polypropylene sample Thermoplastic*

Figure 5: SEM image of the turns collected from an Epoxy/CNT sample Thermoset

Images by CRANFIELD UNIVERSITY.



The different behaviour of the two types of materials reacting to the drilling can be observed at the microscale since the turns collected from the drilling of polypropylene (and so thermoplastic) materials appear like an agglomeration of materials that seems to have melted –Figure 2- due to their low thermal conductivity.

Within SIRENA the same drilling conditions for all the samples studied have been applied independently of their thermoplastic or thermoset nature. Considering the heat effect on thermoplastic matrixes, the drilling protocol could have been adapted by extending the machining time with slower feed rates (this is just an example of an alternative approach). This must be seen as a relevant consideration for future studies on nano-release assessment on polymer nanocomposite samples in mechanical degradation studies.

The results obtained within SIRENA suggest that the nature of the host material has a greater influence on the characteristics of particle release from plastic nanocomposites during mechanical abrasion than the characteristics of the nanofillers.

Aligned with the present results, Hirth et al. concluded from their work³ that CNT protrusions are a material-dependent phenomenon related to the toughness of the host matrix and are likely to occur only in particles released from host materials with elongation-at-break values greater than 10%. In materials with large elongation-at-break values (e.g., thermoplastic polymers such as Nylon, PE, PET, etc.), necking of the host matrix is expected to inhibit the formation of CNT protrusions; that is, the host material will “stretch” around nanofillers rather than simply break off to leave nanofillers exposed.

It must be noted that within SIRENA no CNT protrusion has been observed in epoxy samples (same host matrix, filler and filler quantity -2% weight-) in contrast to the reference cited above. The difference relays in the mechanical process tested, thus nano-release needs to be considered to be specific to the mechanical process under consideration.

Finally, in relation to the nature of the samples of interest, no studies have been identified addressing the release/emissions on recycled polymer nanocomposite samples, for any of the possible degradation processes these might undergo (mechanical, chemical, biological...) depending on their specific application and life cycle stage of consideration. This can be pointed out as a research gap to be addressed in the future.

³ Hirth et al., Scenarios and methods that induce protruding or released CNTs after degradation of nanocomposite materials. J. Nanopart. Res. 2013, 15, 1504.



3.5. Monitor (and isolate) background and/or alternative emissions not specifically related to the process that is being simulated

Background nanoaerosols from natural and incidental sources are ubiquitous and present major challenges for the characterization of aerosols in simulated scenarios. Several approaches have been proposed and applied, including subtraction of background concentrations, either measured prior to the activity or during the activity away from the source, and statistical techniques. However, concurrent processes (i.e., use of combustion or electro motors) can be a significant source of other (potentially health relevant) particles (Koponen et al. 2011; Szymczak et al. 2007). Furthermore, these techniques for correcting background levels do not account for the interactions between ambient aerosols and the ENM particles.

Instruments to date do not distinguish ambient particles and ultrafine particles from the nanoaerosols generated in mechanical degradation processes on test samples. Furthermore, it is unclear whether background measurements should be subtracted from the measurements taken during simulated scenarios or reported separately.

The use of enclosures facilitates the discrimination of nano-objects from background particles. An additional benefit of using enclosures is the safety of the testing personnel, who is not directly exposed to the released particles with possible hazardous properties not yet clearly determined.

In the preparatory actions conducted within SIRENA, several particle measurements were carried out as blank tests (no nanocomposite samples being mechanically degraded) on different days. The different particle number concentrations can be observed in the Figure 6. Measured particle concentration corresponds to the activation of the drill with no samples being drilled on 7 different days.

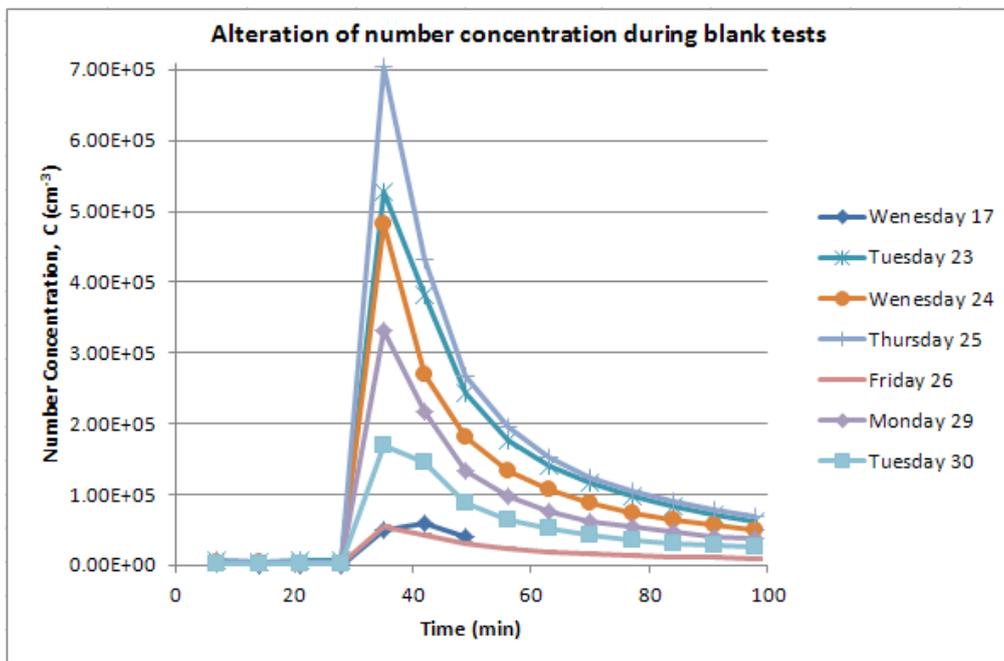


Figure 6: Variations in particle number concentration obtained in blank tests (un-optimized protocol and testing prototype)

Additionally, **emissions associated to the equipment** that is used to generate the release are to be monitored. In fact, several authors (Koponen et al., 2009, van Broekhuizen et al., 2011, Kuhlbusch et al., 2011, Wohlleben et al., 2011) have detected high levels of ultra-fine particles which they attributed to particle emissions from electric motors. Szymczak et al. (2007) and Liroy et al. (1999) showed that certain motors (with carbon brushes sliding over copper commutator contacts) tend to release significant amounts of ultra-fine particles.

Being aware of the present circumstance, a water cooled and sealed spindle drill system to ensure no particles are introduced into the chamber was implemented in the developed prototype by CRANFIELD UNIVERSITY.



Figure 7: Water cooled and sealed spindle drill system implemented in the prototype developed within SIRENA

To address the background noise problem, researchers at RGU and VITO developed a new chamber system that eliminates all the background noise. This new chamber set up includes an enclosed environment which consisted of only "clean air" through a series of HEPA filters. The testing would only initiate once the chamber had cleaned itself and a low concentration of particles was produced on the CPC. The HEPA filters combinations were capable of producing a CPC reading within the chamber of 0 #/cm^3 particle number concentration.



3.6. Use calibrated and sensitive measurement equipment

Instrument and system calibration are of main importance for the successful measurement of aerosol properties and nano-release assessment in a sampling environment. While there are theoretical means for assessing instrument or system performance, calibration provides information which is more reliable and more applicable for the particular sampling conditions.

The ISO 9001:2008 Quality management systems - Requirements are:

7.6 Control of monitoring and measuring equipment

The organization shall determine the monitoring and measurement to be undertaken and the monitoring and measuring equipment needed to provide evidence of conformity of product to determined requirements.

Where necessary to ensure valid results, measuring equipment shall

- be calibrated or verified, or both, at specified intervals, or prior to use, against measurement standards traceable to international or national measurement standards;*
- be adjusted or re-adjusted as necessary;*

In addition, the organization shall assess and record the validity of the previous measuring results when the equipment is found not to conform to requirements. The organization shall take appropriate action on the equipment and any product affected.

Box 1: Extract of the ISO 9001:2008

In general, devices used to assess exposure to nanomaterial or nano-size aerosols can be subdivided into devices that monitor (on-line) a chemical substance or aerosol by “near or quasi” real-time detection and devices that sample (time-aggregated) chemical substances or aerosols on a substrate, followed by off-line analysis.

As a limitation to the state of the art technology it must be noted that the methods and instrumentation generally applied to estimate the particle size distribution make the assumption that the particle’s shape is spherical which is usually not the case.



3.7. Evaluate both aerosols generated and deposited particles, as both materials are relevant to estimate the release

Recent publications by Shandilya et al. (2015) and others, have addressed the release of ENMs by means of abrasion but focus only on aerosolized particles (EAPNC – Emitted Aerosol Particle Number Concentration; PSD- Particle Size Distribution, determined on the basis of PNC –Particle Number Concentration).

When aerosolized, ENM coagulate homogeneously or heterogeneously with other ENM, or attach to ambient background particles; all processes effectively alter the particle size distribution, the particle number concentration, and the chemical composition of the background aerosols (Schneider et al. 2011; Seipenbusch et al. 2008). Many studies of aerosolized ENM focus primarily on measuring nano-sized particles (compared to larger particles), yet particles may no longer be in the nano-size range at the time of sampling. CLARK ET AL 2012

Within SIRENA emitted particles are classified as airborne and deposited. Airborne particles are measured by Cranfield University via SMPS+C whereas deposited particles are collected for ulterior characterization studies. In the case of RGU, the particle size distribution was measured using an SMPS and a DMS50.

In fact, data from the SMPS provide information related to the exposure to the emitted particles. Information related to the nano-release assessment –to the date of present report- can be obtained by actively collecting emitted particles and visually inspecting whether ENMs have released or not from the surrounding matrix. As an alternative, Wohlleben et al. (2011) used XPS and SIMS to show that silica nanoparticles were exposed on the surfaces of composite particles released from silica/polyamide PNCs, but only in concentrations similar to what is found in the bulk composition of the PNCs, if silica nanofillers were released in a free state and then adsorbed onto the surface of particles composed of the host material after aerosolization, XPS and SIMS would reveal disparate concentrations of silicon between the postabrasion released particles and the preabrasion bulk material. According to these authors, a wider application of surface analytical techniques such as SIMS and XPS could reveal more about the conditions under which free nanofiller release is likely and confirm the presence of nanofillers on abraded particle surfaces.

It must be noted that indoor particles are subject to aerosol transport processes such as deposition and therefore released nanoparticles in airborne conditions might eventually deposit. Due to this fact, both airborne and deposited particles are of interest as there might be changes from one status to another and emitted nanoparticles might be in either both. Bearing this fact in mind, preliminary testing studies must evaluate the time needed so that most particles are deposited following a mechanical degradation process and particle levels decrease to the pre-experiment levels. Only after this time should deposited particles be collected.

It is also relevant to encompass the measuring time of the instrumentation used with the testing time during which particles are emitted. The SMPS classifies sequentially the different electrical mobilities of the particles in a DMA and determines their number concentrations with a condensation particle counter. The SMPS thus relies on stable concentrations and size distributions for the full length of the measurement (7 min in the case of Cranfield University).



3.8. Correlate the emission or release taking place with the actual simulation process under assessment

In the case of the drilling approach the amount of particles emitted or ENMs released can be correlated with the volume of material removed by the drill (material removal rate). The same can be applied to other physical processes such as abrasion.

There is, however, one relevant consideration that is to be made at this regard, the mechanical degradation of the sample -if the sample is of plastic nature- can generate heat that would melt the material thus decreasing the number of particles emitted. As an alternative to reduce the heat generated in the mechanical degradation process, wet machining (with a cooling effect) has been evaluated in several studies. Not surprisingly, abrasion during wet conditions often results in a significant reduction in the number of aerosolized particles, although perhaps not in the total amount of material released (in the evaluated literature studies, the liquid were not assessed for particle content).

For samples exposed to environmental degradation, emissions/release can be expressed per area of sample that has been in contact with the environmental stressors (light, water...).



3.9. Collection step

Because particles and objects released by machining of nano-composites are potentially of nanoscale it is necessary to use collection equipment that is suited for presenting such objects to the analysing equipment without change of the relevant characteristics. This can be achieved by sampling “cassettes” that contain membranes for stripping solid aerosol objects from an airstream that passes through the membrane, by diffusion cells that collect ultra-fine particles on open mesh structures (PWRAS), by inertial impactors that deposit particles dynamically onto solid target surfaces (ELPI, PWRAS) as well as by thermophoretic (TP) or electrostatic precipitators (ESP, NAS) that achieve the same using thermal gradients or electrostatic attraction, respectively. Large particles can be collected by simply letting them fall into a particle storage container under the influence of gravity (Schutz & Morris, 2013).

Ideally, if emissions and/or released particles are to be evaluated from the ecotoxicological perspective the storage time should be minimal, since samples might undergo changes during storage. ENMs enclosed in particles of a composite matrix are largely isolated from the surroundings, at least temporarily. This has the consequence that they are not equally biologically available and more persistent. It can generally be said that such chemicals have lower bioavailability and consequently a reduced acute toxic effect. Bioavailability may, however, change if surrounding environmental factors affect the material particle so that it erodes, corrodes or is dissolved. The smaller the particles are, the more rapid the ENM can escape from the particle matrix because the surface to area ratio increases.

The preferred scenario would be to conduct any assessment directly with the released particles; be it *in vitro* or *in vivo* testing. This would allow preventing particle losses in the collection stage as well as particle changes undergone during storage periods, depending on the nature of the emitted particles. The particle deposition rate in the air-liquid interface is a relevant parameter if the present approach is considered.



3.10. Protect personnel carrying out the research

Though the present tip has been placed as the last one, it is possibly the most relevant one. In absence of conclusive data related to the (eco)toxicological potential of ENMs, even less of hybrid materials released during the life cycle of NEPs, personnel working on nano-release needs to be protected. In this sense, EC Guidelines for worker protection are recommended:

- Working Safely with Manufactured Nanomaterials – Guidance for Workers (November 2014)
- Guidance on the protection of the health and safety of workers from the potential risks related to nanomaterials at work – Guidance for employers and health and safety practitioners (June 2013)

In addition to evaluating the release and emissions associated to NEPs, such information should be made available to the public and regulatory bodies.



4. Outlook and steps to standardisation

Having established the main principles for nano-release assessment, the next step and basic consideration with standardization purposes would be to conduct **inter-laboratory assays** that would allow comparing the consistency, repeatability and accuracy of the experiments performed. This is the most immediate need to start a standardization process.

Finally, if a research study finds that the degradation (be it physical or chemical) of a ENM/polymer composite releases ENMs, ENM fragments, or ENM/matrix aggregates, an immediate question that arises is whether the released particles pose a real risk to human health or the environment. Such a question can only be answered by assessing the toxicological or ecological impact of ENMs with the exact form and concentration of the ENMs found to be released during the exposure assessment. The present approach is currently being considered in many European projects undertaking a “life cycle” approach in the conception of NEPs, however, there are a number of challenges yet to be overcome so that results obtained can be considered conclusive.

Relevant standards in the area of Nanotechnology are published by standardization committees and EU Projects addressing nanosafety (nanoREG, amongst other). Amongst other, the reader is referred to ISO/TC 229 to access the latest publications at this regard.



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