New method for the characterization of abrasion-induced nanoparticle release into air from nanomaterials

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ABSTRACT

A new method for the characterization of abrasion induced nanoparticle release into air from nanomaterials using a normalized Taber equipment has been developed. The influence on nanoparticle releases of the abrasion process conditions and the tool type were investigated. Concentrations of nanoparticles released in the air higher than that of micrometric particles were measured by an Electrical Low Pressure Impactor (ELPI): up to 10000 particles/cm^3. The released nanoparticles were then collected on Transmission Electron Microscopy (TEM) grids and filters for further analysis in order to determine if nanoparticles are leached by abrasion in free or agglomerated form. At this stage, Cu nanoparticles were observed nearly detached from a Polymethyl Methacrylate (PMMA) nanomaterial using an SiC grid paper P1200 (ISO classification). This confirms the interest to develop such a method. No standard method for the characterization of nanoparticle release is currently available.

Keywords: Taber method, abrasion, nanoparticles, CNT, release

1. INTRODUCTION

Nanotechnologies are emerging around the world. Nanoparticles are finding new industrial applications every day. Today we are witnessing the advent of a new step of the industrial history of nanoparticles as nanoparticles developed in laboratories are about to be manufactured in mass production. Thus, economists are talking about the emergence of a new industry for the 21st century which could rank alongside automobile and microelectronics industries in terms of turnover as soon as 2015. Nevertheless, this new industry can develop dynamically only if the safety issues are solved and this for the whole life cycle of the nano products: from fabrication to the end of life through usage. Due to the variety of nanoparticles, toxicology studies will take time to define dangerousness of every kind of nanoparticle. Today in the absence of reliable data on the toxicity of nanoparticles, the only way to ensure that nanomaterials are not dangerous is to verify that they do not release their nanocharges. No standard method for characterization of nanoparticle release is currently available.

A test bench capable of measuring the release of nanoparticles from nanomaterials using a linear normalized Taber equipment has been achieved in the frame of Nanosafe 2 project [1], [2]. The purpose of this bench is to quantify whether nanomaterials after abrasion leach particles in free or agglomerated form. Our first results showed that only a few released nanoparticles were detected from nanoproducts by abrasion [2]. Another study proposes a similar method using a circular Taber equipment instead of a linear Taber [3]. This work shows that the total number of submicrometric particles or nanoparticles generated by abrasion was extremely low [3].

In this paper, efficiency of standard and non-standard abrasion tools to aerosolize nanoparticles from polymer matrix was quantified. The most efficient tool to aerosolize the nanodust by abrasion was searched. The release of nanoparticles from PMMA containg 10% wt Cu nanoparticles and from polycarbonate containing 3% wt carbone nanotubes (CNT) were quantified and analyzed.

2. EXPERIMENTAL METHOD

All manipulations are performed in a sealed glove box equipped with a HEPA filter in order to limit the initial presence of particles in the atmosphere. The background noise in the sealed glove box is quantified less than 10 part./cm^3. These special conditions are obtained by creating a vacuum at the top of the box, that will suck the air rich in particles at a rate of 150 l / min and a clean air is obtained using an absolute filter placed in the bottom of the glove box. Nanomaterials are mechanically solicited by abrasion using a standardized linear Taber equipment. The tool is rubbed on the sample in order to generate a dynamic friction.

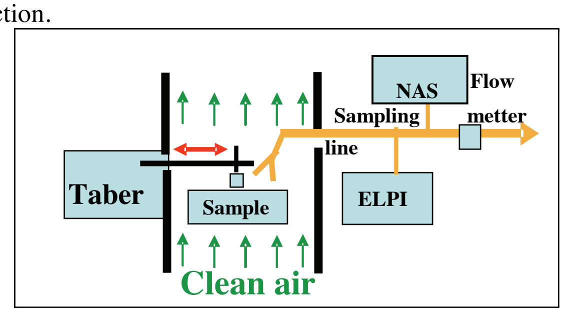

Fig. 1 Schematic of the measurement tool.

The friction is linear and cyclical on the surface of the sample. The cycle speed, number of cycles are parameters that can be modified for the abrasion process. The normal force applied can be modified as well adding mass on the sample.

The characterization of the particles released by the abrasion process requires the detection of the particle concentration and the number size distribution. One instrument was used for measuring the number size distribution: an ELPI. The ELPI allows the determination of particle number distribution in the range of 7 nm to 10 μm. This device is capable of achieving real-time measurements and displays, for each size class, changes in concentration

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over time. It also allows depositing released particles on filters after putting them on impactors. These filters (hydrophilic polycarbonate membrane) are then analyzed by scanning electron microscopy (SEM) to observe the morphology and size of the collected particles. Thus, it is possible to measure the size distribution and to perform physical-chemical characterization of the collected particles.
An electrostatic nanoaerosol sampler (NAS-Nanometer Aerosol Sampler,model 3089, TSI Incorporated, USA) was used in parallel with the ELPI. The released particles were collected on TEM grids in order to determine if nanoparticles are leached by abrasion in free or agglomerated form and for an elemental identification of the nanoparticles of interest by EDX analysis (Energy dispersive X-ray spectroscopy).

3. RESULTS

3.1 Influence of abrasion conditions on nanoparticle release

First, the influence of the abrasion process conditions on nanoparticle release were investigated. All the measurements shown here were performed on polycarbonate sample containing 3% wt CNT.

The abrasion was performed using a steel brush and the speed of the tool generating friction on the sample was increased. As shown on the Fig. 2 the abrasion effect is enhanced when the abrasion speed increases.

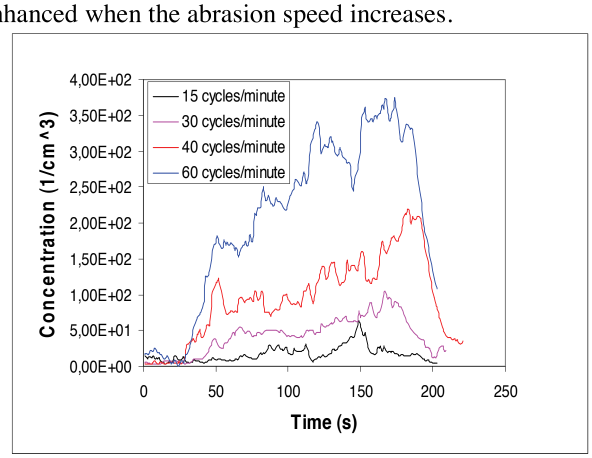

Fig. 2: Concentration of particles at different abrasion speed measured with an ELPI.

The concentration of released particles reaches a value of 370 part./cm^3 for a speed of 60 cycles per minute by comparison with 50 part./cm^3 particles for a speed of 15 cycles per minute. Further, all experiments were carried out with the maximum abrasion speed, 60 cycles per minute.

In a second step the abrasion was performed using a steel brush and the normal force applied on the sample was increased. As shown on the Fig.3b the abrasion effect is enhanced when increasing normal force without changing the size distribution of released particles (Fig.3a, 3b). Up to 1800 part/cm^3 nanoparticles were measured using an ELPI, the maximum number of nanoparticles were measured at stage 2 (Fig 3b).

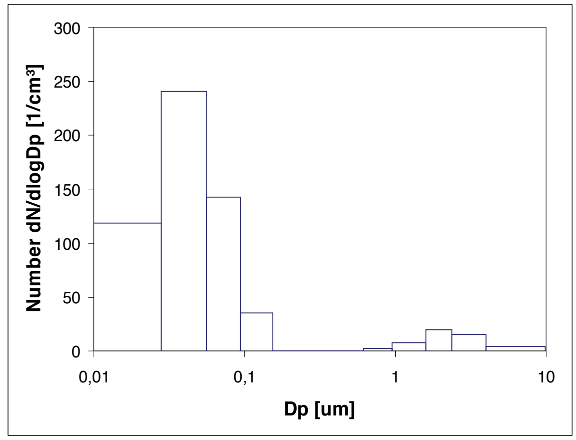

Fig.3a Effect of applied force (m = 1200g) on particle distribution.

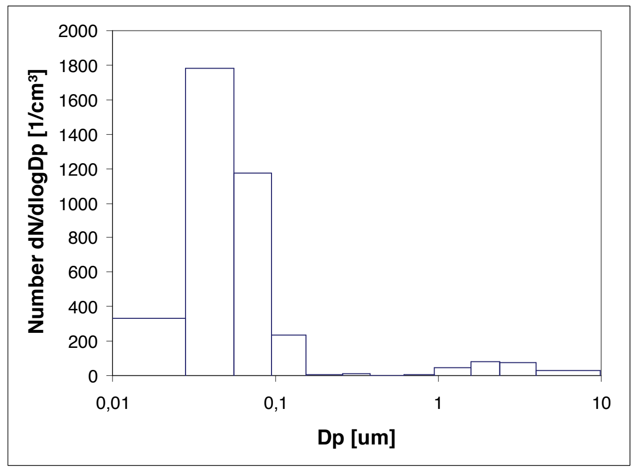

Fig.3b Effect of applied force (m = 2100 g) on particle distribution.

3.2 Quantification of nanoparticle release using different tools

An efficient tool to aerosolize the nanodust by abrasion was searched. Standard and non-standard tools were quantified. PMMA containing up to 10 wt % nanoparticles was investigated. Polycarbonate samples containing 3% wt CNT was investigated as well. Normalized standard tools efficiency- abrasive ribbons of SiC -were tested (ISO 7784-1). Non standard steel brushes efficiency has been evaluated as well.

3.2.1 Abrasion using a non-standard tool brush

First abrasion test was performed using a steel brush tool. Polycarbonate containg 3% wt of CNT was investigated. Higher concentrations of nanoparticles than micrometric particles were released in the air (Fig. 4).

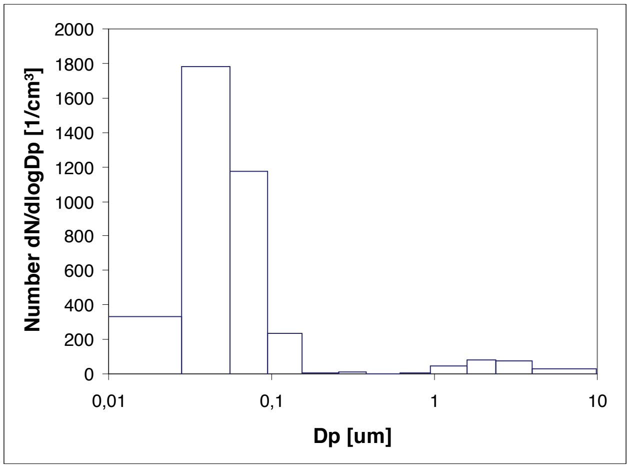

Fig.4 Size distribution from polycarbonate polymer containing 3% wt CNT (Carbone Nanotubes) abraded using a steel brush. A normal force was applied (m = 2100g).

Significant release of nanoparticles was detected: up to 1800 particles/cm^3 were measured at stage 2 of the ELPI.

3.2.2 Abrasion using a standard tool

Polymethyl Methacrylate PMMA polymer containing 10 % wt of nanoparticles with a mean size around 40 nm was investigated. The influence of the type of abrasive paper (which can also simulate a sanding) on the release of nano particles in the air was quantified. Silicon carbide-type abrasive paper P120 and P1200 with variable grit size (from 125µm up to 15.3µm) were used. The influence of the abrasive grit size on the number size distribution was estimated.

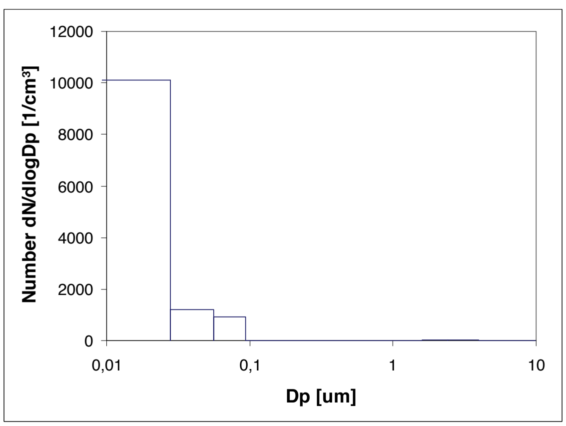

Fig.5a Size distribution from PMMA polymer containing wt 10% Cu nanoparticles abraded using a P1200 SiC abrasive paper. No normal force was applied.

Using a P1200 paper, up to 10000 particles/cm^3 were measured at stage 1 of the ELPI.
Using a P120 paper with abrasive grains larger than in the case of P1200, smaller concentrations of nanoscale objects are detected while larger concentrations of sub micron objects are issued.

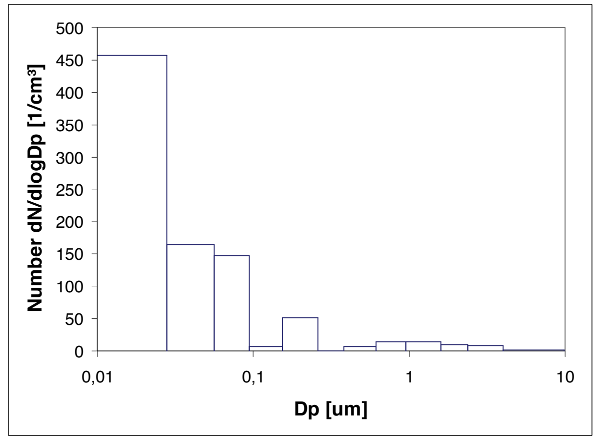

Fig.5b From PMMA polymer containing 10% wt Cu nanoparticles abraded using a P120 SiC abrasive paper. No normal force was applied.

20 time less nanoparticles can be observed on channel 1 of the ELPI in this case by comparison with results obtained using P1200 abrasive paper .
The type of abrasion tool has a high impact on the quantity of nanoparticles releases in the air from the polymer.

3.3 Analysis of released particles from samples

In order to identify which kind of particles are released, analysis on TEM grids are performed. The dust was deposited on a TEM grid using the NAS and on filters on different stages of the ELPI (as described in the section 2).

In a first step the presence of free or agglomerate nanoparticles or CNT and polymer embedded with nanoparticles were analyzed by TEM and SEM. In a second step the samples were examined with EDX (energy dispersive X-ray spectroscopy) for an elemental identification and the presence of Cu nanoparticles was confirmed.

3.3.1 Polycarbonate containing 3% wt CNT

Nanoparticles emitted from polycarbonate samples containing wt 3% CNT by abrasion was investigated. These particles were collected on the filter in stage 2 of the ELPI and analyzed by SEM. The particle number distribution performed on this sample is showed on fig. 4.

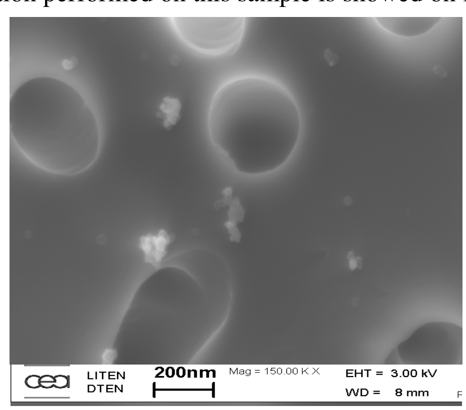

Fig.6 SEM observation of detected particles on filter out on the ELPI channel abraded using a steel brush.

At this stage particles with aerodynamic diameter between 28 and 56 nm are deposited (Fig 3b).

The presence of nanometric polymer particles on the filter can be observed. No free NTC was observed. These observations were also confirmed by TEM.

3.3.2 PMMA containing 10% wt Cu

Nanoparticles emitted by abrasion from polycarbonate samples containing 10% wt Cu was investigated further by TEM (Fig.7 and 8). No visible free Cu nanoparticles were observed when the surface was abraded using a brush. Micrometric and submicronic polymer particles were visible on TEM grids. The TEM image proves that Cu nanoparticles are still embedded in the polymer (Fig 7).

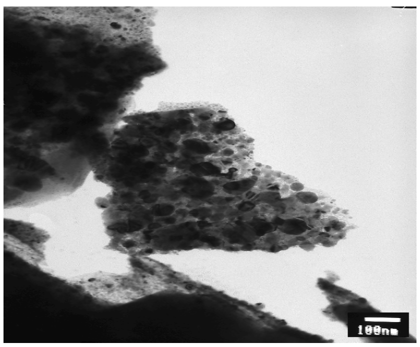

Fig.7 Observation of abraded particles on TEM grids.

When the surface was abraded using a P1200 SiC paper, nanoparticles nearly detached from PMMA polymer were observed (Fig.8).

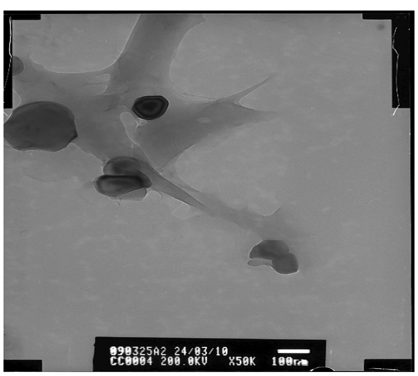

Fig.8 Observation of abraded particles on TEM grids.

In a second step Cu nanoparticles were identified by EDX (Fig.9). The size of nanoparticles from TEM image corresponds to the size expected and given by the manufacturer.

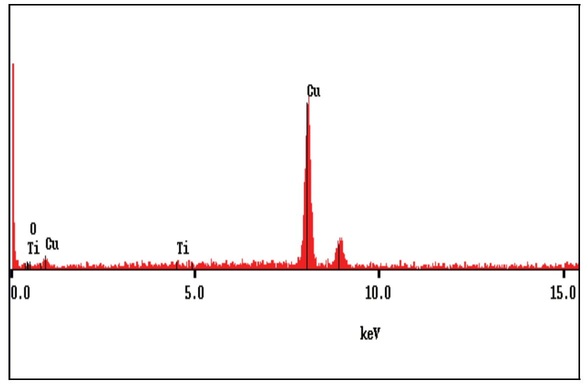

Fig.9 EDX graph of abraded polymer and nanoparticles identified on Fig.8.

4. CONCLUSION

The abrasion process itself was optimised to give the highest release and then the highest aerosolization of the nanodust.

- Increase of nanodust was obtained by increasing the abrasion speed and the normal force on the sample.
- The sandpaper P1200 friction on PMMA containing 10% wt Cu promotes the formation of nanoscale dust in higher quantity than P120.
- Abrasion performed on polycarbonate containing CNT and PMMA containing Cu using stainless brush produced nano-sized dust but no isolated CNTs or Cu nanoparticles.
- In the case where PMMA was abraded using an SiC grid paper P1200, free Cu nanoparticles were nearly detached.

At this stage standard SiC standard paper seems to be efficient to detach Cu nanoparticles from PMMA polymer. This confirms the interest to develop such a method.

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Acknowledgments

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