

LIFE11 ENV/ES/596





IEEdd ENIV//EC/206

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STATE OF THE ART IN NANORELEASE ASSESSMENT FOR POLYMER NANOCOMPOSITES [Abstract REF: 91]*.

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IEE44 ENIV/IEC/EAG

LIFE Overview

➤ The LIFE programme is the EU's funding instrument for the environment. The general objective of LIFE is to contribute to the implementation, updating and development of EU environmental policy and legislation by co-financing pilot or demonstration projects with European added value.

SOURCE: http://ec.europa.eu/environment/life/about/index.htm#life2014







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LIFE Overview

> The programme has three components:

- ✓ LIFE+ Nature and Biodiversity,
- ✓ LIFE+ Environment Policy and Governance, and
- ✓ LIFE+ Information and Communication.







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LIFE Overview

LIFE+ Nature and Biodiversity - It will co-finance best practice or demonstration projects that contribute to the implementation of the Birds and Habitats Directives and the Natura 2000 network. In addition, it will co-finance innovative or demonstration projects that contribute to the implementation of the objectives of Commission Communication (COM (2006) 216 final) on "Halting the loss of biodiversity by 2010 – and beyond".







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LIFE Overview

LIFE+ Environment Policy and Governance- It will co-finance innovative or pilot projects that contribute to the implementation of European environmental policy and the development of innovative policy ideas, technologies, methods and instruments.







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LIFE Overview

LIFE+ Information & Communication- It will co-finance projects relating to communication and awareness raising campaigns on environmental, nature protection or biodiversity conservation issues, as well as projects related to forest fire prevention (awareness raising, special training).





LIFE11 ENV/ES/596





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 €



Inkoa



General Information (II)

Coordinating Beneficiary

Associated Beneficiaries







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 size¹

Where can we find them?

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

















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}.

www.life-sirena.com

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







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







Demonstrative character

2 Ways to physically process samples simulating different LC scenarios: drilling // crashing



The demonstration character of SIRENA relies on the fact that developed methodology can be transferred to additional materials from different origins, not necessarily plastic based, and to additional industrial sectors www.life-sirena.com





Envisaged 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"

First International Workshop of the SIRENA LIFE Project

1 May 2014, Madrid (Spain)





NANOCOMPOSITES: MARKET and TRENDS

- In terms of volume, the global market for nanocomposites is expected to grow at a CAGR (Compound Annual Growth rate) of 17.5% between 2012 and 2018.
- Vehicle safety & need for light-weight materials to improve vehicular performance have been the most important factors driving the market in the past few years.
- An increased consumption of nanocomposites in building & construction and their importance in the field of electronics and semiconductors have been other factors driving the market of late.
- The most commonly used filler materials are **nanoclays**. Glass fibers and metal fibers are also in huge demand and are expected to be major markets in the coming years. Other nanofibers, platelets, carbon nanotubes and graphene are also expected to show healthy growth over the forecast period.





NANORELEASE FROM NANOCOMPOSITES

B Annual Overall Nano-Release Publications & Experiments



Stephan J Froggett, Shaun F Clancy, Darrell R Boverhof and Richard A Canady A review and perspective of existing research on the release of nanomaterials from solid nanocomposites. Particle and Fibre Toxicology 2014, 11:17

We review fifty-four studies that investigate release from solid, non-food, nanocomposites. These early efforts to understand release from nanocomposites, examined a variety of materials and methods under five general scenarios – **machining, weathering, washing, contact** and **incineration**.





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







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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.





EVOLUTION - NUMBER OF ITEMS RELATED TO THE RELEASE SIMULATION TECHNOLOGIES

NUMBER OF ITEMS					
Мо	Мı	M1-M3	M4-M8	M12	M13-M15
4	32	37	45	64	78

"ITEM" means:

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







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)





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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)¶
Comple observatorization prior	Glass-fibres-Taiwan-glass-industry-Co./473H)¤
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. m
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 obtained 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. a





Release Scenario	Measurement Methods	References
Cutting	 Fast Mobility Particle Sizer (FMPS: Model 3091); Aerosol Particle Sizer (APS: Model 3321); Thermophoretic Precipitator (TP); Electrostatic Precipitator (ESP); Condensation Particle Counter (CPC: Model 3007); SEM TEM 	Bello, D., B. Wardle, N. Yamamoto, R. De Villoria, E. Garcia, A. Hart, K. Ahn, M. Ellenbecker and M. Hallock (2009) <i>Exposure to nanoscale</i> <i>particles and fiber during machining</i> <i>of hybrid advanced composites</i> <i>containing carbon nanotubes</i> . Journal of Nanoparticle Research. 11: 231-249.
Abrasion	 Scanning mobility particle scanner (SMPS; model 3934), Condensation particle counter (CPC model 3022) TEM 	Vorbau, M. L. Hillemann and M. Stintz (2009) <i>Method for the</i> <i>characterization of the abrasion</i> <i>induced nanoparticles release into</i> <i>air from surface coatings</i> . Aerosol Science. 40: 209-217.





NANO-RELEASE LABORATORY SCALED SIMULATIONS







32 MECHANICAL SIMULATIONS (Items related to MECHANICAL & MECHANICAL + WEATHERING Simulations)



■ Sanding ■ Drilling ■ Abrading ■ Cutting ■ Grinding ■ Other (Shredding, Impact tests...)

NOTE: 1 single item can simulate multiple scenarios (32 TSS Items VS 44 Mechanical scenarios)





PRELIMINARY CONCLUSIONS – Under development

- 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.





Thank you all!



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