



**Innovative strategies, methods and tools for occupational risks management
of manufactured nanomaterials (MNMs) in the construction industry**

BEST PRACTICE GUIDE FOR RISK PREVENTION IN RELATION WITH MANUFACTURED NANOMATERIALS (MNMs) IN THE CONSTRUCTION SECTOR

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Disclaimer

This document was prepared following extensive consultation with a range of stakeholders (via workshops, meetings, surveys, interviews and document reviews):

- Representatives of the construction sector, including:
 - o European Construction Industry Federation (FIEC);
 - o European Federation of Building and Wood Workers (EFBWW);
 - o OHS Managers from several construction companies.
- Manufacturers of construction products;
- European and Spanish agencies for occupational safety;
- Manufacturers of personal protection equipment;
- Experts in nanosafety;
- Policy makers at European and national (Spain) levels.

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The views expressed herein are solely those of the authors.

Presentation

This Best Practice Guide aims to help Occupational Health and Safety managers assess the potential risks derived from the use of nano-objects, and their aggregates and agglomerates NOAAs (ISO 12901-2) in the construction sector. It provides quick advice on methods, examples and good practices to perform the risk assessment when NOAAs are incorporated in the products or the production processes in the sites.

This guide has been developed inside the SCAFFOLD project (Grant agreement Nº 280535, 2011-2015) which address five specific NOAAs that are the focus of this document: nano-TiO₂, nano-SiO₂, nano-clays, carbon nano-fibers and nano-cellulose. Apart from this guide, three other Best Practice Guides have been developed in the framework of SCAFFOLD, which would complete a set of documents whose main goal is to help the management of risks derived from the use of NOAAs in the construction sector. Additionally, the project has produced a Handbook where the topics of the quick guides are treated more extensively.

Knowledge in this area is emerging as research and experience grows. This guide is an initial step to assist the risk assessment in the sector and its practical application jointly with future inputs from the science would lead to new improvements.

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Introduction

Construction in the European Union is a dynamic sector and the biggest industrial employer (3.1 million enterprises - 95% have less than 20 workers - and 14.9 million jobs). The increasing use of NOAA and nano-enabled products in construction might pose new health and safety risks to workers at different stages of the life cycle in construction. Consequently companies need to address the management of these potential occupational emerging risks.

This guide aims to help Occupational Health and Safety managers assess the potential risks derived from the use of NOAAs in the construction sector. This guide has been developed inside the SCAFFOLD project (Grant agreement Nº 280535, 2011-2015).

It is important to highlight that this guide only addresses the potential risks derived from NOAAs by inhalation and other risks that may be relevant for this sector are not considered.

1. Mapping the construction sector & exposure scenarios to NOAAS

NOAA and nano-enabled products are being considered for various uses in the construction industry and related infrastructure industries, not only for enhancing material properties and functions but also in the context of energy conservation.

So far, only a limited number of nano-products make it to today's construction sites, the main ones are based on silicon and titanium oxides. The key areas of application are in: cement based materials, insulation materials, infrastructure coatings and coatings and paints for wood, glass and other materials as well as for self-cleaning purposes.

In the Scaffold project we have selected five nano-objects: clay nanoparticles, carbon nanofibers, cellulose nanofibers, nano-SiO₂ and nano-TiO₂; each of the above mentioned NOAAs are being studied in one particular application, due to the properties that they give to the matrix in which they are added (see table 1).

Table 1. NOAAs and applications selected in the SCAFFOLD project

NOAA	Application/matrix	Expected benefit
n-SiO ₂	Concrete	Improvement of rheology and mechanical properties
n-TiO ₂	Mortar	Self-cleaning and decontamination
n-TiO ₂	Self-cleaning coating	Self-cleaning and decontamination
Nano-clay	Fire resistance panels	Improvement of creep resistance and thermal stability
Cellulose NFs	Insulations	Improvement of mechanical and thermal properties
Carbon NFs	Coating/paint	Improvement of mechanical, thermal and electrical properties

Cementitious materials such as concrete experience changes in their properties by the incorporation of nano-SiO₂; nano-particles of SiO₂ can fill the spaces between particles of gel of C–S–H, acting as a nano-filler and basically improving the strength and durability of the materials. In contrast to the bulk TiO₂ (>100 nm) that is considered chemically inert, nano-scale TiO₂ can act as a photo-catalyst, and can generate reactive oxygen species upon illumination. A wide range of applications exist, exploiting the various properties of TiO₂ nanomaterials. For instance, in coating paints nano-sized TiO₂ is used as a photocatalyst producing reactive oxygen that may degrade other organics. The addition of TiO₂ to the common mortar implies the improvement of barrier properties of the material. These NOAAs add to the mortar the capacity to maintain the surface of the product clean more time than the common mortar, therefore the maintenance tasks of the product will be reduced during the use of the product. Nanoclays are usually incorporated into polymeric matrixes in order to improve or modify one or more characteristics of the material: improve their mechanical properties, increase their resistance to thermo-oxidative processes, modify their surface properties, increase their crystallinity, improve their creep behavior, reduce the gas permeability, give antibacterial

properties, etc. This nano-filler is industrially used in the automotive and packaging sectors as well as in the construction for the preparation of materials and elements with improved fire resistance, since the clay layers reduce the gas permeation and act as protection to the polymeric matrix. Cellulose fibers are extensively used in paper production, cotton textiles, and as insulation and structural strengtheners in construction products. Finally, carbon nanofibers (CNF) are used in construction, for example, in composite materials to improve strength, stiffness, electrical conductivity, or heat resistance.

Although the use of NOAAs in the construction sector is growing, they have found some barriers; the main ones have been identified:

- the expensiveness of NOAAs compared to traditional solutions,
- the conservative profile of the sector and the lack of awareness about emerging technologies,
- the general uncertainty with respect to health and safety risks **related to NOAAs** and to how to properly manage them in order to protect the workers and be in compliance with the existing OHS legislation.

Workers exposure to NOAA may occur over the life cycle of nano-enabled products: during the nano-objects manufacturing process, in the manufacturing of products containing NOAAs, their application and installation, during their use (e.g. maintenance tasks) and finally in the products end of the life including demolition/disposal and recycling processes. In all these steps, many enterprises from the sector with different profiles are implied.

Exposure predominantly can occur via inhalation, dermal, oral and ocular routes. The major possible portals of NOAAs entry are lung, skin, gastrointestinal tract, nasal cavity and eyes. Exposure through inhalation of dust is the scenarios most likely to pose health risks. Skin penetration may in theory play a role as well, but most studies have shown little to no transdermal absorption through healthy skin. However, the uptake via damaged skin cannot be ruled out. Oral exposure can occur from intentional ingestion and from unintentional hand-to-mouth transfer. Swallowing inhaled particles that are cleared via the mucociliary escalator, and of drainage from the eye socket via the nasal cavity following ocular exposure are less important ways of exposure.

Critical factors affecting exposure to NOAAs include the amount of material being used, the ability of the material to be dispersed (in the case of a powder) or form airborne sprays or droplets (in the case of suspensions), the degree of containment, and duration of use.

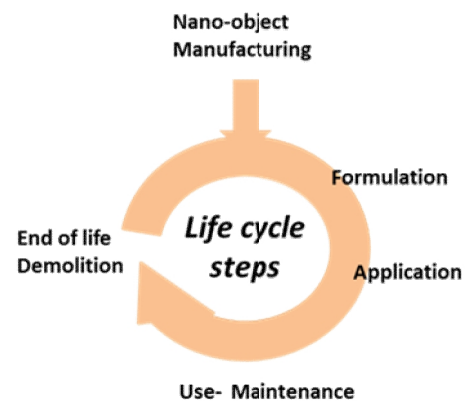


Figure 1. Life cycle steps of nano-enabled products and applications

Jobs and operations that may increase the likelihood of exposure to nanoparticles include for example:

- Generating nanoparticles in the gas phase in non-enclosed systems.
- Handling nanostructured powders.
- Working with nanomaterials in liquid media without adequate protection (e.g., gloves).
- Working with nanomaterials in liquid during pouring or mixing operations or where a high degree of agitation is involved.
- Machining, sanding, drilling, or other mechanical disruptions of materials containing nanoparticles (e.g. during the installation of materials, in demolition/recycling processes).
- Conducting maintenance on equipment and processes used to produce or fabricate nanomaterials, or the clean-up of spills or waste material.
- Cleaning of dust collection systems used to capture nanoparticles.

In Scaffold the occupational exposure to the five selected NOAAs has been measured in scenarios covering the life cycle of the six applications; see next matrix summarizing the scope of the scenarios investigated in the project (**Table 2**).

Life cycle step	Nano-object and application					
	nano-TiO2 depollutant mortar	nano-TiO2 self-cleaning coating	nano-SiO2 self-compacting concrete	nano-Clay/fire retardant panels	carbon nano-fibers coating laminates	nano-cellulose insulations
Nano-object manufacturing	X	X	○			
Manufacturing nano-enabled products and application	X	○	○	○	X	X
Use/maintenance: Machining	X	X	X	○	X	X
Demolition	X	X	X	○	X	X
Accidental fires	X	X	X	X	X	X

Table 2. Scope of the scenarios investigated in SCAFFOLD project.

Note: cells marked with X have been investigated at lab/pilot scale; cells marked with the red circle have been investigated in the case studies.

The results found are encouraging and in general workers performing the tasks measured were not overexposed to NOAAs in the scenarios investigated. Data of occupational exposure were below the limits proposed for the NOAAs by Scaffold (Stockmann-Juvala H. et al, 2014), NIOSH (NIOSH 2011) and the nano-reference values proposed by IFA (IFA, 2014, SER 2012); the limits used are showed later in this document. For that reason, the scenarios in the matrix are showed in green color although some remarks have been marked for some of them.

- (1) Considering the metric of mass concentration (mg/m³), the occupational exposure measured in all scenarios was below proposed limits by NIOSH and SCAFFOLD. As expected, the highest mass concentration measured was found in tasks where nano-objects were handled directly and in significant quantities as for example, during cleaning operations in the nano-TiO₂ manufacturing process or during the spraying of a self-cleaning coating in a wall (marked with (1) in table 2). It is worth mentioning, that although measurements are below the limits, cleaning operations in nanoparticle production are not daily activities and do not involve continuous periods of 8h.
- (2) Considering the metric of particles concentration (particles/cm³), the occupational exposure measured in all scenarios was also below the recommended nano-reference value of 40000 particles/cm³ (IFA, 2014). As expected, common activities in this sector produced a high release of particles. For instance, the highest values measured were during the machining of quite hard materials such as the self-compacting concrete and the laminates filled with CNF marked with (2) in table 2. However two issues should be underlined here. On the one hand, the release of particles is intrinsic to the machining process and in fact, no sticking differences have been found for processes performed with control materials (without NOAAs) and materials filled with NOAAs. On the other hand, the machining processes were performed during short times and, consequently, the concentrations averaged to the 8 h-day did not exceed the OELs; however, other working conditions with longer processes may lead to higher exposures.
- (3) Fire tests performed with the materials from the six applications did not observe the release of the NOAAs added to the materials with the exception of the fire retardant panels where there may be indications of possible release of nano-clays during the combustion of the materials.

Nowadays there are still very few data available on workers exposure to NOAAs in the construction sector. The data achieved in Scaffold contributes to clarify if the use of new nano-enabled products may increase the risk of workers handling these materials. It should be noted that most of the measurements have been taken at pilot scale, so short times and small quantities have been handled. More data from real scenario would help to incorporate in a safe way these new materials in the sector. Finally, it should be underlined that construction work environments are rather complicated, typically handling different activities and chemicals, and where other hygienic risks may be more relevant than exposure to NOAAs.

2. Risk analysis

2.1. Risk

According to the Guidance on risk assessment at work, risk is defined as the likelihood that the potential for harm will be attained under the conditions of use and/or exposure, and the possible extent of the harm.

2.2. Exposure

In the successive steps that involve the use of MNMs in the construction, an exposure to MNMs predominantly can occur via inhalation, dermal, oral and ocular routes. The major possible portals of MNM entry are lung, skin, gastrointestinal tract, nasal cavity and eyes.¹

Exposure through inhalation of dust generated when processing materials (e.g., from cutting, sanding, drilling or machining) or aerosols from paint-spraying are the scenarios most likely to pose health risks.²

Skin penetration may in theory play a role as well, but most studies have shown little to no transdermal absorption. Oral (gastrointestinal) exposure can occur from intentional ingestion, unintentional hand-to-mouth transfer, from inhaled particles (>5 µm) that are cleared via the mucociliary escalator, and of drainage from the eye socket via the nasal cavity following ocular exposure.

Critical factors affecting exposure to MNMs include the amount of material being used, the ability of the material to be dispersed (in the case of a powder) or form airborne sprays or droplets (in the case of suspensions), the degree of containment, and duration of use.

In the case of airborne material, the particle or droplet size and its aerodynamic behaviour will determine the deposition of material. Respirable particles may deposit in the alveolar (gas exchange) region of the lungs, which includes particles smaller than ca. 10 µm in diameter. Approximately 30%–90% of inhaled nanoparticles are likely to deposit in any region of the human respiratory tract depending on, e.g., breathing rate and particle size. Even 50% of nanoparticles in the 10–100 nm size range may deposit in the alveolar region, while nanoparticles smaller than 10 nm are more likely to deposit in the head and thoracic regions.³

¹Yokel and Mac Phail 2011

²van Broekhuizen and van Broekhuizen 2009

³NIOSH 2009

Table 3. Predominant exposure routes and portals

Route	Portal	Exposure
Inhalation	Lungs, nasal cavity	Inhalation of dust formed during handling and processing of NP-containing materials or e.g., aerosols from paint-spraying
Dermal	Skin	Exposure likely, but little to no transdermal absorption
Oral	Gastrointestinal tract	Intentional ingestion, unintentional hand-to-mouth transfer
Ocular	Eyes	Drainage from the eye via the nasal cavity following ocular exposure

It is important to underline that, according to the research carried out within the SCAFFOLD project based on scientific and informative literature review as well as by means of successive surveys, **the most concerning exposure route by far is inhalation**. This is due to the fact that most of nanoadditives are synthesized, commercialized and used in the form of very low bulk density powders that can generate aerosol and respirable droplets.

Table 4 lists the types of operations which are most likely to lead to release of nanoparticles and which therefore have the potential to result in worker exposure.

Table 4. Operations implying exposure to MNMs in an occupational context

Operation	Potential risk
Generating nanoparticles in the gas phase in non-enclosed systems	Aerosol release to the workplace, inhalation risk
Handling nanostructured powders	Possible aerosolization, inhalation risk
Working with nanomaterials in liquid media without adequate protection (e.g., gloves)	Probability of skin exposure
Working with nanomaterials in liquid during pouring or mixing operations or where a high degree of agitation is involved	Possible formation of airborne, inhalable, and respirable droplets. Inhalation risk.
Conducting maintenance on equipment and processes used to produce or fabricate nanomaterials, or the cleanup of spills or waste material	Potential for exposure to workers performing these tasks. Risk of dermal exposure, inhalation risk
Cleaning of dust collection systems used to capture nanoparticles	Increases the potential for both skin and inhalation exposure
Machining, sanding, drilling, or other mechanical disruptions of materials containing nanoparticles	Can lead to aerosolization of nanomaterials. Inhalation risk

3. Best practices for prevention

The use and manipulation of MNMs in an occupational scenario involves uncertainties due to the lack of information about their potential effect in human health that is available. Best-practices strategies and measures for prevention are presented in the next sections.

3.1 Prevention strategies

Risk Prevention tends to avoid the possibility of exposure to the potentially hazardous compounds, by avoiding the very presence of these compounds in exposure media, e.g. through:

- Substitution of MNMs by conventional particles or by MNMs known as non hazardous
- Confinement of MNMs in the process, in the product, or in a stable matrix.
- Isolation of potentially hazardous tasks and materials.

The most traditional way is to observe the material safety data sheet (MSDS) provided by the supplier and use the specified personal protective equipment indicated in each case. This is generally supervised by the OSH staff. However, as a matter of fact MSDS very seldom contain information about MNMs in the product and related prevention or protection measures⁴.

3.2 Confinement and isolation (safe work practices)

General confinement and isolation strategies against hazardous compounds, and especially against toxic dust in the construction sector, fully apply for MNMs, with some adaptations:

- For the management:
 - *“Educating workers on the safe handling of engineered nano-objects or nano-object-containing materials to minimize the likelihood of inhalation exposure and skin contact.*
 - *Providing information, as needed, on the hazardous properties of the precursor materials and those of the resulting nanomaterials product with instruction on measures to prevent exposure [including through spills].*
 - *Encouraging workers to use hand washing facilities before eating, smoking, or leaving the worksite.*
 - *Providing additional control measures (e.g., use of a buffer area, decontamination facilities for workers if warranted by the hazard) to ensure that engineered nanomaterials are not transported outside the work area.*
 - *Providing facilities for showering and changing clothes to prevent the inadvertent contamination of other areas (including take-home) caused by the transfer of nanomaterials on clothing and skin.”* (NIOSH, 2009)
 - Elaborating a specific emergency plan for spills or accidents.
 - Elaborating a specific waste management plan.

⁴ The Scaffold Project recommends a dramatic amelioration of MSDS on this point.

- For Workers:
 - “Avoiding handling nanomaterials in the open air in a ‘free particle’ state⁵.”
 - *Storing dispersible nanomaterials, whether suspended in liquids or in a dry particle form in closed (tightly sealed) containers whenever possible.*
 - *Cleaning work areas at the end of each work shift, at a minimum, using either a HEPA-filtered vacuum cleaner or wet wiping methods. Dry sweeping or air hoses should not be used to clean work areas. Cleanup should be conducted in a manner that prevents worker contact with wastes. Disposal of all waste material should comply with all applicable Federal, State, and local regulations.*
 - *Avoiding storing and consuming food or beverages in workplaces where nanomaterials are handled.” (NIOSH, 2009)*
 - Avoiding application of cosmetics in areas of ENM handling, use or storage.
 - Avoiding contact to the face or other exposed body parts with dusty fingers.
 - Spraying water on the construction place, so that dust sticks to the solid structures or to the soil.
 - Reducing the energy in mixing processes when adding nano-additives, so as to reduce potential splits (manufacturing of construction products (off site) or preparation of the final construction material from a conventional construction material and a MNM-containing additive (off site or on site))⁶.
 - Adequate control/mitigation of spills:
 - Use a vacuum cleaner fitted with a HEPA filter;
 - Humidification of the powder;
 - Use wet wipes;
 - Use adsorbent if the spill is a liquid;
 - Manage the material generated in the collection of spill as a residue.

When the contact of (potentially hazardous) MNMs cannot be excluded through the prevention measures described above, workers are required to wear personal protective equipment, such as goggles, respirators, gloves and special clothes, **Figure 2**. Scaffold’s Guide on risk protection (*et al.*, 2015) provides a complete set of recommendations for collective and personal protection in relation with manufactured nanomaterials (MNMs) in the construction industry. Existing equipment for fine dusts prove appropriate. Given the uncertainties about the toxicity of MNMs, one should pay specific attention that:

- the personal protection equipment (PPE) fit perfectly to the worker’s body, so as to avoid leakage. Particularly, for respirators (e.g. half-masks), filters for smaller particles (P3) are correlated with increased resistance to air, therefore increased under-pressure when breathing and finally increased risk of leakage;
- the PPE is not damaged. For instance, gloves may have to be changed more often.

⁵ For instance, van Broekhuizen and van Broekhuizen (2009) mention, in the case of silica fume (powders) for high performance and self compacting concrete, “*a packaging material (large bags) that dissolve in water and which material does not affect the foreseen product characteristics (concrete)*”.

⁶ But care must be taken to ensure that the additive is well incorporated.



Figure 2. Workers might be exposed to MNMs when performing habitual activities, such as cement handling (left) and spray painting (right)

3.3 Substitution (safer products)

Truly nano-specific prevention strategies for the construction sector essentially concern the choice of safer MNM-containing products.

- Increase of the size of the particles: rather big than small ENMs, rather micro- than nano-particles;
- Use of nanoparticles supported on larger structures (e.g. n-TiO₂ supported on sepiolite microfibers: see Annex 3).
- Use of rather wet than dry (powdery) additives.
- Use of highly (rather than poorly) concentrated aqueous suspensions so as to reduce the volume to transport and handle⁷ (e.g. for n-TiO₂ and n-SiO₂: see Annex 3).
- Use of products containing modified, safer MNMs (ex. thermally and chemically modified nanoclays against smoke emission in case of fire: see Annex 3).
- Use of products with an effective dispersion and compatibilization of MNMs in the matrixes (e.g. nanofibers in polymers: see Annex 3): a good dispersion and compatibilization of MNMs in matrixes reduces the formation of agglomerates and poorly attached particles and the likelihood to release free NOAAs from solid matrix.

⁷ This measure also reduces the transportation costs and leak risks.

Annex 1. Definitions

Agglomerate

Collection of weakly bound particles or aggregates or mixtures of the two where the resulting external surface area is similar to the sum of the surface areas of the individual components [ISO/TS 27687:2008, 3.2].

Aggregate

Particle comprising strongly bonded or fused particles where the resulting external surface area may be significantly smaller than the sum of calculated surface areas of the individual components [ISO/TS 27687:2008, 3.3].

Bulk material

Material of the same chemical nature as the NOAA, at a non-nano scale (ISO/TS 12901-2).

Exposure

Contact with a chemical, physical or biological agent by swallowing, breathing, or touching the skin or eyes (ISO 12901-1:2011).

Health hazard

Potential source of harm to health [ISO 10993-17:2002, 3.7].

Health risk

Combination of the likelihood of occurrence of harm to health and the severity of that harm [ISO 10993-17:2002, 3.8]

Nanomaterial

material with any external dimension in the nanoscale (2.1) or having internal or surface structure in the nanoscale (ISO/TS 80004-1).

Nano-object

Material with one, two or three external dimensions in the nano-scale [ISO/TS 27687:2008].

NOAA

Nano-objects, and their aggregates and agglomerates greater than 100 nm (ISO/TS 12901-2).

nanoscale

size range from approximately 1 nm to 100 nm [ISO/TS 27687:2008].

Particle

Minute piece of matter with defined physical boundaries [ISO/TS 27687:2008, 3.1].

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ASTM D7439 Standard Test Method for Determination of Elements in Airborne Particulate Matter by Inductively Coupled Plasma–Mass Spectrometry

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Asbach et al (2012). NanoGEM Tiered approach for the assessment of exposure to airborne nanoojects in work-places.

NIOSH (2013) Bulletin 65. Occupational Exposure to Carbon Nanotubes and Nanofibers)

NIOSH 0500 Particulates not otherwise regulated, total

NIOSH 0600. Particulates not otherwise regulated, respirable

NIOSH 5040. Elemental Carbon

NIOSH 7300 Elements by ICP

NIOSH 7402 Asbestos by TEM

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Annex 3. Prevention strategies applied in the Scaffold project

In the SCAFFOLD project we have focused our work in the risk prevention by developing and using nanoadditives that are **safer-by-design**.

Prevention-through-design can be approached developing safer nano-objects, designing processes containments and controls and developing new risk management systems. In the SCAFFOLD project, basically we addressed the first approach, developing the so called “safer-by-design” nanoadditives.

This idea is going to be illustrated in this document, but prior to it, the nature of each of the MNMs, their associated problem and used strategies are defined, **Table 5**.

Table 5. MNMs summary and associated strategy

Nanoparticle	Associated problem	Strategy
TiO ₂	Very low density, powdery nature. Possible chemical modifications of uncertain nature	Use concentrated and stable dispersions Use n-TiO ₂ supported on sepiolite microfibers
SiO ₂		Use concentrated and stable dispersions
Nanoclay		Reduction of energy in agitation processes to reduce potential splits Safer-by-design process approach: nanoadditives less likelihood to release smoke in case of fire
Cellulose nanofibers	Fibrous and powdery nature. It is necessary to ensure that no problems similar to those caused by asbestos might occur	Achieve good dispersions-NOAA bounded to the matrix (to reduce the likelihood to release free NOAAs from solid matrix)
Carbon nanofibers		

1) n-TiO₂: Support of nanoparticles on microparticles

In the case of n-TiO₂, the first strategy has been to use an additive in which the nano-spheres had been adhered on the surface of bigger structures in order to obtain **products whose size is in the range of the micro-scale but maintain the properties of the nanoscale, Figure 3**.

These bigger structures are sepiolite fibers. Sepiolite is a type of mineral clay that occurs naturally in form of micro-fibers. The surface of these fibers is highly active and is often used as catalyst.

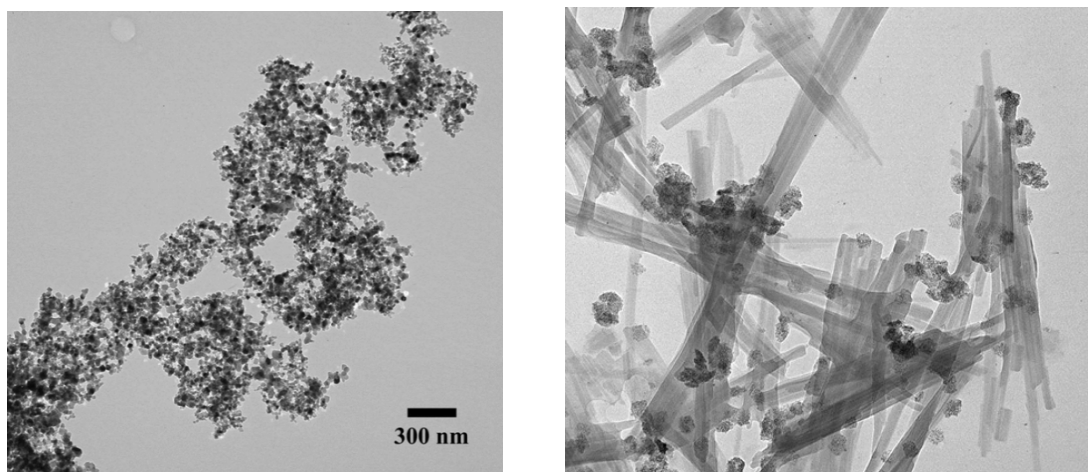


Figure 3. TEM micrograph of a conventional TiO_2 nanoadditive (left) and a safe-by-design nanoadditive composed of TiO_2 supported on sepiolite microfibers (right)

It has been demonstrated that the photocatalytic effect of the TiO_2 nanoparticles is actually enhanced because:

- The agglomeration problem, that nanoparticles often experience, is decreased and these offer a larger surface for photo-decomposition
- The very active surface of the sepiolite attract and fix pollutant molecules which therefore are more likelihood to undergo the reaction

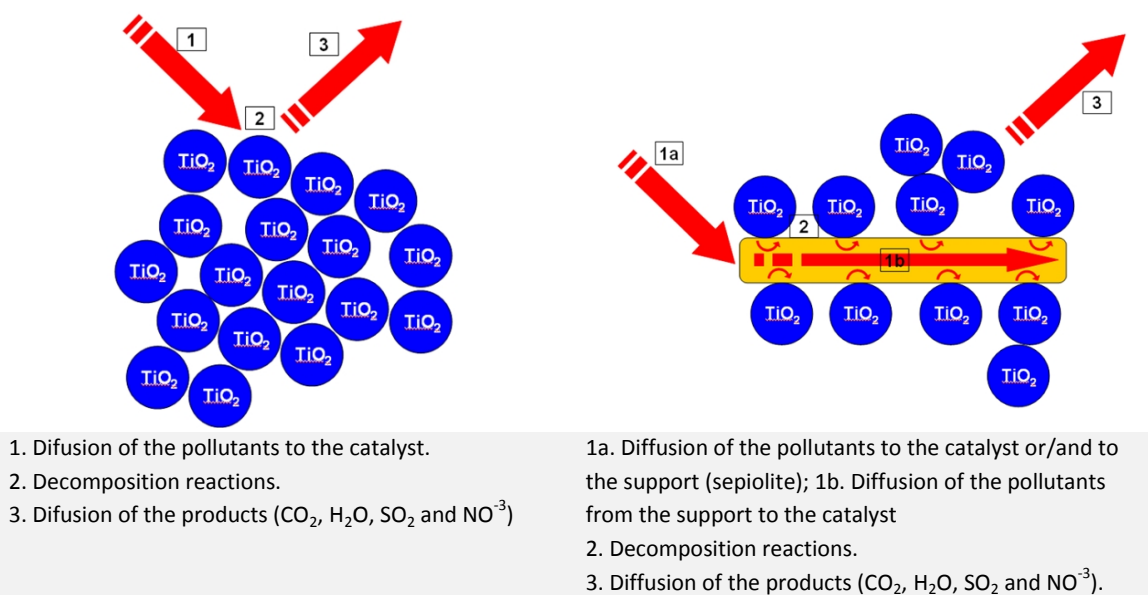


Figure 4. Representation of the two exposed photocatalytic mechanisms

Experimental data from SCAFFOLD shows that occupational exposure to nano- TiO_2 was smaller when using the additive of nano- TiO_2 supported on sepiolite than when using nano- TiO_2 powder directly.

2) n-TiO₂/n-SiO₂: preparation of highly concentrated aqueous suspensions

Additives and nanoadditives are often commercialized and used in liquid media in order to reduce the risks associated to the use of powders. These liquid additives typically contain about 10%wt. of the solid suspended in water or water/alcohol. This is a much safer way to handle the additives, since the risk by inhalation is minimized or cancelled.

In order to reduce the volume of commercial products and risks associated to the manipulation of large quantities, more concentrated suspensions were synthesized by optimizing the diverse preparation steps including sonication, stirring and chemical stabilization, turning out that suspensions with a concentration up to 30 %wt. were possible to achieve with suitable final properties

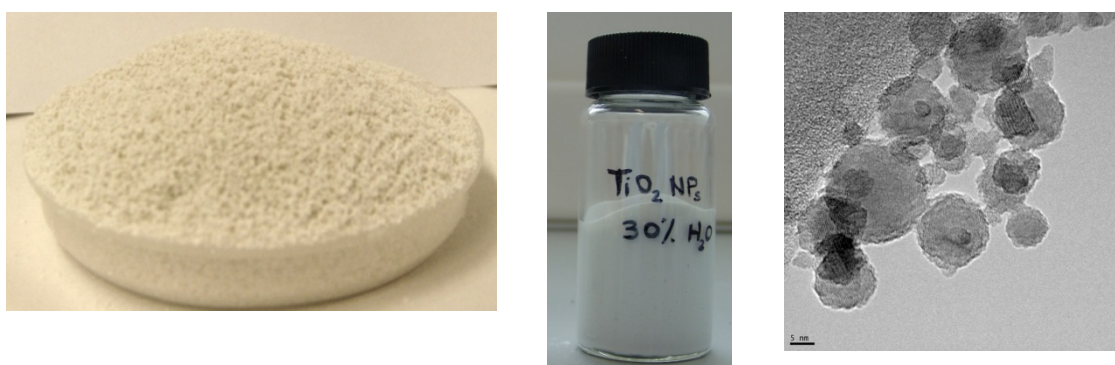


Figure 5. n-TiO₂ in form of powder (left), 30%wt aqueous suspension (center) and TEM image of the nanoparticles (right)

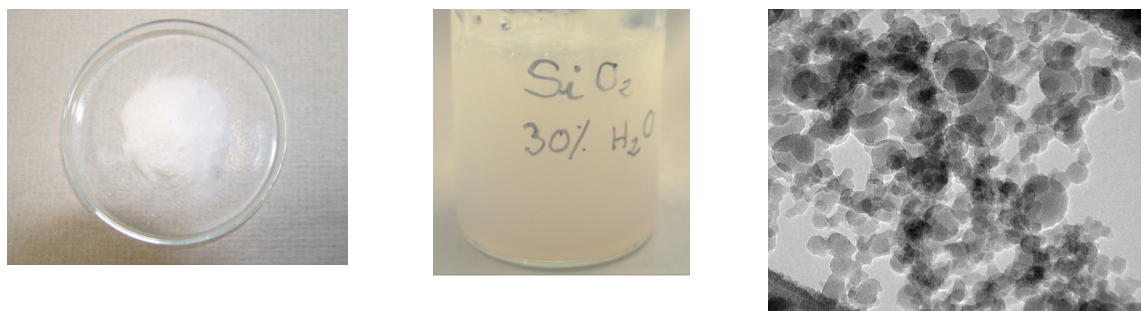


Figure 6. n-SiO₂ in form of powder (left), 30%wt aqueous suspension (center) and TEM picture of the nanoparticles (right)

Table 6. Summary of more relevant dispersions prepared by TECNAN in SCAFFOLD

	TiO ₂ (10% in water)	TiO ₂ (20% in water)	TiO ₂ (30% in water)	SiO ₂ (10% in water)	SiO ₂ (20% in water)	SiO ₂ (30% in water)
Average particle size (nm)	70	150	140	50	150	102
pH	7	7	7	7	5	5
Conductivity / μ S/cm	4.2	6.2	18.9	52.3	83	258
Viscosity / c.poise	6	11	16	21	38	62
Density / g/ml	1.3	1.4	1.5	1.2	1.3	1.4

3) Nanoclays

As it was previously mentioned, in the case of nanoclays, two safer-by-design approaches have been considered from different perspectives: the process and the material.

1. Designing the clay-polymer mixing process in order to minimize inhalation exposure risk

The energy used in the mixing process was found to have no discernible effect on ultimate fire performance. Therefore in practice, lower energy processes, with reduced likelihood of raising dust, should be used. The only requirement is that the clay be properly wet-out, such that subsequent cutting and trimming operations do not hit upon any dry patches and lead to particle release.

2. Thermal modification to reduce the risk of toxic smoke emission during fire

Polymer clay nanocomposites are most commonly produced using bentonite clays – a class of aluminium phyllosilicate consisting of alternating tetrahedral and octahedral layers. In order to improve compatibility with hydrophobic polymers and subsequently aid exfoliation of the individual clay layers (which is believed to lead to maximum property improvements), it is necessary to replace the small cations which occupy the inter-layer spacing (typically sodium and lithium) with long chain surfactant molecules to produce organomodified clays.

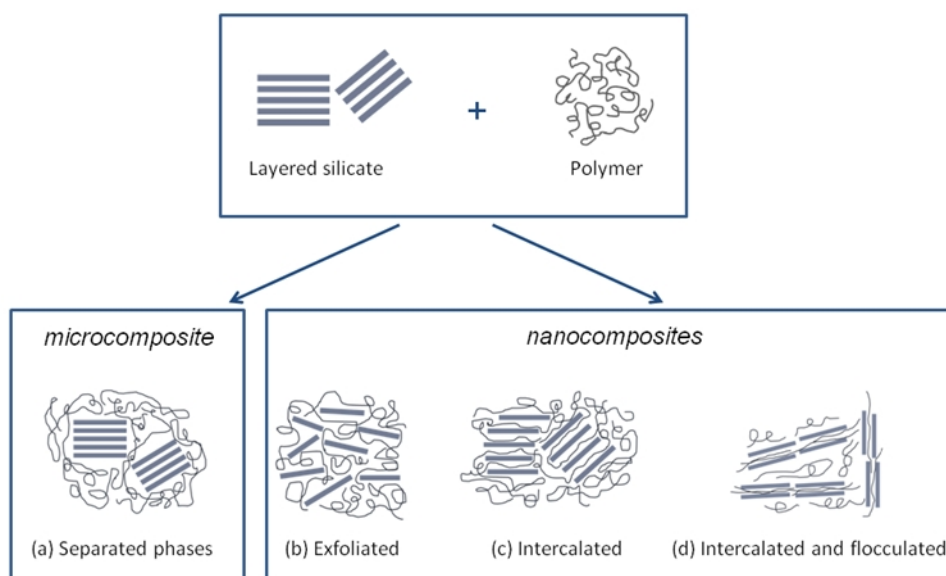


Figure 7. Representation of polymers and layered clays in their different formats of composite and nanocomposite materials

A drawback of this process however, is that these surfactants contribute to the release of toxic smoke in case of fire. To address this, one strategy that has been applied in SCAFFOLD was to reduce the amount of surfactant prior to its incorporation in the polymeric matrix – attempting to balance improved clay-polymer compatibility with minimal additional contribution to toxic smoke. In this project, a thermal treatment method was used to lower the modifier-content of one commercially available organomodified clay. It should be noticed, that in practice, one would look to the supplier to produce organoclays with lower modifier content.

It is envisaged that the simple reduction of organic modifier results in worse compatibility of the clay within the matrix, and although less smoke could be generated due to organic load reduction, clays could be more easily released from the matrix so the solution was not totally achieved. Therefore, apart from the first strategy, a second alternative was also used to prepare safer nanoproducts. Concretely, it was designed a combined alternative which implied a partial reduction of organic modifier as well as the introduction of inorganic silanes to increase matrix compatibilisation. Thus, nanoclays would be well incorporated while the smoke and heat generated is reduced when subjected to fire.

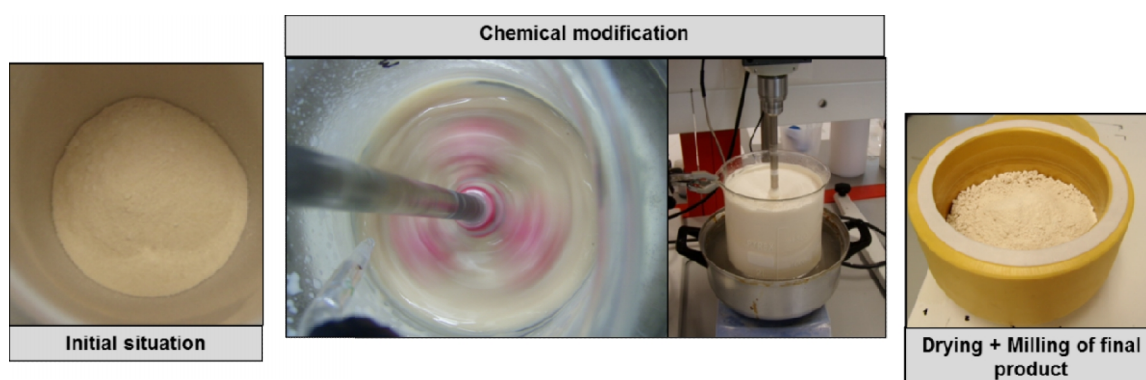


Figure 8. Preparation of modified nanoclay

These modified nanoclays were then used to prepare polymeric nanocomposite panels, using an unsaturated polyester resin as the matrix (which would be the case in the production of interior cladding panels), **Figure 9**.



Figure 9. Fabrication of a PS/nanoclay composite panel

The fire behavior of panels containing treated and non-treated clay was analyzed, revealing that the panels produced using the thermally treated nanoclay displayed a slightly lower total heat emission and smoke production, compared to the commercially-available organomodified clay (**Figure 9**).

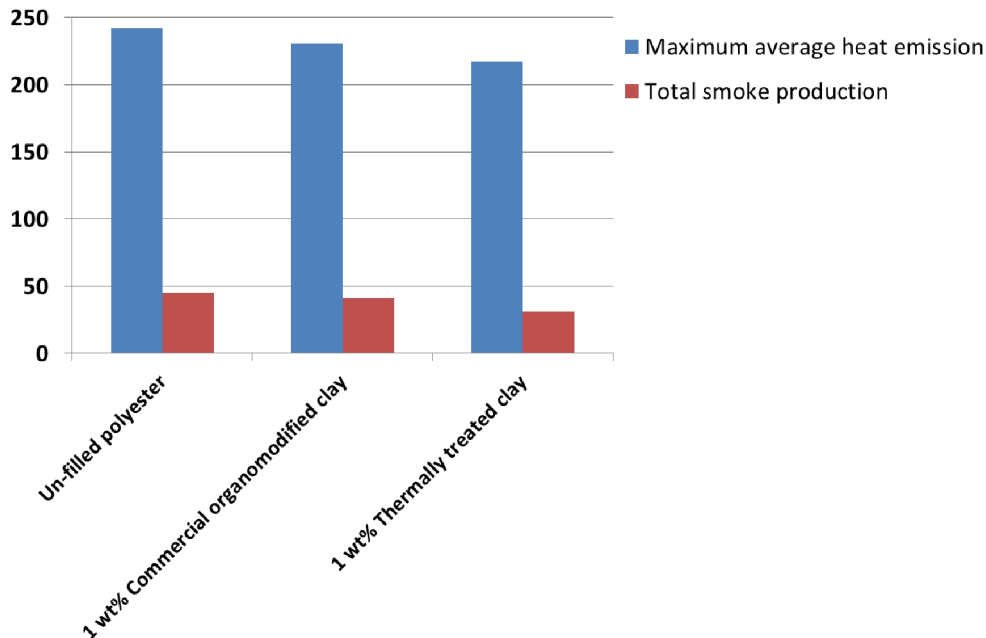


Figure 10. Heat emission and smoke production measurements for PS matrix and nanocomposites filled with 1 wt% of both nanoclays

4) Nanofibers: improvement of the dispersion and compatibilization matrix/MNMs

The nanofibers that have been studied in this project are cellulose and carbon nanofibers, **Figure 10**. These fibers are generally used in polymeric matrixes, such as polyurethane and epoxy resin, improving the mechanical and thermal properties of the matrixes. Additionally, carbon nanofibers which possess conductive properties are added used in the construction sector in order to shield the electromagnetic interferences in security buildings.

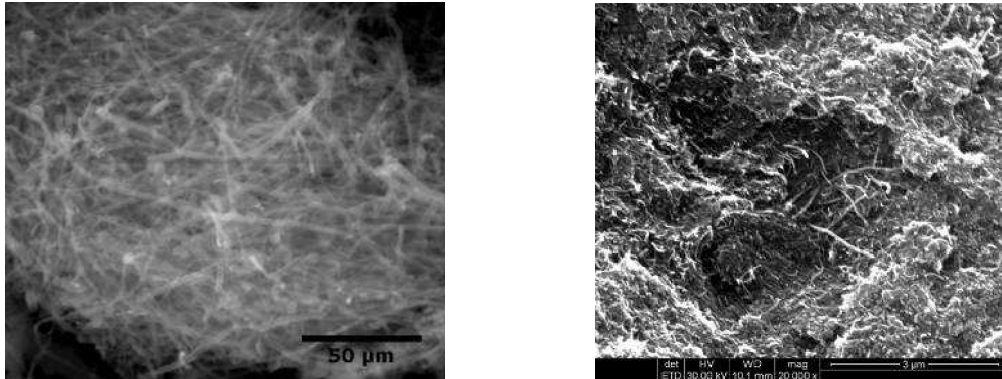


Figure 11. SEM pictures of carbon nanofibers (left) and cross-section of a carbon nanofiber/resin composite (right)

These fibers are very stable and usually very strong interactions between the surfaces of the fibers occur, leading to poor dispersions and compatibility with the polymeric matrixes.

Generally these type of MNMs are incorporated as received in the commercial polymer pre-mix, which is usually a system composed by: monomer/s (might include more than one monomer or/and a crosslinker), activator/s, catalyst/s, solvent/s, etc.

In practice, this incorporation is usually carried using sub-optimal simple mixing procedures, with the result that poor compatibilization between the matrix and the reinforcement might occur. If this happens, the risk of MNMs being released from the matrix when machining (cutting, drilling, etc.) the fabricated pieces/panels is greatly increased.

In order to prevent the potential MNMs release, our strategy has been to **improve the dispersion** of the MNMs in the matrix, reducing the probability of having poorly attached agglomerates and **improve the compatibility** between phases, by using superficially modified nanofibers.

Experimental data showed that no free nanofibers, released during the machining process of the matrixes filled with the nanofibers, were observed by electronic microscopy analysis.

The preparation strategies were the following:

- In the case of the carbon nanofibers, superficially active nanofibers were purchased and pre-dispersed in the monomer system by using a high energy mixer (dispermat with cowles blade). Then, the activating component of the resin was added to the pre-mix containing the nanofibers well dispersed.
- In the case of the cellulose nanofibers, also superficially active nanofibers were used. In this case, the MNMs were dispersed by ultrasound bath in the least viscous component (polyol) and added to the poly-isocyanate component.