R&D of Polymer Composite Materials Modified With Nano-Oxides and Phosphinates: Related Risk Assessment

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INTRODUCTION: A new amazing and exponentially growing field of knowledge to the scientific community is nanotechnology. It is expected that related industries will have an annual turnover by 2015 over 1.5 trillion euros (Savolainen et al., 2010). However, new technologies are usually related to new risk factors and researchers are most of the times the first ones to be exposed to them (e.g., the revolutionary research on radioactivity made by Marie Curie and how her discovery led to her death). Recent inquiries have shown that many researchers do not have internal occupational safety regulations relative to nanomaterials (Groso, Petri-Fink, Magrez, Riediker, & Meyer, 2010). This lack of knowledge about nanomaterials (NM) safety came under the attention when, some years ago, seventy seven persons complained of severe respiratory problems and some of them were even hospitalised with fluid in the lungs after using "Magic Nano", a bathroom cleaning product (Miles, 2006). Another dramatic case occurred in a paint factory in China. Nanoparticles (NP) were found in the lungs of seven female workers who become sick, and two of them died later. These tragic events could have been avoided had there been implemented preventive measures and adequate monitoring in occupational safety health (Groso et al., 2010).

OBJECTIVES: This study aims to evaluate the risk in research and development (R&D) of polymeric composite materials modified with nano-oxides and phosphinates, focusing on exposure to NP in a known research laboratory.

MATERIALS AND METHODS: This study has been developed under a national Portuguese project (PTDC/ECM/110162/2009) at the Institute of Mechanical Engineering and Industrial Management (INEGI). The production of different polymer composites used a commercially available unsaturated polyester resin, with trade name Aropol® FS3992 (Quimidroga Portugal-Produtos Químicos Unipessoal Lda) as matrix. The fillers, a phosphinate based flame retardant (FR) and alumina (Al_2O_3) NP, were used with different contents as specified in Table 1. The FR was Exolit® OP 1240 (Clariant-Químicos, Lda., Portugal) which consists of a fine white grain-based organic phosphonate powder (37.50 μm average size) with high phosphorus content. The NanoDur® (99.5% purity, Alfa Aesar®) alumina NP (45.0 ηm average size and a 36.0 $m^2.g^{-1}$ specific surface area) were purchased from Cymit Quimica S.L. (Spain). The production process of polymer composites and sequent analysis were conducted under the same conditions as usually observed in the industry (general exhaustion). In order to obtain exposure data control, air particle measurements before the production or testing are essential. To measure the particles concentrations in the workplace air, the Dust-Trak TM Aerosol Monitor (model 8520) was used, which is a reference equipment for sampling and measuring indoor air quality under buildings' HVAC systems regulation. This equipment, measures the fine and coarse particles concentration by weight between 1-10 μm, and for this study the 1 μm nozzle was used, to try detecting particles with lower dimension than those of the used FR. The established maximum concentration limit in Portugal is 0.15 $mg.m^{-3}$ for particles smaller than 10 μm. (M.O.P.T.C., 2006).

RESULTS AND DISCUSSION:
During the production and testing of polymer composite materials (Figure1), it was observed that particles go through different "states": in the pre-production phase, particles are at powder state; throughout production, particles are dispersed in a resin (solution); and finally, in the post-production and testing phases the particles are embedded in the solidified resin matrix. In order to analyze the mechanical properties of the different composite materials under study, it was necessary to cut the samples according to the required standard specimen sizes. It was found that both the cutting and testing operations led to dust release into the work environment, which potentially contains NP. Additionally, during all the steps involved in the production process, the handling of a variety of chemicals is required which can also expose the workers to potentially dangerous substances. Usually, occupational disorders are the result of cumulative exposures and not the consequence of a single severe incident. There is still no adequate legislation applicable to NM; however, some standards appropriate to these materials have begun to emerge. In the traditional risk assessment, the exposure doses are compared with the occupational exposure limit values (OELs). However, there are no specific OELs for NP; so, these new standards propose a pragmatic orientation, referring that for insoluble or

poorly soluble NM not included in the fibrous or carcinogenic, mutagenic and reprotoxic chemicals category, the final OEL should be reduced 15 times (Schulte, Murashov, Zumwalde, Kuempel, & Geraci, 2010). It was found by observation that many tasks involved in samples' production show different risk levels of exposure to NP. Considering the statutory limit values for the used NM, they were not exceeded or even reached (OEL for nano Al_2O_3 = 10 mg.m^{-3}). However, considering the proposed reduction and that all the dust could potentially be NP, it was verified that the value (adjusted OEL for nano Al_2O_3 = 0.67 mg.m^{-3}) is higher than the suggested for the cutting task (Table 1). The same is observed relative to the recommended maximum limit values for air quality, for the same task. One point must however be stressed: the used equipment is standardized and it is only appropriate to detect particles lower than 1.0 μm and not specifically NP. With these results, some precautionary and prevention measures should be made and enforced. Even for situations within the exposure limits, there is still lack of specific toxicological data for NPs. Therefore, the potential presence of NPs in the workplace should require that workers always use collective and individual safety equipment.

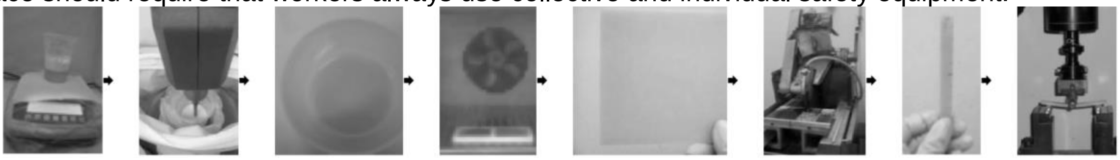

Figure 1 – Main phases in the in R&D of polymer composites

Table 1 – Measurements obtained with the dust track during different tasks

Aerosol Concentrations	Production with:							Cutting	Measuring	Testing
	Control	15%FR	20%FR	2.5%NP + 15%FR	2.5NP + 20%FR	5%NP + 15%FR	5%NP + 20%FR			
Mean (mg/m^3)	0.015	0.049	0.044	0.019	0.037	0.010	0.007	0.173	0.021	0.112
Minimum (mg/m^3)	0.009	0.024	0.038	0.005	0.013	0.007	0.003	0.009	0.008	0.057
Maximum (mg/m^3)	0.045	0.118	0.054	0.034	0.068	0.013	0.019	0.707	0.052	0.136

CONCLUSION: Recommendation 2011/696/EU (definition of NM) and the Commission Communication "Regulatory Aspects of Nanomaterials" indicate that the legal basis exists; however, there is still a long way to go through in terms of safety in handling and use of NM and derivative products. Current knowledge about the NP toxicity is insufficient and preliminary scientific assessments show there is enough evidence to suspect that, at least some NP can be hazardous to human health. Still, with the present and impending legislation applicable to NM, it is possible to implement prevention and protection based on generic technical (e.g., adequate ventilation, manipulation under fume hood or glove box and access restriction), organizational (e.g., education and training), personal (e.g., eye protection, laboratory mask for respiratory protection – at least a ffp3 mask, body protection – non-woven lab coat and overshoes and hand protection – more than 1 pair of adapted gloves) and cleaning management safety measures (e.g., wet cleaning only).

These measures should be undertaken to ensure safety during R&D of materials with NP. Future challenges relative to NP monitoring and health risk assessment should focus on the development and use of more sensitive instruments specific for NP with realistic potential for real-time measurement, with capacity for shape identification, and determining other important properties that could influence the NP hazard.

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