# Measurement of nanofiller removal by abrasion

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## ABSTRACT

In the frame of the European NanoSafe2 project, CEA designed and qualified a specific bench test to measure the release of nanofillers from nanomaterials. In the proposed set up the material to be tested is mechanically solicited by abrasion using a normalized Taber equipment. The sensitivity of the method has been drastically optimized by reducing the background noise counts and the streaming air flow.

The results show that even materials without any nanofiller can generate nanoparticles when submitted to abrasion. Furthermore, tests show that nanofillers can be released in usage by abrasion for non optimised nanoproducts. This confirms the interest to develop such a method.

The normalized abrasion process itself is critical for the removal and the aérosolisation of the nanoparticles which both drive the sensitivity of the method. The abrasion process has to be optimized in a realistic and consensual way for standardization.

***Keywords***: nanosafety, Taber method, nanofillers, release, abrasion

## 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 21$^{st}$ century which could rank it alongside the automobile and microelectronics industries in terms of turnover.

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 i.e. the 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 therefore necessary.

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 already presented by the same authors at NanoSafe2008 [1] conference using a normalised Taber equipment is further discussed for measuring the release-ability of the nanofillers embedded in the nanoproducts under abrasion in order to mimic realistically one of the main types of solicitation in usage. An interesting recent paper from Vorbau et al. [2] reports on the development of a similar technique based on the circular Taber tool instead of the linear approach used in this paper.

The objective of developing such a measurement tool is double: optimization of the “hooking” of the nanoparticles in the matrix and perhaps one day, certifying the nano products before introducing on the market through new standards.

## 2 EXPERIMENTAL SETUP AND METHOD

In the frame of the European NanoSafe2 project [3], 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 1 000 nm.

The critical parameters to take into consideration to set up such a method for a standardization purpose is the sensitivity -appropriate solicitation, detection of the first few released nanoparticles- and to obtain 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. Another important point is to identify the more efficient abrasion method.

- 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 step by step to collect the maximum of the generated particles with the minimum collecting flow in spite of the abrasion head displacement.

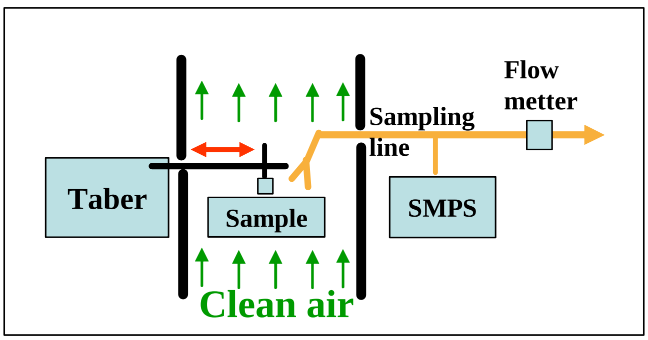


Figure 1: Schematic of the measurement tool.

Figure 2: Picture of the equipment set up designed at CEA.

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 nanoparticles embedded in matrix particles. On the other hand the CPC gives the number of nanoparticles only but is much more sensitive. To illustrate that, ones 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 wee need 10 events in the same 4 minutes in order to get a relevant number. This means that it is necessary 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 3 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 in order to mimic the nanoparticles released by the sample.

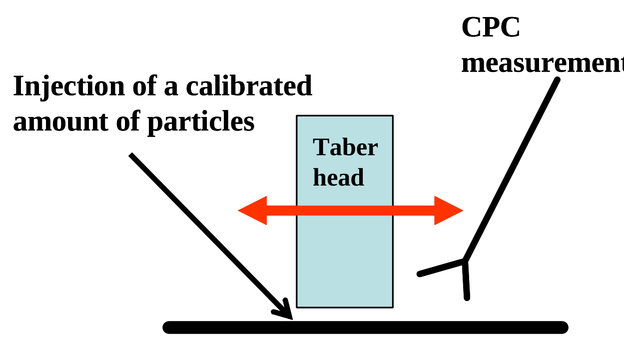


Figure 3: Schematic of the collection efficiency test.

Experimentally it was seen that the smallest nanoparticles are the most difficult to collect efficiently. As seen in Figure 4, for 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.


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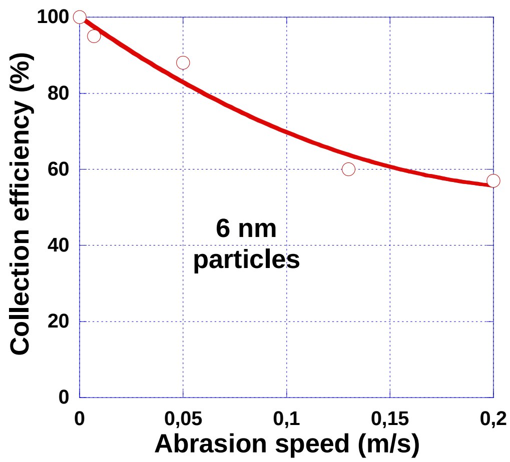


Figure 4: Collection efficiency versus the abrasion head speed for the smallest measured nanoparticles (6 nm).

Then a first qualification 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 leading to a poor attachment of the nanoparticles onto the media. First the background was quantified and estimated to be negligible. As seen in Figure 5, the measurements performed with the SMPS show a clear release of the deposited nanoparticles.

A second measurement after the first 4 minutes of abrasion (corresponding to the duration of the first SMPS measurement) 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.

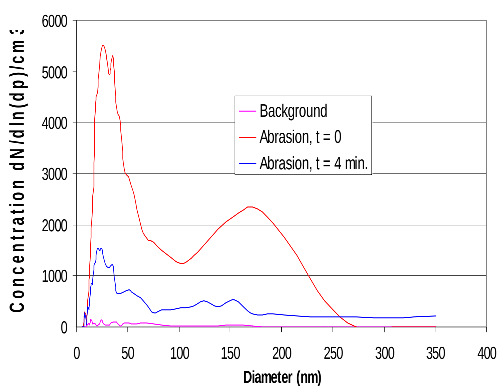


Figure 5: Release measurements of 20 nm $SiO_2$ particles deposited on a cotton fabric after 2 successive runs.

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 6 show that the abrasion aerosolizes the actually deposited nanoparticles as the SMPS detect the same nanoparticles sizes than deposited.

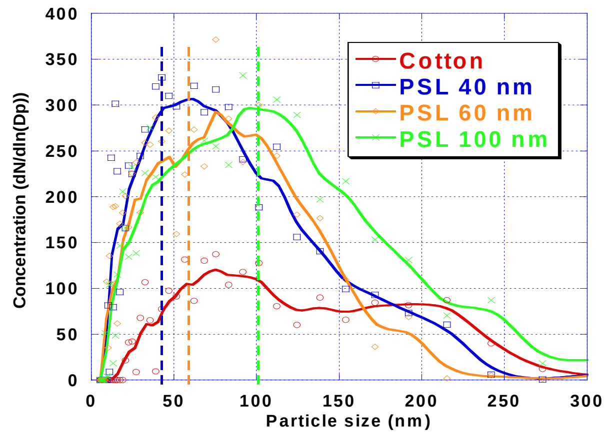


Figure 6: Release of calibrated PSL nanoparticles of 40, 60 and 100 nm intentionally deposited on a cotton fabric.

## 4 FIRST MEASUREMENTS

Then the qualified abrasion tool was used to characterize the nanoparticle release of different nanomaterials.
First, 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) was investigated.

Surprisingly, Figure 7 shows that the abrasion of the PET fabric and the PVC coating which do not contain any nanoparticles, generates nanoparticles close to 80 nm!
This indicates that even conventional fabrics without nanofillers can release nanoparticles.
A bigger nanoparticle peak is detected when testing the PVC coating containing nanoclays.

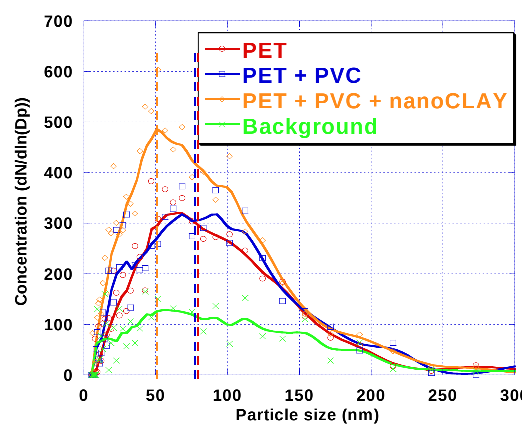


Figure 7: Abrasion test results obtained on a fabric constituted of a PET layer coated with a PVC coating containing or not nanoclays.

Subtracting the background contribution from the PET + PVC without nanofillers allows obtaining a peak centered at 50 nm corresponding to the nanoclays (see Figure 8). The maximum of this pick corresponds well to the actual size of the nanoclays mixed in the polymer.

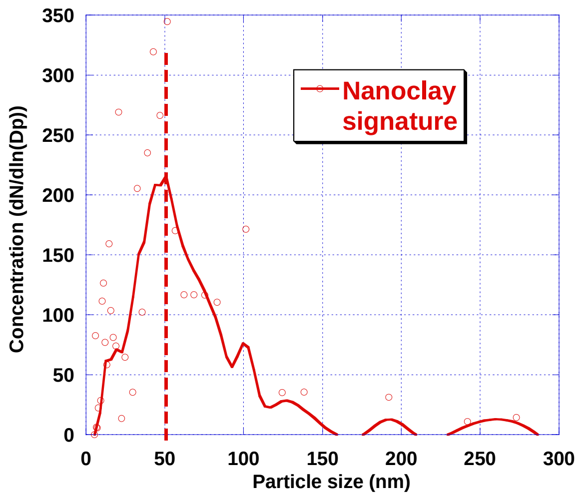


Figure 8: Calculation of the nanoclays contribution by subtracting the background contribution from the PET + PVC sample containing no nanofiller.

Many other tests have been performed with the described set up, on different industrial samples actually containing nanoparticles such as: socks with nano silver, paints containing nano $TiO_2$, etc. Only a few released nanoparticles were detected which does not allow giving significant data here. This, questions the relevant aspect of the normalised Taber test which could not be the most efficient method to aerosolise the nanoparticles from matrix by abrasion. Indeed, in the Taber tests, the just released nanoparticles may be sticked back to the media. Other abrasion solicitations have to be evaluated (brush, comb, etc.). We have to take into consideration the realistic aspect of the mechanical solicitation too. This is an interesting debate for future discussions in the frame of standardisation commissions.

## 5 CONCLUSION

A new equipment to test the release-ability by abrasion of nanoparticles contained in nanoproducts was developed in the frame of NanoSafe2 project. Progresses have been obtained in terms of sensitiveness and accuracy.

- The first results show that even materials without nanoparticles can generate nanoparticles by abrasion.
- Another conclusion is that nanofillers can be released in usage by abrasion for non optimised nanoproducts.
- The abrasion process itself has to be optimised to give, in a realistic way, the higher release and then the higher aérosolisation of the nanofillers.

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 certify 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.

## REFERENCES


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