Measurement of nanoparticle removal by abrasion

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Abstract. A strong release limitation of single nanoparticles from commercial manufactured “nanoproducts” is necessary to decrease potential exposure risks of consumers and represents also a pragmatic way to facilitate acceptance for nanomaterial commercialization before obtaining definitive toxicological results. So, it is of prime importance to know how to characterize the release of small materials during usage solicitations such as mechanical, thermal, UV stress: are they single nanoparticles, aggregates or nanoparticles included in a bigger piece of the matrix?
In the frame of NanoSafe2 project, CEA developed and qualified a specific bench test where the material to be tested is mechanically solicited by abrasion using a normalized Taber equipment. The first results show that nanofillers can be released in usage by abrasion for non optimised nanoproducts.

1. Introduction
The nanoparticles are finding new industrial applications every day in fields as diverse as electronics, biomedicine, pharmaceutics, cosmetology, chemical catalysis, new materials, and others. We are about to witness the advent of a new era in the industrial history of nanoparticles. New types of nanoparticles that until now were under laboratory development are on the verge of mass-production. Economists are now talking about the dawn of a new industry for the 21st century which could rank it alongside the automobile and microelectronics industries. Nevertheless, this new industry can develop dynamically only if the safety issues are solved during all the life cycle long of the nano products: from fabrication to the end of life through usage.

Due to the complexity of the nano toxicology in particularly due to the multitude of shapes, sizes, surface charges, etc. even for nanoparticles presenting the same chemical formula, it will probably take a long time to identify if some nanoparticles are dangerous and even a longer time to declare some nanoparticles as benign.

However the relevant parameter for safety issues is the risk. The risk depends on 2 factors: the hazard and the exposure. If the exposure is decreased toward zero, then the risk becomes low whatever the hazard (toxicity in this case). The only pragmatic way to secure the nanomaterials today consists in reducing the exposure to nanoparticles of the potentially exposed workers, the consumers and the environment.

A strong release limitation of single nanoparticles from commercial manufactured “nanoproducts” is necessary to decrease the potential exposure risks for consumers and represents also a pragmatic way to facilitate acceptance for nanomaterial commercialization. So, it is of prime importance to know how to characterize the release of single nanoparticles, aggregates or nanoparticles embeded in a bigger piece of the matrix during usage solicitations such as mechanical, thermal, UV, stress, etc.
In this paper, a new method is presented for measuring the release-ability of the nanofillers embedded in the nanoproducts under abrasion in order to mimic one of the main types of solicitation in usage. The objective of developing such a measurement tool is double: optimization of the “hooking” of the nanoparticles in the matrix and perhaps one day, qualifying the nano products for the market.

2. Experimental setup and method

In the frame of NanoSafe2 project, CEA developed and qualified a specific bench test where the material to be tested is mechanically solicited by abrasion using a normalized Taber equipment ASTM C1353-07. In this test, 2 parts of the same material are alternatively rubbed against each other to generate a dynamic friction. Then, the nanoparticles are streamed into an ultra clean air flow before analysis performed by a Scanning Mobility Particle Sizer (SMPS) and a Condensation Particle Counter (CPC). Removed nanoparticles can be measured from 5 to 1000 nm.

The critical parameters to take into consideration to set up such a method for a standardization purpose is the sensitivity (detection of the first few released nanoparticles) and to get an absolute measurement.

- To get a good sensitivity of the method, it is necessary to decrease the background noise level of nanoparticles external to the system and to minimize the dilution of the flow collecting the released nanoparticles to the more sensitive counter.

- To get an absolute measurement, it is necessary to collect all the released nanoparticles and to know the deposited fraction before the counter.

As seen in Figure 1, the sample is disposed in a clean air flow filtered with an H14 HEPA filter. The collecting device has been optimized to collect the maximum of the generated particles with the minimum collecting flow in spite of the abrasion head displacement.

![Figure 1. Schematic of the measurement tool and a picture of the equipment set up at CEA.](image)

A 100 x 30 mm sample is placed at the bottom of the device and a 30 x 30 mm part of the same sample is placed at the moving upper part. The displacement length is 100 mm at the frequency of 60 cycles/min.

The measurement of the released nanoparticles is performed with a SMPS (Grimm 5.5-300) presenting a flow rate of 0.3 L/min and a CPC (Grimm 5.403) presenting a flow rate of 1.5 L/min. The SMPS gives the concentration of nanoparticles and their distribution which is very interesting to know if the abrasion releases single nanoparticles or bigger parts of the matrix. On the other hand the CPC gives the number of nanoparticles only but is much more sensitive. To illustrate that, we can calculate the theoretical Low Limits of Detection in the best case: when the collection flow equals the measurement flow of the counter.

- Assuming that an average of one particle in each of the 44 channels of the SMPS has to be detected during the 4 minutes measurement to get a relevant value and taking into account the flow rate of the SMPS: 0.3 L/min, calculations show that we need to release more than 1200 particles during the 4 minutes.
For the CPC we assume that we need 10 events in the same 4 minutes in order to get a relevant number. This means that we need to release more than 10 particles during the 4 minutes. Measurements performed alternatively with a SMPS and a CPC are therefore complementary.

3. Qualification of the measurement tool

Thanks to the clean air flow the background noise count was measured under 5 particles @ 6 nm during 4 min whatever the TABER system is switched on or not.

As seen in Figure 2 the collection efficiency was estimated as a function of the Taber head speed by injecting intentionally a calibrated amount of Pt nanoparticles very close (1 mm) to the abrasion area. For small nanoparticles around 6 nm the collection efficiency is 100% when the TABER system is off and decreases to 60% when the abrasion speed is maximum (0.2 m/s) due to losses induced by the head displacement. This means that it is necessary to correct the measured values for the smallest nanoparticles.

![Figure 2. Schematic of the collection efficiency test and obtained results for small nanoparticles (6 nm).](image)

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Then a first test was performed on a cotton fabric sample covered with 20 nm silica particles deposited by dropping a colloidal suspension (liquid) followed by a simple air dry. First the background was quantified and estimated to be negligible. Than, the measurements performed with the SMPS show a clear release of the deposited nanoparticles. A second measurement after the first 4 minutes of abrasion indicates an important decrease of the released nanoparticles in spite the quite high level of deposited nanoparticles at the surface of the fabrics. This means that in practice it is necessary to use a new sample for each measurement in certain cases.

![Figure 3. First results obtained on cotton fabrics containing nanoparticles. Left: results from 2 successive trials with SiO$_2$ nanoparticles. Right: results obtained with different sizes of PSL nanoparticles.](image)

Figure 3. First results obtained on cotton fabrics containing nanoparticles. Left: results from 2 successive trials with SiO$_2$ nanoparticles. Right: results obtained with different sizes of PSL nanoparticles.
The method has been then also qualified with calibrated polystyrene-latex, PSL nanoparticles of size ranging from 40 to 100 nm intentionally deposited on cotton fabric pieces. The results of Figure 3 show that the abrasion aerosolizes the deposited nanoparticles as the SMPS detect the same nanoparticles sizes than deposited.

4. First measurements

Then the qualified abrasion tool was used to characterize an advanced fabric piece made of a PET layer coated with an additional PVC layer containing or not nanoclays used as nanofiller (from IFTH, Lyon, France).

Submicron particles close to 80 nm are emitted by abrasion from both PET fabric and the PVC coating. This indicates that even conventional fabrics without nanofillers can release nanoparticles. A bigger nanoparticle peak is detected when testing the PVC coating containing nanoclays. Subtracting the background contribution from the PET + PVC without nanofillers allows obtaining a peak centered at 50 nm corresponding to the nanofiller (see the right curve of Figure 4). The maximum of this peak corresponds to the nanoclays size.

5. Conclusion

A new equipment to test the release-ability of nanoparticles contained in nanoproducts by abrasion is in progress at CEA to be more sensitive and accurate. The first results show that nanofillers can be released in usage by abrasion for non optimised nanoproducts. Other solicitations such as chocks and UV have also to be evaluated.

This type of equipment may be useful to protect the consumers by optimizing the hooking of nanoparticles in their matrix and perhaps one day to qualify the nanoproducts before their introduction on the market.

For this objective, a standardisation procedure at ISO is necessary in order to make this type of method recognised by all the stakeholders and regulation bodies.

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