Nanoparticles monitoring in workplaces devoted to nanotechnologies

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Abstract. The impact of engineered nanoparticles (ENP) on human and environmental health is largely unknown at the moment, although their applications involve a wide range of fields from electronics, medicine, environmental remediation, packaging, etc. and their use are becoming very common. Currently the best way to estimate the human exposure to ENP is by monitoring the workplaces, which are the first environment involved in their involuntary release.

This study has been carried out in the research laboratories of the CIVEN Association, devoted to the promotion of research and training activities in different fields of nanotechnology. Its aim is to evaluate the emission of particles in the full range from 5 nm to 20 µm from two different deposition processes of thin film (plasma enhanced chemical and physical vapour deposition, PECVD and PVD respectively) and from the compounding of polymers with nanofillers by means of twin screw extruder.

The results show very different scenarios of emissions. In particular a significant increase of particles concentration has been detected at the opening of the PECVD vacuum chamber and during nanocomposite compounding. In the first case it rises to 3 000 particles cm⁻³, while in the second one the emissions are two orders of magnitude larger, reaching more than 1.5 x 10⁵ particles cm⁻³.

1. Introduction
Nanotechnologies are emerging processes that involve materials at the nanoscale dimension, which applications include a wide range of fields and are becoming very common and of ordinary usage. The debate is open about the impact of engineered nanoparticles on human and environmental health; currently workplaces are the most likely places of exposure, and recently Boccuni et al. [1] have estimated that workers potentially exposed to engineered nanoparticles in Italy are more than 350 000. However, exposure can not be easily evaluated in workplaces because ultrafine particles are emitted by many industrial activities, such as hot processes (melting and refining of metals, welding), combustion and fumes [2], and actually the real-time sampling instruments are not able to differentiate between the sources of emission. Moreover, the indoor concentrations of particles can vary largely due to the other activities occurring in the background, the number of people present, the differences in workers techniques, the changes in ventilation and the variation in outdoor concentration [3].
The aim of this study is to assess the number concentration of particles in the fine and ultrafine ranges in research labs devoted to nanotechnology, and to evaluate their sources as first approach to estimate the potential exposure of involved workers to engineered nanoparticles. Samplings have been carried out at the CIVEN laboratories, an association devoted to the promotion of research and training activities in different fields of nanotechnology, belonging to the Italian Cluster of Nanotechnology. The production techniques investigated in this study are widely used in industrial processes and concern surface coating via vapour deposition (both Plasma Enhanced Chemical Vapour Deposition PECVD and Physical Vapour Deposition PVD) and polymer nanocomposite production. The former processes allow deposition of thin film on substrates to improve its surface characteristics (tribologic, protecting and functional coatings), while the second one improves the bulk properties of polymers, such as their permeability to gases or flame resistance.

2. Experimental
Indoor aerosol was sampled in the different lab rooms, both during the process run and in non-working conditions, with a Condensation Particle Counter (CPC model 5403 Grimm Aerosol Technik) to characterize the temporal variation of the concentration of particles lower than 370 nm. Successively, samplings were done with a Wide Range Aerosol Sampler (WRAS, Grimm Aerosol Technik) composed by the CPC equipped with the Classifier “Vienna” Type DMA (model 5.500) and the portable aerosol spectrometer (model 1.108) to assess the dimensional distribution of particles in the full range from 5 nm to 20 µm.

Instruments were put on a trolley, 115 cm high above the floor, as near as possible to the operator (about 120-130 cm) to estimate his potential exposition to emitted particles but avoiding the interferences with the worker movements.

3. Results and discussion
The results show very different scenarios of contamination regarding both the background concentrations and the emission of particles.

PECVD lab is a clean room class 10 000, so the background concentration (particles with aerodynamic diameter less than 370 nm) is very low and stable: it is about 500 particles cm\(^{-3}\) when the instrument pumps are switched on and less than 50 particles cm\(^{-3}\) when they are off. The particles concentration sharply increases when the operator opens the door of the vacuum chamber, growing up to 800-2 900 particles cm\(^{-3}\). Afterwards it rises more than one order of magnitude, reaching the value of 10 000 – 17 000 particles cm\(^{-3}\), because of the vacuum cleaner used for removing the waste products from the chamber. That great increase could be due to nanoparticles emitted from the vacuum cleaner or may be recycled from it. In any case, the great influence of the vacuum cleaner on the air concentration has been previously reported by Maynard [4].

Samplings performed by WRAS do not evidence the peak emission due to the chamber opening, because of the limited time of the event (about 4 minutes), however, they clearly show that the particles emitted by the vacuum cleaner belongs to the < 100 nm range.

The importance of the background level is confirmed by the results obtained from the monitoring of the PVD process (Figure 1), which instrumentation is located in a laboratory with conventional air conditioning and filtering system, and where the concentration in non working conditions is quite high and not stable (about 1 000-3 000 particles cm\(^{-3}\)). The chamber opening, occurring at the end of different deposition processes, does not result in concentration peaks, but it could not be stated that it is due to the absence of particles emission or because of the too high level of the room baseline.
The largest particles concentration has been detected during the compounding of polymers with nanofillers by means of a twin screw extruder heated up to 180-240°C. In fact during this activity the room concentration grows up to $2 \times 10^5$ particles.cm$^{-3}$, and it is mainly due to particles smaller than 100 nm, as depicted in Figure 2. These emissions occur both when the operator introduces the polymer and the nanofillers into the mixing chamber and during the cleaning by polyethylene (without any nanoparticles).

As claimed by Tsai et al. [5], who monitored a similar process into an industrial plant, detecting concentration larger than $10^5$ particles.cm$^{-3}$ (size range: 5.6 - 560 nm) during the production of nanofilled polymers, it is reasonable to suppose that the nature of the detected nanoparticles is not engineered, but composed by condensed polymer fumes and degraded carbonaceous materials.
4. Conclusions
This study discusses the temporal concentration of fine and ultrafine particles in research laboratories involved with nanotechnological processes, namely vapour deposition in vacuum conditions (both plasma enhanced chemical VD and physical VD) and compounding of polymers with nanofillers. The results obtained are very different in respect to the processes involved and the background conditions, and are briefly resumed in Table 1.

Table 1. Particles number concentration and likely sources.

|                      | PECVD           | PVD             | nanocomposite compounding |
|----------------------|-----------------|-----------------|---------------------------|
| background concentration [particles cm$^{-3}$] | $5 \times 10^2$ | $1 \times 10^3 \cdot 3 \times 10^3$ | $3 \times 10^3$ |
| maximum concentration [particles cm$^{-3}$] | $3 \times 10^2 \cdot 3.5 \times 10^6$ | $7 \times 10^3$ | $7 \times 10^3$ |
| geometric mean $^\dagger$ [nm] | 10 | - | 30-80 $^\ddagger$ |
| likely source | silica nanoparticles from deposition chamber and nanoparticles from vacuum cleaner respectively | unknown | polymers fumes and degraded materials |

$^*$ measured by CPC; $^\ddagger$ measured by WRAS; $^\dagger$ non working conditions; $^\ddagger$ mixing

The results agree with those reported by other authors [6], and confirm the difficulties to detect the engineered nanoparticles emissions due to the production processes, because of the presence of interferences from other sources. However, to the best of our knowledge this study should be the first attempt to estimate the potential operator’s exposure to nanoparticles produced by the involved processes, in particular from the PECVD technique.

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