QUALITATIVE RISK ASSESSMENT DURING POLYMER MORTAR TEST SPECIMENS PREPARATION – METHODS COMPARISON

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Abstract. Polymer binder modification with inorganic nanomaterials (NM) could be a potential and efficient solution to control matrix flammability of polymer concrete (PC) materials without sacrificing other important properties. Occupational exposures can occur all along the life cycle of a NM and “nanoproducts” from research through scale-up, product development, manufacturing, and end of life. The main objective of the present study is to analyse and compare different qualitative risk assessment methods during the production of polymer mortars (PM) with NM. The laboratory scale production process was divided in 3 main phases (pre-production, production and post-production), which allow testing the assessment methods in different situations. The risk assessment involved in the manufacturing process of PM was made by using the qualitative analyses based on: French Agency for Food, Environmental and Occupational Health & Safety method (ANSES); Control Banding Nanotool (CB Nanotool); Ecole Polytechnique Fédérale de Lausanne method (EPFL); Guidance working safely with nanomaterials and nanoproducts (GWSNN); Istituto Superiore per la Prevenzione e la Sicurezza del Lavoro, Italy method (ISPESL); Precautionary Matrix for Synthetic Nanomaterials (PMSN); and Stoffenmanager Nano. It was verified that the different methods applied also produce different final results. In phases 1 and 3 the risk assessment tends to be classified as medium-high risk, while for phase 2 the more common result is medium level. It is necessary to improve the use of qualitative methods by defining narrow criteria for the methods selection for each assessed situation, bearing in mind that the uncertainties are also a relevant factor when dealing with the risk related to nanotechnologies field.

1. Introduction

The need for a building material with high strength and durability afforded the development of a relatively "new" composite material: polymer concrete (PC) [1]. Although the PC advantages, its usage is only competitive in applications in which durability, strength or other particular requirements render conventional materials unusable, where the initial higher price of PC is mitigated by their superior short and long-term performances. PC present, however, some drawbacks brought by resin matrix like high sensitivity to high temperatures and creep phenomena, and mainly, the deficient behaviour under fire [2-4]. Polymer binder modification with inorganic nanomaterials (NM), leading to nanocomposites (NC), could be a potential and efficient solution to control matrix flammability without sacrificing other important properties. Although the NM use as flame retardant (FR) is promising, this technique is still giving the first steps [5, 6]. The majority of research work on the subject of polymer flame retardancy by means of NM has been carried out on polymer-clay NC. Other emerging nanoparticles that have also shown likely effects on polymer thermal degradation are metal oxide nanoparticles such as aluminium oxides (Al_2O_3). The few studies focusing on this issue show promising results attesting that alumina nanoparticles incorporation can improve thermal stability and other relevant properties of final composite [5-9]

There is a lack of knowledge on the effects of engineered nano-Al_2O_3 in the human body, as existing studies are divergent. In a comparative inhalation study, it was clearly showed that Al_2O_3 nanoparticles (20 nm) induced an inflammatory reaction in rat lungs; however, others similar studies showed that there were no or only slight acute effects on animals due to nanoalumina inhalation, even after high doses [10]. For a final assessment additional research will be needed [10].

The global market for NC will be worth 3.000 billion dollars in 2015, since they have an increasingly decisive role in various industries [11]. However, this new technologies rise is related with new human and environmental risk factors [12]. Occupational exposures can occur all along the life cycle of NM and "nanoproducts" from research through scale-up, product development, manufacturing, and end of life. Quantitative toxicity studies on engineered NM are still relatively sparse and until now there are not known direct implications to the humans health [13].

Risk assessment is an important part of the process to achieve safer workplaces in the nanotechnology field. Because of the limited amount of data on NM, many of the assumptions and estimations are based on the traditional chemical risk assessments. Recently, several exposure assessment approaches have been developed, since the traditional risk and exposure assessment methods seem to be not fully adequate to assess risk related to nanotechnologies, mainly due to existing doubts on the most adequate dose metrics and to the lack of data on the chronic health effects [14]. In this scenario, qualitative risk assessment helps on supporting decisions in the risk management process [15]. The validation of the different proposed qualitative risk assessment methods is an on-going work in the scientific community, and it is expected that modifications could occur [16].

Meanwhile, it is necessary to raise the awareness of the nanotechnology potential risks and one of the ways is through qualitative risk assessment. Under this framework, the present study is an effort to contribute to an enhanced performance and use of qualitative risk assessment methods during the production of polymer mortars (PM) materials with NM. The research question underlying this study is: Do different qualitative risk assessment methods identify comparable risk levels for the same tasks?

This research work was developed at INEGI laboratories, and the tasks were performed in typical work conditions.

2. Materials and Methods

2.1. Tasks under evaluation

In the production process of PM, a commercially available unsaturated polyester resin (Aropol® FS3992, Quimidroga Portugal-Produtos Químicos Unipessoal Lda) was applied as polymer binder. Alumina NM (NanoDur®, Al_2O_3, 99.5% purity), for polymer binder modification, was purchased from Cymit Quimica S.L. (Spain), with 45 nm average size and 36.0 $m^2.g^{-1}$ specific surface. Siliceous foundry sand (SP55, Fundipor), with an average diameter of 245 µm, was applied as mineral aggregate. Manual stirring and ultrasound sonication techniques were used to disperse the NM into the resin system (2.5% by weight of resin), and afterwards, the mixture was added to the sand aggregates (with a binder to sand ratio of 1:4) and thoroughly mixed in a mechanical mix device. The final mixture was casted into standard prismatic moulds.

The laboratory scale production process was divided in 3 main phases: 1 - Pre-production: handling, weighing, adding nanoalumina to the resin and cleaning; 2 - Production: stirring, pouring the

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mixture into the mould and cleaning; and 3 - Post-production: demoulding, cutting and cleaning. During the production process, the nanoalumina is present in powder (phase 1), suspension (phase 2), or inserted in a cured polymer matrix (phase 3), which allowed testing the assessment methods in three different situations.

The production process only involved a single operator who used collective protection measures existing in the lab (mechanical ventilation/general exhaust), and personal protective equipment (two pairs of nitrile gloves, three latex gloves, a mask with ABEK1 P3 filters, protection goggles, type 5 category III disposable coverall and disposable polypropylene shoe covers).

2.2. Risk assessment methods

The risk assessment involved in the manufacturing process of PM was made by using the qualitative analyses based on: French Agency for Food, Environmental and Occupational Health & Safety method (ANSES), from France; Control Banding Nanotool (CB Nanotool), from United States of America; Ecole Polytechnique Fédérale de Lausanne method (EPFL), from Swiss; Guidance working safely with nanomaterials and nanoproducts (GWSNN), from. The Nederlands; Istituto Superiore per la Prevenzione e la Sicurezza del Lavoro (ISPESL), from Italy; Precautionary Matrix for Synthetic Nanomaterials (PMSN), from Swiss; and Stoffenmanager Nano, from The Nederlands.

2.2.1. French Agency for Food, Environmental and Occupational Health & Safety method (ANSES)

ANSES is a risk assessment method by control bands. The risk values are obtained by overlapping the hazard bands and emission potential bands. The hazard bands are defined according to the severity level of the hazard, resulting from the analysis of the available information of similar chemicals. The hazard levels may assume five classifications from HB1 - very low (no significant risk to health) to HB5 - very high (severe hazard requiring a full hazard assessment by an expert). The exposure bands are defined according to the nanomaterial emission potential, whether raw or included in a matrix. The exposure bands can assume four levels: EP1 – solid, EP2 – liquid, EP3 – powder, and EP4 – aerosol. From the resultant matrix it can be defined the control level that corresponds to technical solutions for collective prevention to be implemented at the workplace (CL1 - natural or mechanical general ventilation to CL5 - full containment and review by a specialist required) [17].

2.2.2. Control Banding Nanotool (CB Nanotool)

CB Nanotool is a four by four factors matrix that relates severity parameters on one-axis and probability parameters on the other. The severity parameters consider that the physicochemical and general properties of NM are often unknown. Adding information about the parent material solves partially this problem. The overall severity score is determined based on the sum of all the points from the severity factors. The probability axis fits with traditional information. The probability scores are based on factors determining the extent to which employees may be potentially exposed to NM. The obtained control bands by risk level can be classified in RL1 – general ventilation to RL4 – seek specialist advice [18].

2.2.3. Ecole Polytechnique Fédérale de Lausanne method (EPFL)

EPFL method consists in a decision tree for "nano-laboratories" with three risk classes, which correspond to similar approaches applied to other hazards types (biological, chemical or radiation). This decision tree analyses the established collective protection measures, NM form/state handling typology, NM quantity use, possibility to release dust or aerosol and NM agglomeration ability. The risk classification can be Nano1 (low) to Nano3 (high). With the risk classification it can be defined several safety measures [19].

2.2.4. Guidance working safely with nanomaterials and nanoproducts (Guidance)

GWSNN risk assessment method analyses different scenarios through a three by three decision matrix, informing the policy options and procedures to guarantee safe working conditions with NM. The hazard category can be classified as: 1 - soluble NP, 2 - synthetic, persistent NM, and 3 - fibrous, nonsoluble NM. The exposure classification is made based on the NM potential exposure in the different activities related with the polymeric NC production: I - no emission of free NP due to working in full containment, II - emission of NP embedded in a matrix is possible, and III - emission of free NP is possible. The recommended control measures range from level A (applying sufficient ventilation, if needed local exhaust ventilation and/or containment of the emission source and use appropriate personal protective equipment) to level C –(the hierarchic Occupational Hygienic Strategy will be strictly applied and all protective measures that are both technically and organizationally feasible will be implemented) [20].

2.2.5. Istituto Superiore per la Prevenzione e la Sicurezza del Lavoro, Italy method (ISPESL)
The ISPESL risk assessment method is based on ten different factors (A to J). The aforesaid factors are denominated “factors level risk” and each one of them may assume three increasing values, 1 (low) to 3 (high), referred to as “risk levels”. Since the use of NM presents uncertainty about danger level, the risk assessment takes into consideration these aspects through the index denominated “corrective factor” (within the range 0.5 and 2.0) [15]. The risk is estimated through the “factor level risk” (flr) sum (from A to J) and then multiplied by the “corrective factor” (cf). The evaluation result consists in three risk levels (risk level "low" 5-15, "medium" 16-35, and "high" 36- 60) [21].

2.2.6. Precautionary Matrix for Synthetic Nanomaterials (Precautionary Matrix)
The PMSN estimates the precautionary need that represents the relation between the parameters: "Nano-relevance according to the precautionary matrix" (N), “Potential effect” (W), “Potential exposure” (E), and “Specific framework conditions" (S). The precautionary matrices are logically completed and evaluated in two iterative steps: 1st - a rapid evaluation to demonstrate knowledge gaps and uncertainties, which leads to a preliminary precautionary matrix; 2nd - exact clarifications on the fundamentals of the results from 1st step and from the specific answers to knowledge gaps that afford a finished and definitive evaluation of precautionary matrix. The potential risk can be classified into class A (the nanospecific need for action can be rated as low, even without further clarification) or class B (nanospecific action is needed; existing measures should be reviewed, further clarification undertaken and, if necessary, measures to reduce the risk associated with development, manufacturing, use and disposal implemented in the interest of precaution) [22].

2.2.7. Stoffenmanager Nano
The Stoffenmanager Nano is a risk-banding tool to prioritize health risks occurring as a result of exposure to NP for a broad range of occupational scenarios and to assist implementation of control measures to reduce exposure levels. In order to prioritize the health risks, it is made the combination between the available hazard information of a substance with a qualitative estimate of potential for inhalation exposure. Input parameters for the hazard assessment of NP are selected based on the available information (e.g.: safety data sheets, product information sheets). The method was converted into an online tool that offers a practical approach for risk prioritization in exposure situations where quantitative risk assessment is currently not possible. The obtained priority bands by risk assessment can be classified in 1 (highest priority) to 3 (lowest priority) [23].

3. Results and discussion

3.1. Results

3.1.1. Inputs for the assessment – risk determinants
From the previous sections it is possible to verify that the different methods consider different characteristics from the nano-objects (hazard band) and take in consideration different aspects from the tasks performed (exposure likelihood band). Are also relevant the scale considered to each

parameter, and the weight that each parameter assumes in the final result of the assessment. These differences will influence the obtained results with each method.

In short it is possible to have a wide view of the considered hazard factors of each method in Table 1.The toxicity of the nanomaterial, or its bulk form, is directly considered by five of the methods. Solubility of the nanoparticles and fibrous form are also considered by the majority of the methods, although the toxicity itself could result from these factors, and also from reactivity and size, considered as relevant factors in three of the seven methods. The ISPESL method includes the fire and explosion hazard factor which is relevant for safety risk assessment, biasing the result when only the health effects are considered.

Table 1 – Hazard band factors

Hazard factor	ANSES	CB Nanotool	EPFL	Guidance	ISPESL	Precautionary Matrix	Stoffen-manager
Toxicity (nano and/or bulk material)	●	●		●	●		●
Solubility	●	●		●		●	●
Fibre form (particle shape)		●	●	●			●
Reactivity	●	●				●	
Size		●			●		●
Fire and explosion					●		

In Table 2 the factors that could determine the worker's exposure are presented.

Table 2 – Exposure (or likelihood) band

Exposure factor	ANSES	CB Nanotool	EPFL	Guidance	ISPESL	Precautionary Matrix	Stoffen-manager
Quantity		●	●			●	●
Duration/ frequency (time) factor		●			●	●	●
State of material (e.g. solid, liquid)	●		●				●
Release of nano-objects (e.g. dustiness)	●	●		●		●	●
Aggregation/ agglomeration			●		●		
Embedded in a matrix				●		●	●
Number of workers		●			●		
Risk control / organization					●		●
Containment			●	●			
Type of process/task	●		●				●

The ISPESL and Precautionary Matrix methods include also general factors that influence the final result of the assessment, taking in account the uncertainty on the information gathered. These factors are related to the knowledge on the materials and, in the Precautionary Matrix also on the size and state of aggregation/agglomeration of the nanomaterials present. CB Nanotool leads with the uncertainty, introducing a score for "unknown" in several parameters corresponding to 75% of the scale.

3.1.2. Inputs for the assessment – information gather
The information on nanoalumina and the tasks performed is of major importance for the risk assessment result. The aluminium oxide is a relatively inert material. For the risk assessment it was considered that nanoalumina is a non-soluble, non-fibrous material and its carcinogenicity, mutagenicity and toxicity for reproduction are unknown. In Phase 1, nanoalumina is a solid (powder), in Phase 2 it is in liquid suspension and finally, in Phase 3 it is embedded in a matrix. Based on the assumption that the materials in nano-form are more reactive than its bulk material, nano-Al_2O_3 is considered more reactive than the parent material. Some doubts arise due to information lacking about dustiness, styrene evaporation rate influence on NP release and agglomeration/aggregation of the airborne nanoparticles.

The total amount of nanoalumina used in each phase is 30 g and the tasks durations are around 50 min for Phase 1, 1h50 min for phase 2 and around 30 min for Phase 3. For the frequency factor it was considered that the tasks were performed on a monthly basis.

Figure 1 shows the obtained results of the application of the 7 different risk assessment methods for all the considered stages.

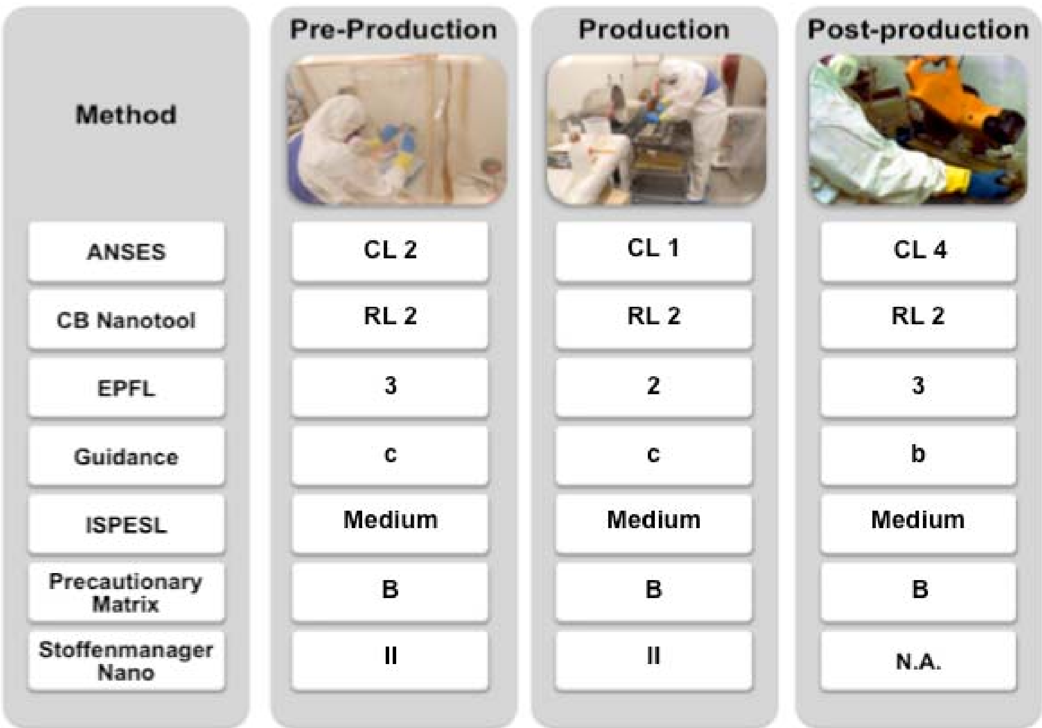

Figure 1 - Comparing the results of the different risk assessment methods (N.A. – Non Applicable)

3.2. Discussion
Analysing the results, it was found that the most critical operation in the PM processing is the pre-production phase, because it deals with NMs in powder state and may lead to typical scenarios of

exposure. However, it was verified that the used qualitative risk assessment methods had different final results (Figure 1).

In phases 1 and 3 the risk assessment tends to be classified as medium-high risk, while for phase 2 the more common result is medium level. The consideration of different assumptions as risk determinants could explain some of the found differences. It is also relevant to consider the sensibility of the methods regarding the different exposure scenarios, as some of them give the same risk level for the three different phases.

In respect to phase 3, divergent results are obtained: while ANSES and EPFL methods point to an increasing risk level, when comparing with the other phases, with the Guidance and Stoffenmanager Nano lower risk levels are obtained (CB Nanotool, ISPESL, and Precautionary Matrix present the same risk level, despite some variations on the exposure scores).This divergence arises from the consideration that NP embedded in a matrix are released together with other material in large particles, thus not resulting in exposure to free NP, assumed by the Guidance and Stoffenmanager Nano methods.

Bearing in mind that these assessment methods are risk management tools it is also relevant to compare their outputs considering the risk control measures. In Table 3 the control measures recommended or necessary to low the risk to an acceptable level, according to each different method.

Table 3 – Risk control measures

Method	Phase 1	Phase 2	Phase 3
ANSES	Local ventilation	Natural or mechanical general ventilation	Full containment
CB Nanotool	Fume hood or local exhaust ventilation	Fume hood or local exhaust ventilation	Fume hood or local exhaust ventilation
EPFL	High level technical, organizational and individual control measures	Medium level technical, organizational and individual control measures	High level technical, organizational and individual control measures
Guidance	Mandatory technical and organizational protective measures	Mandatory technical and organizational protective measures	Technical and organizational protective measures considering economical feasibility
ISPESL	Existing controls are sufficient	Existing controls are sufficient	Existing controls are sufficient
Precautionary Matrix	Review existing control measures and if necessary improved	Review existing control measures and if necessary improved	Review existing control measures and if necessary improved
Stoffenmanager Nano	Medium priority, enclosure necessary to reduce exposure level	Medium priority, enclosure necessary to reduce exposure level	N. A.

As observed on Table 3, the risk control measures recommended (when there are specific recommendations) by each method are different. Depending on the method considered, the user could be led to implement technical, organizational or individual control measures with different degrees of efficacy and/or complexity.

The use of various parameters and/or differences in their interpretation can lead to differences in risk level results. These methods should be reviewed in order to give more convergent results avoiding unequal final outcomes, and their selective and/or complementary application could also help to improve risk management in the workplaces.

4. Conclusions

The occupational risks are a key issue to be considered especially in the early stages of any new material production. By studying proactively emerging risks, one can prevent future problems. The risks are inherent to any technology and nanotechnology is no exception.

Within this scope, in this study the different qualitative risk assessment methods were used to evaluate the risk during the production stages of PM with nanoalumina. The experimental study was conducted in a laboratory environment but provides an overview of the measures that could be applied during the PM production at an industrial scale.

The results obtained with the qualitative methods were divergent; however, generally the methods consider that the pre-production stage is the one with the higher risk.

The results of this study highlight the need to improve the qualitative methods, together with the definition of narrow criteria for the methods selection for each assessed situation, bearing in mind that the uncertainties are also a relevant factor when dealing with the risk related to nanotechnologies field. Thus, more research work is needed to fill existing gaps.

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