INVASSAT

Institut Valencià de
Seguretat i Salut en el Treball

Plan de formación 2014

Jornada técnica

Proyectos LIFE. Riesgos con nanomateriales

Ponencia

Nuevas soluciones para la evaluación de los riesgos de los nanomateriales sectores tradicionales. Proyecto LIFE SIRENA

Ponente

María Blazquez

Burjassot, 4 de diciembre de 2014

GENERALITAT VALENCIANA

CONSELLERIA D'ECONOMIA, INDÚSTRIA, TURISME I OCUPACIÓ

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

LIFE11 ENV/ES/596

www.life-sirena.com

Contents of presentation

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4-DEVELOPMENT OF ENVIRONMENTAL EXPOSURE SCENARIOS

General Information (I)

- **Project location:** Basque Country // UK
- **Project start date:** 01/01/2013
- **Project duration:** 36 Months
- **Project budget:** 1.122.942 €
- **EC LIFE+ Programme contribution:** 560.235 €

General Information (II)

- Coordinating Beneficiary — Inkoa
- Associated Beneficiaries

Cranfield UNIVERSITY — tecnalia Inspiring Business — ROBERT GORDON UNIVERSITY • ABERDEEN

Background (I)

What is a COMPOSITE?

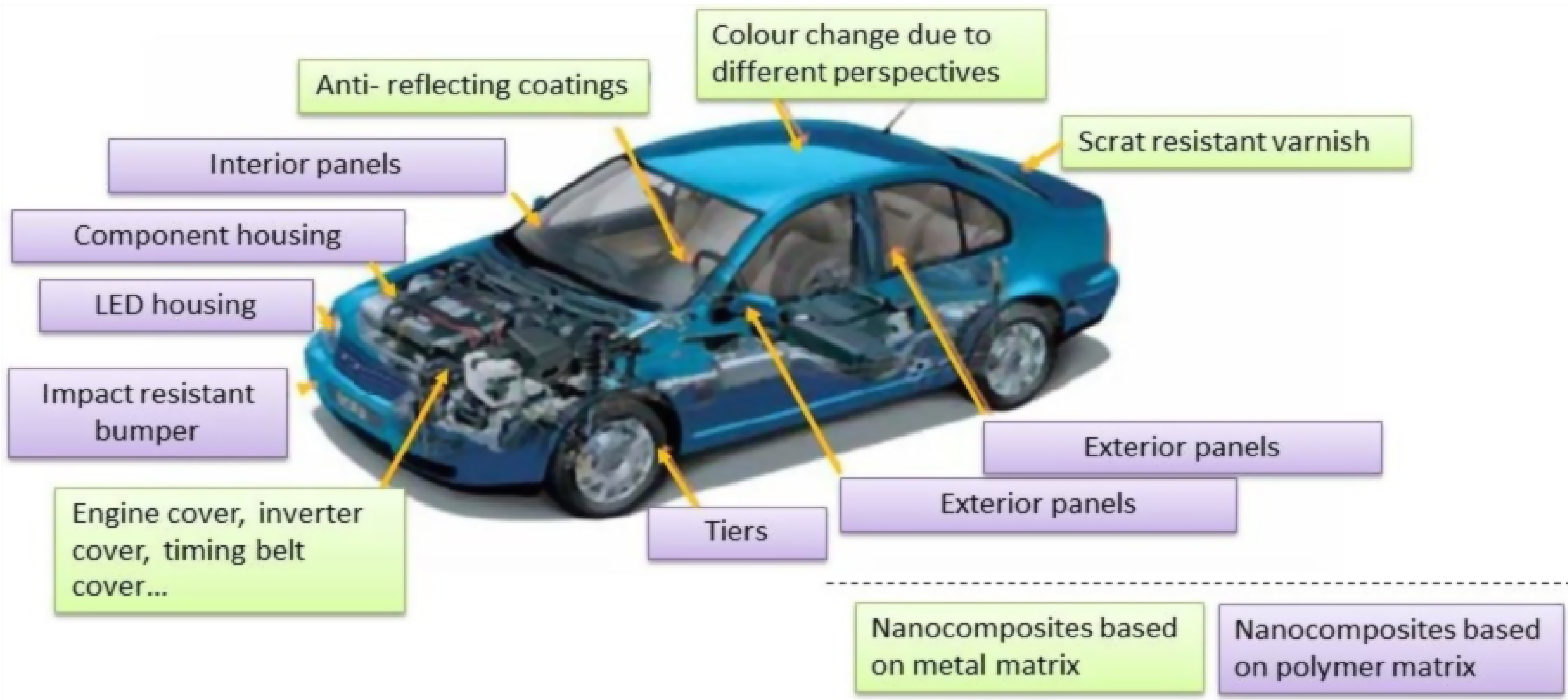
Combination of two or more different materials mixed in an effort to blend the best properties of both

What is a NANOCOMPOSITE (NC)?

Composite material in which one of the components has at least one dimension that is nanoscopic in size[1]

Where can we find them?

NOTE 1: Reference: Society of Plastics Engineers - http://www.4spe.org/plastics-encyclopedia/nanocomposites



"Cada una de las facetas de nuestra vida cotidiana va a quedar alterada en una o dos décadas, por los desarrollos provenientes de la nanotecnología" (SERENA DOMINGO, PEDRO A.) [Madrid I+D; 01/12/2014]

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Background (II)

- Use of NCs in more applications and products will inevitably also result in their introduction into ecosystems.

- Risks of an unintended release of ENMS from these products along their LC?

- Need of ***standardized*** methods for estimating the release of NMs to the environment (permarketing).

Background (III)

- Industry must **evaluate and quantify the risk** of embedded nanoparticles release throughout the life cycle

- Necessary **adaptations of existing regulation** in relation to chemicals and environmental protection for nanomaterials.

- Maximum benefits of Nanotechnology while minimized risks.

Background (IV)

Beyond NEPHH…

NEPHH FP7 founded Project has demonstrated that physical processing at manufacturing, use and recycling phases actually conveys NPs release from nanocomposites that need to be evaluated in relation to their (eco)toxicological potential[2,3,4].

NOTE 2: *S. Sachse, F. Silvia, A. Irfan, H. Zhu, K. Pielichowski, O. Kuzmenko, O. Kazmina, V. Ermini, M. Blázquez, J. Njuguna Physical characteristics of nanoparticles emitted during drilling of silica based polyamide 6 nanocomposites, IOP Conf. Ser.: Materials Science and Engineering 40 012012 doi:10.1088/1757-899X/40/1/012012*

NOTE 3: *S. Sachse, F. Silvia, A. Irfan, H. Zhu, K. Pielichowski, O. Kuzmenko, O. Kazmina, V. Ermini, M. Blázquez, J. Njuguna "The effect of nanoclay on dust generation during drilling process of polyamide 6 nanocomposites", Journal of Nanomaterials, 2012.*

NOTE 4: *S. Sachse, A. Irfan, H. Zhu, J. Njuguna, "Morphology studies of nanodust generated from polyurethane/nanoclay nanofoams following mechanical fracture" Journal of Nanostructured Polymers and Nanocomposites, 2011; 7;5-9*

nephh

Background (V)

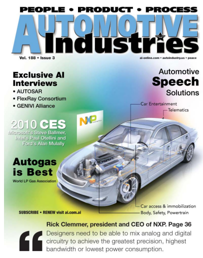
Beyond NEPHH...

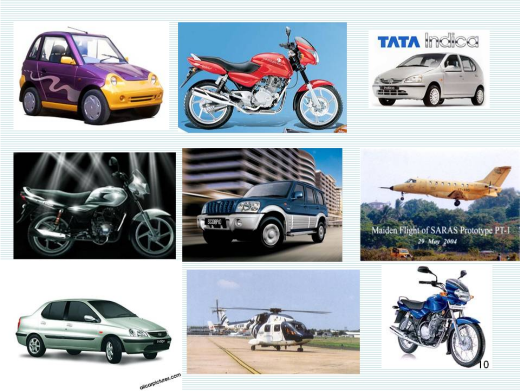
NEPHH's Approach	SIRENA's Approach
Composites VS Nanocomposites LAB Scale	Materials in PRE-MARKET stage
Non reinforced plastic as baseline for comparison	Composites with traditional fillers (mixed combinations) as baseline for comparison
Composition and life cycle processes non related to functionality	EES and composition especifically evaluated for typical applications and industrial sectors of interest

For a given comparison, materials with the same or similar functionalities should be assessed!

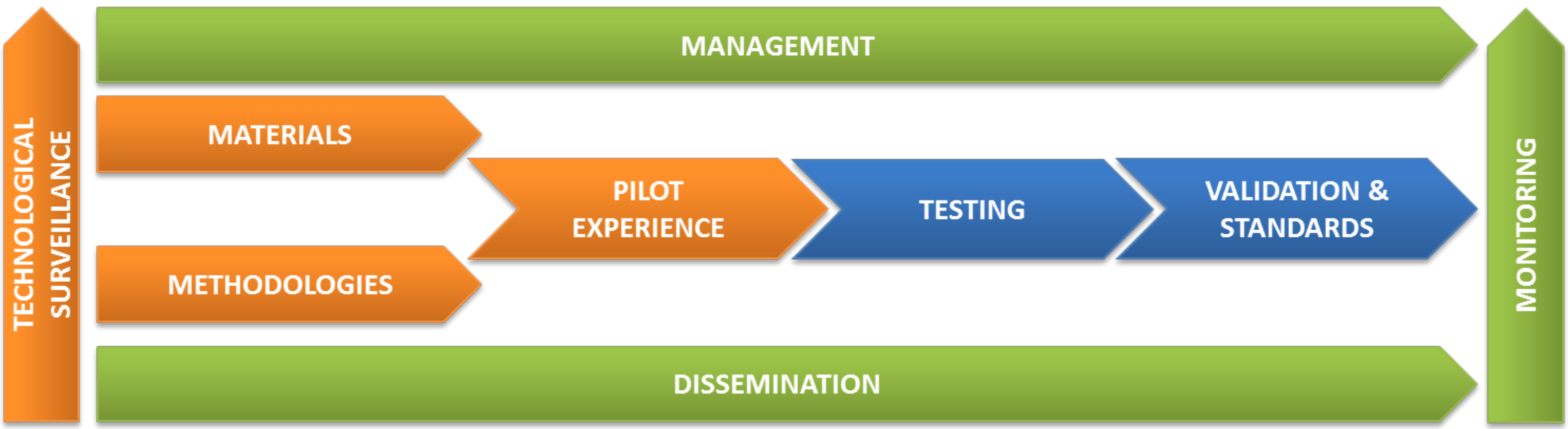
Main Target

SIRENA's main objective 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 three industrial sectors in order to get the necessary information for the exposure assessment





Project Actions



Expected Results (I)

- A searchable **database** including outcomes from the TSS
- **Sample specimens** of different industrial sectors
- A STOA report in relation to the methods to simulate the release of NMs from consumer products in different LC stages. Best practices manuals.
- Evaluation of **EE** of applications selected for testing.

Expected Results (II)

- Set of physicochemically characterized NMs from release simulation processes for safety evaluation

- Validated **methodologies and best practice guidelines for EES Replication** in different stages of the LC

- **Exposure data** to support risk-management decision-making and regulations development to protect human health and environment.

- List of suggested actions to be implemented at a **regulatory level** for environmental protection.

"STATE OF THE ART IN NANORELEASE ASSESSMENT FOR POLYMER NANOCOMPOSITES"

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TECHNOLOGICAL SURVEILLANCE

A technological surveillance system has been designed, established and managed by TECNALIA in collaboration with INKOA in order to identify the state of the art and all the innovations related to the issues of interest.

EXPECTED MAJOR OUTCOMES:

- Feeding the tasks where updated information is essential. Contribution to related deliverables.

- A searchable database of all the documents

- A document evaluating the most relevant outcomes occurred in the implementation of the project

TECHNOLOGICAL SURVEILLANCE (TS)

On line registration to access the database including the outcomes of the TS.- Periodic updates (every 3M)

Nanomaterials release simulation technologies. Physico-chemical characterization of generated samples in the release and associated (eco)toxicological profile Methods to quantify the release	Protocols and methodologies used by the different research groups in order to simulate the release to the environment of Engineered Nanomaterials from solid polymeric matrixes throughout an item´s lifecycle are listed under this topic. All the information related to the physical, chemical and (eco)toxicological characterization and quantification of particles released to the environment in these simulated processes is compiled under this topic. The simulation processes of release of particles from drug therapy applications and from composite debris from medical devices are out of the scope of present topic.	95

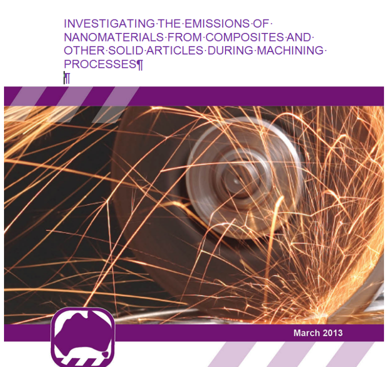
EVOLUTION - NUMBER OF ITEMS RELATED TO THE RELEASE SIMULATION TECHNOLOGIES

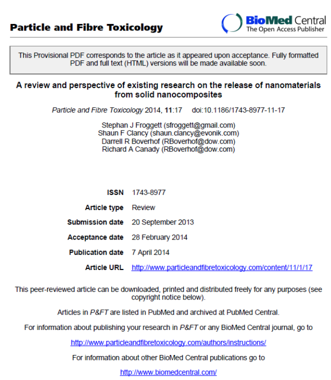
NUMBER OF ITEMS

M0	M1	M1-M3	M4-M8	M12	M13-M15	M16-M18	M19-M21
4	32	37	45	64	78	86	95

"ITEM" means:

- Research articles (original or review)
- Thesis
- Contributions to congresses (abstracts, presentations, extended papers)




Particle and Fibre Toxicology

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This Provisional PDF corresponds to the article as it appeared upon acceptance. Fully formatted PDF and full text (HTML) versions will be made available soon.

A review and perspective of existing research on the release of nanomaterials from solid nanocomposites

Particle and Fibre Toxicology 2014, 11:17 doi:10.1186/1743-8977-11-17

Stephan J Froggett (sfroggett@gmail.com)
Shaun F Clancy (shaun.clancy@evonik.com)
Darrell R Boverhof (RBoverhof@dow.com)
Richard A Canady (RBoverhof@dow.com)

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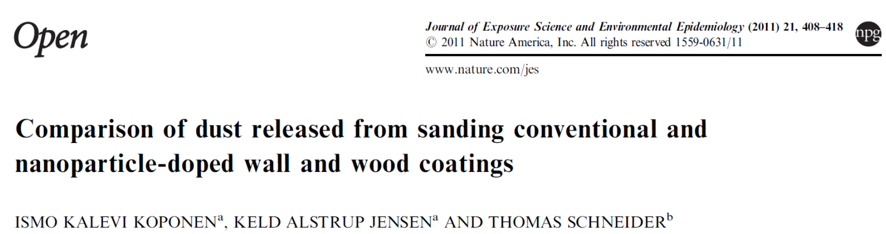

Open

Journal of Exposure Science and Environmental Epidemiology (2011) 21, 408–418
© 2011 Nature America, Inc. All rights reserved 1559-0631/11
www.nature.com/jes

Comparison of dust released from sanding conventional and nanoparticle-doped wall and wood coatings

ISMO KALEVI KOPONEN[a], KELD ALSTRUP JENSEN[a] AND THOMAS SCHNEIDER[b]

SELECTION CRITERIA

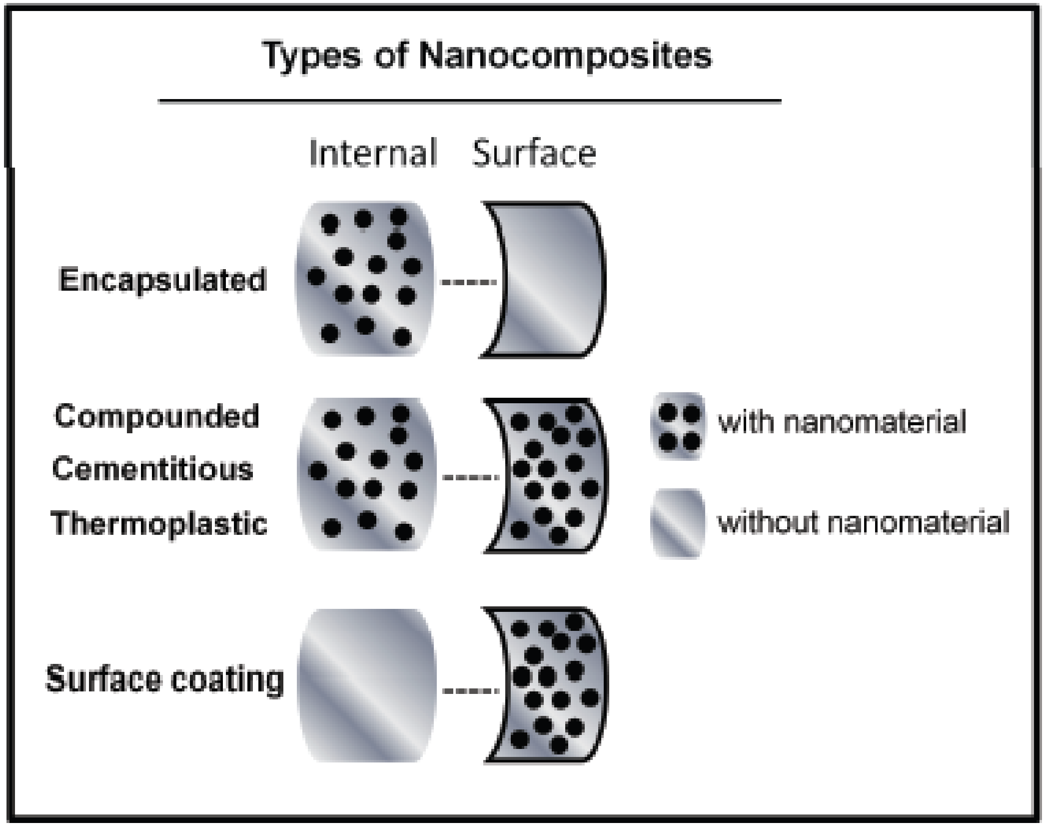
Protocols and methodologies *used by the different research groups in order to* ***simulate*** *the release to the environment of ENMs from* ***solid polymeric matrixes*** *throughout an item´s lifecycle will be compiled in this topic.*

All the information related to the physical, chemical and toxicological characterization and quantification of particles released to the environment in these simulated processes will also be compiled under this topic.

The simulation processes of release of particles from **drug therapy applications** and from composite debris from medical devices are not covered. Migration studies **from food composites** are not covered.

Probabilistic methods and kinetic modelling are not covered.

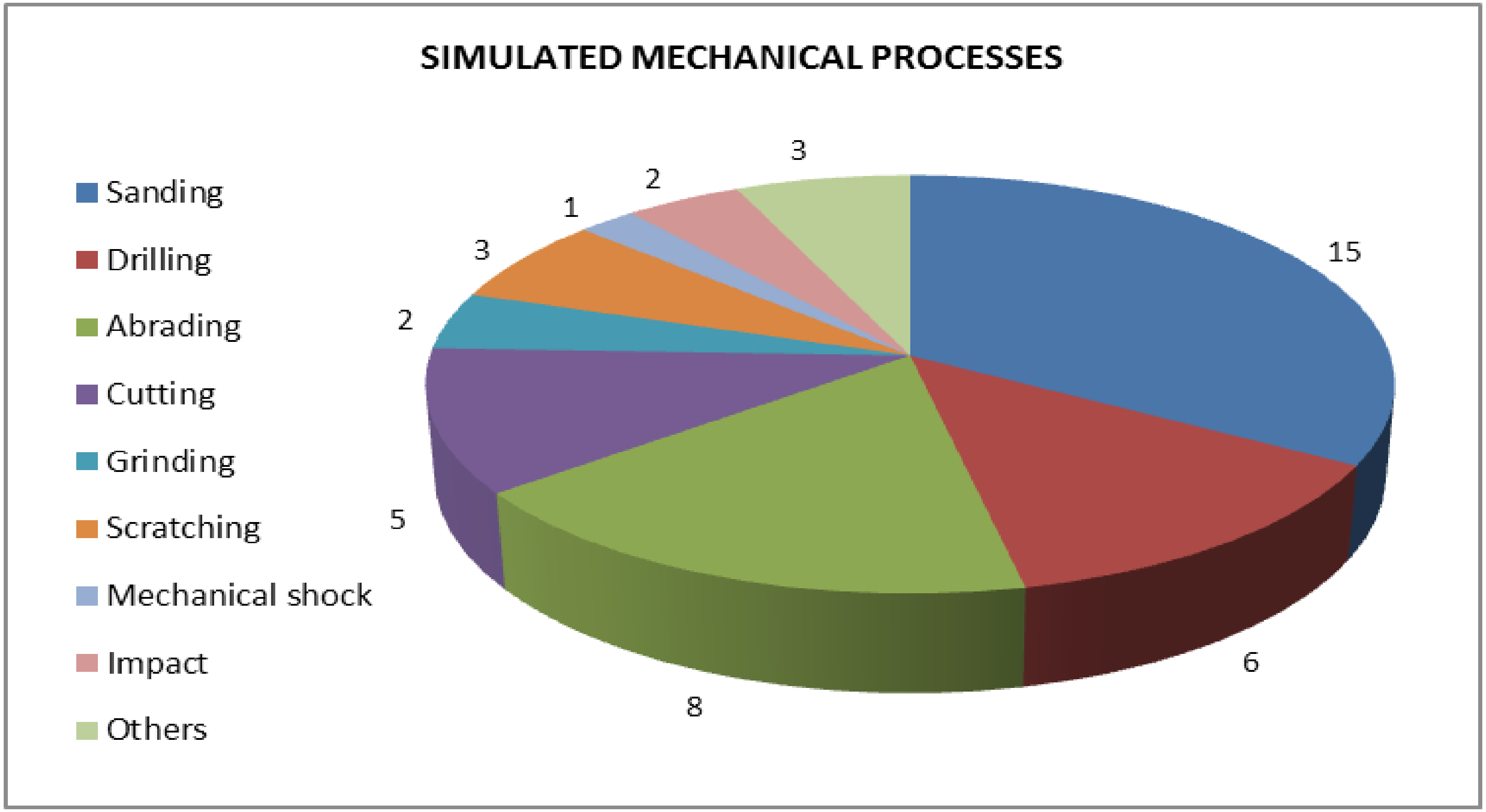
Information about **real processes or in situ measurements** that may cause environmental release (caused by intentional or incidental mechanisms) of ENMs from solid polymeric matrixes through an item´s lifecycle is covered by TOPIC 2.



Simulated proceses degrading nanocomposites in all possible configurations are targeted (surface coatings are, therefore, included)

Process: MECHANICAL DRILLING	Physical characteristics of nanoparticles emitted during drilling of silica based polyamide 6 nanocomposites. Sachse S. et al. doi: 10.1088/1757-899X/40/1/012012 (23)
Reference sample	Unreinforced PA6 pannels (Polyamide 6:Tarnamid T30, Azoty Tarnow, Poland)
Nanoadditivated test specimens	5 wt% Nanosilica fibers: Montmorillonite layered nanosilicates (Laviosa/Dellite 43B) Nanosilica (Degussa /Aerosil 200) Macrosilica fibers: Foam glass crsytal materials (Produced by Toms Polytechnic Unversity) Glass fibres Taiwan glass industry Co./473H)
Sample characterization prior ENMs release simulation	No data
Approach used for laboratory scale ENMs release simulation	Composite panels were fixed in a chamber and an angle drill (Makita BDA 351Z 18V LXT Angle Drill) was used with a maximum speed of 1800 mi-1 adapted with a conventional drill bit of 10 mm diameter. Prior to measurements, the chamber was purged with laboratory air for about 20 min. Each sampling cycle comprised a 60 min background monitoring in the chamber, 14 min of active drilling and a 60 min postdrilling period.
Approach used for the recovery of released ENMs	Particle emissions were measured using a Condensation Particle Counter "CPC" 5.403 with Classifier "Vienna" DMA 5.5-U (SMPS+C, Grimm Aerosol. To support the results obrtained by SMPS+CPC particles were sampled via an electrostatic precipitator and subjected to JFEI XL30 field emission scanning electron microscope.
Relevant outcomes in terms of release and associated exposure	In general, nano and ultrafine airborne particles were emitted from all materials, even the non reinforced polymer. However, emission increased by 56 times for the nanosilica filler and between 20-45 times for the glass fiber and foam-glass crystal filler. Integration of nanoclay into the PA6 matrix reduced particle emission during drilling by 1.5 times. However, the characterization of deposited particles showed exactly the opposite particle behavior, as with decreasing airborne particle concentration the deposit particle concentration increased and vice verse.

NANO-RELEASE LABORATORY SCALED SIMULATIONS



32 References (45 Scenarios)

PRELIMINARY CONCLUSIONS

- In general, laboratory scaled materials are assessed: what about industrial materials or consumer –nanocomposite- products integrating ENMs?

- The real potential of the laboratory scaled materials to replace traditional formulations (data related to increased performance) is generally not assessed.

- The absence of standard operating protocols to be used for scenarios simulation makes inter-assays comparison highly challenging (in some cases not even reference samples have been used).

- The instrumentation used is highly variable.

- Two major critical steps can be observed; the development of an **appropriate set-up** for nano-release assessment (confinement, clean air supply…) AND the **collection step** in which released nano-objects are characterized.

INTRODUCTION TO THE TEST CHAMBER PROTOTYPE BY CRANFIELD UNIVERSITY FOR EXPOSURE ASSESSMENT TO NPS EMITTED BY MECHANICAL DEGRADATION PROCESSES

MAIN FEATURES OF DEVELOPED CHAMBER

Precise control of mechanical degradation parameters:

- CNC Machine & Software assuring the control of the parameters related to the mechanical degradation of samples by drilling processes: spindle seep, feed rate.
- Isolated engine to avoid background contamination (water cooled spindle drill).

Precise control of the conditions inside the chamber:

- Negative pressure
- Air recirculating system (Fan)
- HEPA 14 Filter

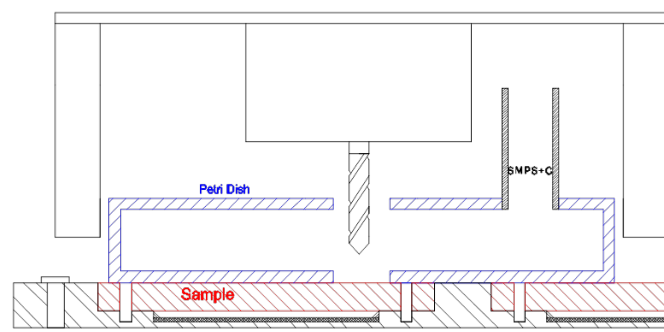
MAIN FEATURES OF DEVELOPED CHAMBER

Precise system for the assessment and collection of generated particles in the mechanical degradation process:

- Scan Mobility Particle Sizer with Particle Counter (SMPS+C) for generated airborne particles measurements. ElectroStatic Precipitator (ESP)

- Newly developed system for the one-single step collection of deposited samples.

MAIN FEATURES OF DEVELOPED CHAMBER



MAIN FEATURES OF DEVELOPED CHAMBER

CONFIGURATION 1

Air from outside is blown into the chamber going through the HEPA filter to clean it and recirculated. Thus, only clean air is getting into the chamber.

Positive pressure inside the chamber [avoiding "dirty" air to get into the chamber].

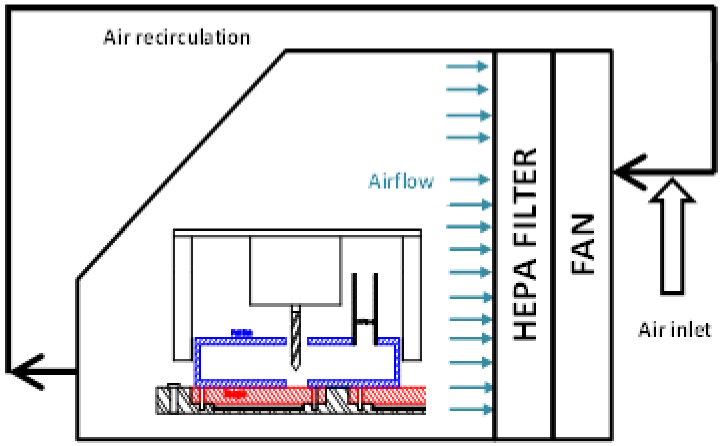
Average Particle concentration: **150-300 cm^{-3}**

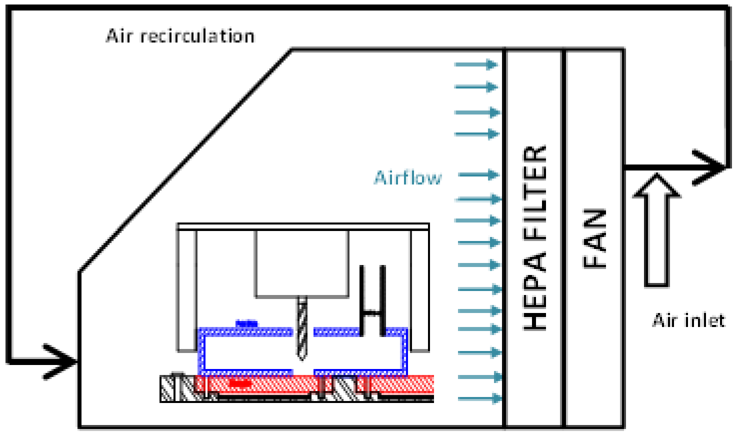
CONFIGURATION 2

The fan takes the air out of the chamber through a HEPA filter and recirculates it again inside the chamber.

A negative pressure iinside the chamber. In case of leakage, the air will get into the chamber with no possibility of particles going out.

Average Particle concentration: **600-1000 cm^{-3}**





a)

b)

MAIN FEATURES OF DEVELOPED CHAMBER

ENVIRONMENTAL EXPOSURE SCENARIOS

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POLYMERS AND REACH

All polymers are **exempt from registration and evaluation under REACH**. However, any manufacturer or importer of a polymer might need to submit a registration to the European Chemicals Agency (ECHA) for the **monomer** substance (s) or any other substance (s), that have not already been registered by an actor up the supply chain.

In this sense, **only additives used to preserve the stability of the polymer and impurities** are regarded as one part of the polymer and **do not need to be registered separately** under REACH.

If **other additives** have been added to **improve the performance of the polymer** (for example, flame retardant), those additives shall be registered separately if:

- **the concentration of such additives are above 2% w/w and**
- **the annual quantity of such additives are above 1 tonne per year**

(both conditions must be met).

Polymers

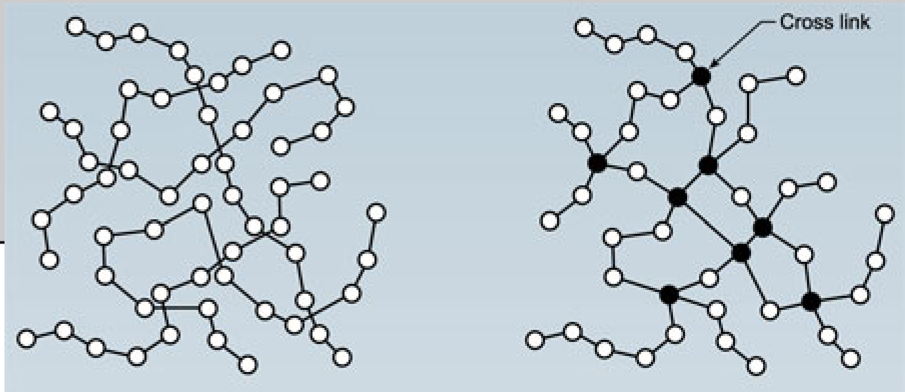
Virgin products of the chemical/petrochemical industry that have undergone no significant post-reactor treatments. This group includes those polymers which may have been modified within the reactor as part of a subsequent chemical process.

Thermoplastic polymers

Melted or softened in order to be formed under pressure into the required shape which is established on cooling the product. The process is reversible and the plastics materials can be reshaped and reused.

Thermosetting resins

Are converted into finished products with the application of heat and pressure. Chemical cross-linking takes place and the process is not reversible. The materials cannot readily be recovered and reused.



(a) Thermoplastic (b) Thermoset

+ADDITIVES

Plastics Materials

Polymers which have been modified in some way, such as the addition of additives and processing under pressure and/or heat. They are then ready to be converted into plastics artifacts.

Masterbatches

Compounds which are made up to contain high concentrations of specific additives. These are then supplied to processors who disperse them into the main polymer matrix by simple mixing. There is a growing trend towards the use of masterbatches, especially where the additive requires careful handling for reasons of cleanliness or health.

Type	Short Description
Fillers (Mineral Loading)	Inert materials which reduce polymer costs, improve processability and can be used to improve the mechanical properties of the resulting plastics material. They are SOLIDS, which are incorporated into polymers but which remain as a separate phase. In general terms fillers are either powders or fibres.
Plasticisers	Liquids or waxy (low melting) solids which fall into two general classes: Permanent plasticisers (with low propensity to migration); Latent plasticisers (removed during post-fabrication oven drying).
Antioxidants	Chemicals such as amines, phenols, phosphates… To inhibit degradation of polymers such as polyethylenes, polypropylenes and styrenic materials during the life of the product.
Coupling agents	Silane and titanate compounds are used to improve the bond between polymer matrices and mineral fillers and fibre reinforcements.
Colourants	A wide range of dyes and pigments are used throughout the industry.
UV & other weathering stabilisers	Generally these are benzo derivatives. However, polymers with good weathering properties such as PVC are sometimes blended into other polymers. They are mainly incorporated into plastics for applications requiring long life, such as building products, automotive and other engineering components. As in the case of permanent plasticisers, the stabilisers are required to function throughout the life of the product.
Polymeric impact modifiers	These are often elastomers or elastomer/polymer blends, used to retard or inhibit brittle fracture by absorbing the crack-initiating energy. By definition, the elastomers and the matrix polymers may not be fully compatible.
Anti-static agents	The purpose of these substances is to inhibit the development of static. In general, these are conductive powders and metal flakes but intrinsically conductive polymers may also be used in certain circumstances.
Flame retardants	Key application areas include packaging, the electrical and the electronic industries. Compounds based on halogens, boron and phosphorous are used to reduce the risk of ignition and retard combustion.
Preservatives	Fungicides and bacteriostatics are occasionally used in plastics which may be expected to be exposed in service for long durations.

ENMs added to composites and functioning as all types of additives described earlier have been identified.

Final Report: Nanocomposite Anchored Plasticizers

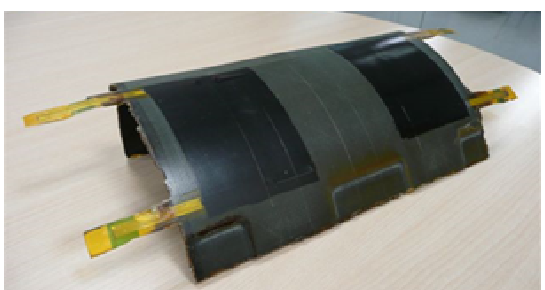
EPA Contract Number: 68D02060
Title: Nanocomposite Anchored Plasticizers
Investigators: Myers, Andrew
Small Business: TDA Research Inc.
EPA Contact: Manager, SBIR Program
Phase: II
Project Period: June 1, 2002 through June 1, 2004
Project Amount: $225,000
RFA: Small Business Innovation Research (SBIR) - Phase II (2002)
Research Category: Nanotechnology , Air Quality and Air Toxics , SBIR - Pollution Prevention , Pollution Prevention/Sustainable Development , SBIR - Air Pollution

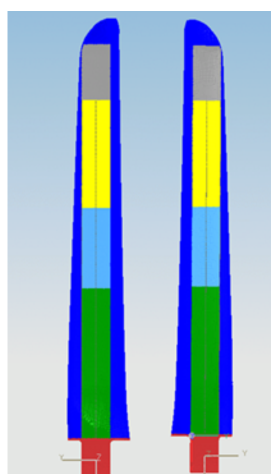
Nano-Silica (Epoxy Resin Only) (VK-SP30S)

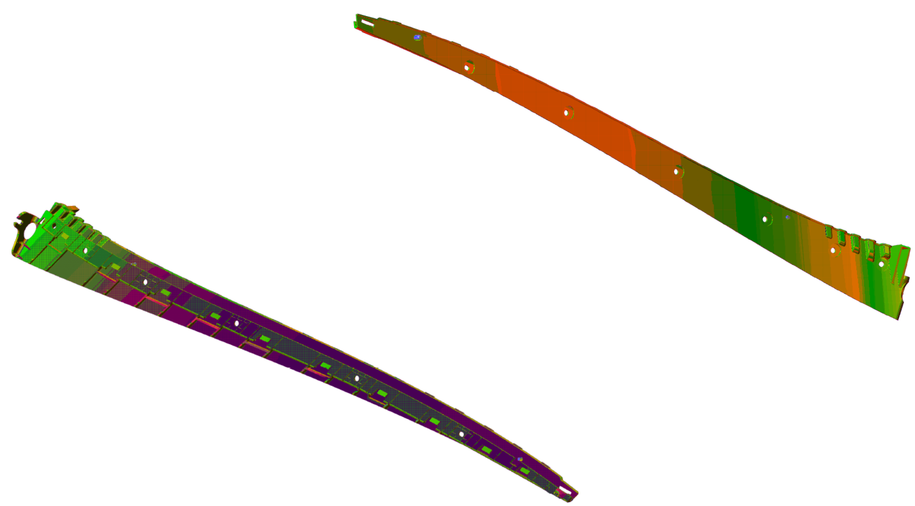
HS Code:	2811220000
Production Capacity:	50mt/Month
Model NO.:	VK-SP30S
Export Markets:	North America, South America, Eastern Europe, Southeast Asia, Mid East, Western Europe
Model NO.:	VK-SP30S
Export Markets:	North America, South America, Eastern Europe, Southeast Asia, Mid East, Western Europe
HS Code:	2811220000
Production Capacity:	50mt/Month

APPLICATIONS SELECTED

SECTOR	MATERIAL	APPLICATION
	Polyester combined with metallic NPs to increase mechanical performance	Wind turbine blade
	Epoxy resin combined with carbonaceous NMs for an increase of the electrical conductivity (CNT; CNFs)	Leading edge of the wing of an airplane
	Polypropylene combined with nanoclays in order to achieve the same properties with a reduced weight	Drip cap







LIFE CYCLE STAGES OF RELEVANCE FOR SIRENA

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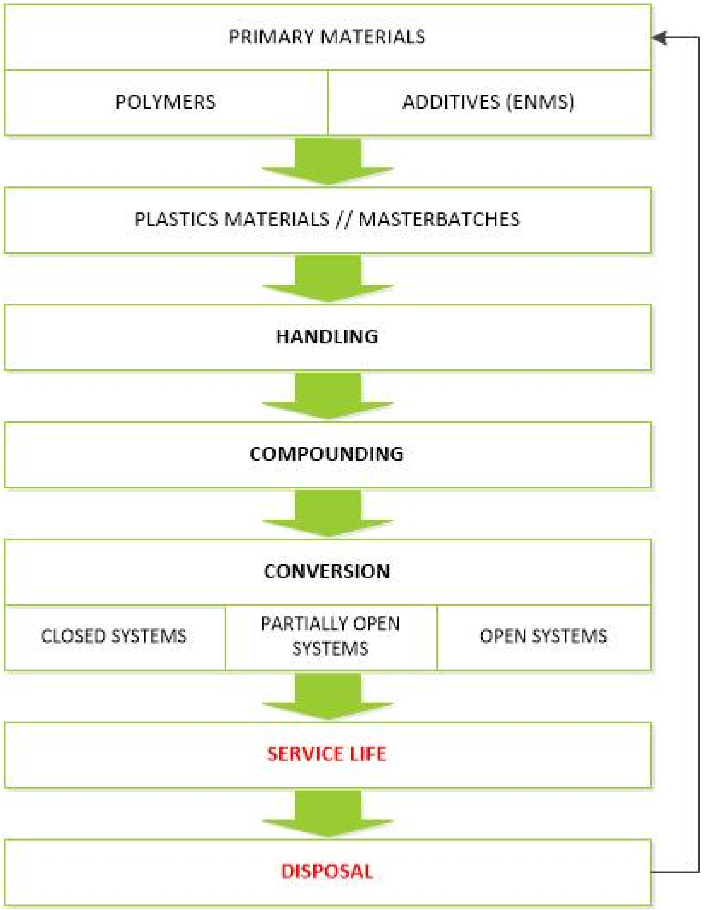

SIRENA

ESTIMATION OF THE EXPOSURE FROM ARTICLES

Release into the environment (air, water, soil and indirectly, sediment) is calculated from the emission rate, the weight of the article(s) and the service life of the article.

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ESTIMATION OF THE EXPOSURE FROM ARTICLES

$Rtot_{comp} = F\ service\ life_{comp} \times Atot \times Fc_{article} \times T_{SL\_article}$

.

Parameter

ESTIMATION OF THE EXPOSURE FROM ARTICLES

For **emission factor** calculation:

1- Compare with similar articles described in ESD's or other sources;

OECD ESD on Plastics Additives (ENV/JM/MONO(2004)8/REV1, reviewed on 09/07/2009.

.

According to the experience of TECNALIA; all of the ENMs used for the manufacturing of the applications of relevance for SIRENA are to be classified as FILLERS

2- Search for data in the literature;

Fadri Gottschalk; Bernd Nowack and Bernd Gawlik (December 2010 - NANEX) reported that empirical (experimental / analytical) release information for the main release sources during the ENM life stages is needed-

3- Use a worst-case assumption or if necessary perform an emission study, leaching study, etc.

ESTIMATION OF THE EXPOSURE FROM ARTICLES

For **emission factor** calculation:

ENMs used in test samples have been assimilated to FILLERS.

.	OECD ESD	Literature (NANEX)	Worst-case assumption (100% release)	SIRENA
Use	Fservice life, water = 0.01% over the service life of the plastic Fservice life, air = 0%	NA	100% Release	*To be provided by the 30th December 2015*
EOL	Fdisposal, air = Fdisposal, water = 0 both for incineration and landfill scenarios	NA	100% Release	*To be provided by the 30th December 2015*

OECD

LIMITATIONS

Production volumes [Atot]:

The OECD estimates the UK consumption of polymers from 1994 together with breakdown by conversion processes (in the ESD for Plastic Additives). NO UPDATED FIGURES AVAILABLE.

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The reliability of the polymers production data is further compromised since, in accordance to the **competence law**, if there are not at least three manufacturers of the same polymer in one country, the manufacturer is not obliged to declare the manufactured quantities.

Not all composites are nanocomposites.

How to determine how many of these nanocomposites are specifically used for the production of selected applications?

Thank you all!

Inkoa
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INKOA SISTEMAS, S.L.
Idoia Unzueta (idoia@inkoa.com)
María Blázquez (maria@inkoa.com)

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Plan de formación 2014
Proyectos LIFE. Riesgos con nanomateriales

Presentaciones de las ponencias

1- Implicación de la Administración Valenciana

2- La nanotecnología en la industria. Tipos y aplicaciones principales de los nanomateriales

3- Impacto de la nanotecnología en la salud laboral

4- Metodologías de evaluación de la exposición y valores límites

5- Equipos de protección respiratoria: selección y estudios de eficacia

6- Estado de situación de la normalización internacional en material de EPIs frente a nanopartículas

7- Metodologías de evaluación del riesgo de nanomateriales

8- Nuevas herramientas para la evaluación del riesgo de los nanomateriales: REACHnano Toolkit

9- Nuevas soluciones para la evaluación de los riesgos de los nanomateriales sectores tradicionales. Proyecto LIFE SIRENA

10- Gestión y control del riesgo en la industria: caso práctico

11- Iniciativas para la prevención y control del riesgo: LIFE NanoRISK y LIFE REACHnano

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