Colloids and Surfaces A xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Colloids and Surfaces A

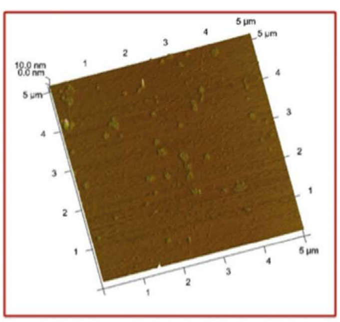
journal homepage: www.elsevier.com/locate/colsurfa

Nanoparticles from paper mills: A seasonal, numerical and morphological analysis

Michele Alderighi[a], Patrizio Carrai[b], Carla Nobili[c], Francesco Lopez[d], Francesca Cuomo[d], Luigi Ambrosone[e,*]

[a] Department of Physics, University of Siena, via Roma, 53100, Siena, Italy
[b] Master in Igiene Industriale, Department of Chemistry and Industrial Chemistry, University of Pisa, Via Moruzzi, 13, 56124 Pisa, Italy
[c] Dipartimento della Prevenzione, Azienda ASL Toscana Nord Ovest, Prov. Lucca, Via IV Novembre 10, 55100 Lucca, Italy.
[d] Dipartimento di Agricoltura Ambiente Alimenti (DiAAA), University of Molise, Via De Sanctis, 86100 Campobasso, Italy
[e] Department of Medicine and Health Science, V. Tiberio, University of Molise, 86100 Campobasso, Italy

GRAPHICAL ABSTRACT



AFM allows examining the real air particle morphology and concentration.

ARTICLE INFO

Keywords:
Paper
Nanoparticles
Light scattering
Sampling
AFM

ABSTRACT

The purpose of this article is to evaluate the potential risk of exposure to nanoparticles of workers in paper mills. In the final stage of the paper production, the very large sheets are wound onto large reels, where these are processed depending on their ultimate use. Paper is smoothed and compacted by passing through metal rollers. During these mechanical treatments nanometric ultrafine particles are generated. In particular, the nanoparticle presence, size and morphology were investigated and differences between particles produced either in summer or winter seasons were explored. To this aim Atomic Force Microscopy (AFM) and Dynamic Light Scattering (DLS) were employed to analyze nano powders filtered in environments of different paper mills to determine structural morphology and sizes. Large breathable particles, with size in the range from 4 µm to 250 nm have been sampled to evaluate the mean level of exposure. By comparing nanoparticles collected from paper mills in summer and in winter we revealed that the number of nanoparticles collected in winter is strictly related to heat generated by the heating system.

1. Introduction

Recent studies have found toxic effects on human beings correlated to particles with very small dimension (typically few hundreds of nanometers or less) originated in different operating sectors where temperature or mechanical work are involved (e.g. foundry, paper

* Corresponding author.
E-mail address: ambroson@unimol.it (L. Ambrosone).

http://dx.doi.org/10.1016/j.colsurfa.2017.06.006
Received 28 February 2017; Received in revised form 3 June 2017; Accepted 5 June 2017

factory mills, welding factory). The study of the shape and morphologies of small nanoparticles is indeed of paramount importance for understanding the mechanism of interaction between particles and human body. In fact, particles having diameter lower than 10 nm cause irritation on the short term and cancer on the long term. Silicosis is a chronic, often fatal, condition caused by micro- and nanoscale particles [1]. Generally, workers can be exposed to air particulate by inhaling, ingesting, and coming into skin contact. The most common way of exposure to aero dispersed nanoparticles in a workplace is inhalation. Ultra Fine Particles (UFP) and Nano Particles (NPs) enter the respiratory trait depending on their dimensions with a diffusive mechanism [2]. Following the deposition, the destiny of the NPs depends on their bio-persistence and their potential transmigration toward other organs and tissues. Factors that regulate such phenomenon and the mechanisms that contribute to the agglomeration and the de-agglomeration of the NPs, as well as their role in the toxic activity after the inhalation are still debated [3].

More recently, experimental evidence has furnished results that point out how the aero-disperse particles exposure with dimensions ranging from ultrafine (UFP) to nanometric (NPs) < 100 nm produced in the working environments and common places (diesel unloading, smokes of welding, ultrafine particles in urban air), is responsible of negative effects for the health. Although the mechanisms of biological action are still not sufficiently known, the considerable sanitary and environmental data based on particles aero-dispersed in the working environments has furnished indications on the characteristics that can influence toxicity and dose-response relationship.

Paper factories are often covered from dusts, a fibrous particulate that sticks to the walls, ceilings, machineries and generally in almost all working areas [4,5]. Currently the dust of paper is considered inactive dust and the TLV-TWA (time weighted average) limit for the ACGIH (American Conference of Governmental Industrial Hygienists) for the professional exposure is 10 mg/m^3 s for the inhalable part and 3 mg/m^3 s for the breathable part. Notwithstanding recently respiratory symptoms as the chronic cough, sense of thoracic constraint and dyspnea start to grow into the workers because of prolonged exposure to paper dust. The paper dust produced from papermaking industry contains around 80% of cellulose fibers and 20% of inorganic material composed by additive substances.

The ability of nanoparticles to induce granulomatus lesions may be consistent with their physicochemical properties which impart to them enhanced structural properties but may also make them more persistent in biological and ecological systems. The bio-persistence of nanoparticles may be a significant occupational safety issue since chronic exposures to low levels could be associated with adverse health effects [6]. Since 1995 Toren et al. [7] signaled that high exposure to chlorine compounds and paper dust was associated with an increased prevalence of impaired lung function, allergic respiratory diseases and death. Today, to investigate patterns of cancer incidence and mortality among employees of the pulp and paper industries, the International Agency for Research on Cancer is coordinating a multicentric epidemiological study involving researchers and representing most paper production regions in the world. Numerous studies regarding environmental epidemiology and toxicology suggest that the toxicological effects of aerosol particles are not only due to mass particles, but also particle size and surface properties has to be considered crucial [8]. Although many studies have been made to correlate the particles size to different diseases, little is known about the role played by particles shape in the spread disease process [9]. The study and the fundamental role of particles size morphologies towards many applications, including nanoparticle templating, environmental remediation, preparative organic chemistry, and a number of supramolecular processes turned out to be important [10–14]. AFM microscopy and DLS were used to study in detail number, morphology and the surface of the particles generated by the processing cycle. To analyze small particles, the use of AFM (Atomic Force Microscopy) is becoming increasing despite the fact that the preparation route should be further optimized. This technology connected with an appropriate DLS (Dynamic Light Scattering) analysis could give important results. For both equipments content of water, hydrophobic forces, bi-continuous phases, aggregate growth play a pivotal role [15–19]. The aim of this work is to monitor workplaces involved in the production of paper. Additionally, the damage to workers in the mills and the developing of an effective prevention plan is also highlighted [20–23].

2. Materials and methods

2.1. Sampling

Sampling of nanoparticles was carried out with aspirators in order to select particles with different sizes. Measurements were performed in order to find an estimation of the number of particles produced. The nanoparticles sampling was performed by means of air pumps and the particles were collected over different filters. For inhalable and fine particles a suction pump (model type air chek 2000 Skc) was exploited to collect particles over IOM filters with a flux of 2.0 L/min. Nanoparticles were sampled over SIOUTAS cascade Teflon and Polycarbonate filters thanks to Leland Legacy Pump with a flux of 9,0 L/min, to select particles with a size range between 250 nm and 2500 nm.

To determine the number of particles in the air, two different types of portable samplers were used. The first one was an OPC (Optical Particle Counter) AeroTrak 9306 of TSI Instruments, based on the optic calculation using the principles of dispersion of the laser light. The tool measures the total number of particles for meter cube of air (particles/m^3) through specific dimensions classes (300, 500, 1.000, 3.000, 5.000 and 10.000 nm). The second tool used was a CPC (Condensation Particle Counter) P-Trak 8525 of the TSI Instruments. CPC measures the particles in the dimensional interval 20–1000 nm, with the expressed data as total number of particles for centimeter cube (particles/cc) of sampled air. The higher limits of detection for the AeroTrak 9306 and for the P-Trak 8525 are respectively of $70 \cdot 10^6$ particles/m^3 and of $100 \cdot 10^6$ particles/m^3.

2.2. AFM measurements

AFM measurements of nano-powders were performed using the Multimode AFM equipped with a Nanoscope IV controller in air and at room temperature, in an amplitude modulation mode (Tapping mode®) with Si tips type with resonant frequencies ranging around a value of 250 kHz and with a tip radius with a dimension less than 10 nm. The microscope was placed on a pneumatic anti vibration desk, under a damping cover. The processing was performed using the Nanoscope 6.13 v software (Bruker) and Igor Pro (Wavemetrics). The measurements were realized in the range from 5 × 5 μm to 500 × 500 nm with a resolution of 512 × 512 pixels.

The analysis of valley-to-valley distances of a line-profile along the line connecting adjacent particles allows us to determine the average of particles. Obviously, the height information from AFM images can be used as an exact particle diameter when spherical particles are investigated.

Filters from different workplaces were suspended in MilliQ water for about 10 min to desorb the particulate. Then 10 μL of the nanoparticle water suspension was deposited onto a freshly cleaved mica surface (Muscovite mica with V-1 quality, EMS Electron Microscopy Science Hatfield, PA). Both casting and spin coating were evaluated to obtain samples suited for AFM analysis.

2.3. Image particle analysis

Image Particle Analysis was performed with the Image Analyze Particles procedure of the Igor Pro 6 software (Wavemetrics Portland,