Release-ability of nano fillers from different nanomaterials

Part 1: Aerosolisation of nanoparticles just deposited at the top surfaces

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ABSTRACT

It is of great interest to set up a reproducible and sensitive method able to qualify the nanomaterials before their market introduction in terms of their constitutive nanoparticle release-ability in usage. The same team already optimized during 3 years a specific method using a normalized abrasion by a Taber tool. In this work, new practical solicitations are investigated on the basis of a theoretical approach of the release phenomena in dry conditions of nanoparticles just deposited on hard and soft surfaces (the "micro football kick out effect"). It is shown that a metallic rake used roughly on both hard and soft nanomaterials surfaces can be 10 times more efficient than the Taber method. Nanoparticles smaller than 50 nm are almost impossible to remove even using very rough solicitations.

Keywords: nanosafety, nanomaterials, nanoparticles, release, shock solicitation

1 INTRODUCTION

Nanosciences and Nanotechnologies provide many opportunities to significantly improve materials properties and sustainability. The current and projected applications of engineered nano particles span a very wide range of industrial and consumer sectors such as: biomedicine, pharmaceuticals, cosmetics, new sources of energy, environmental analysis and remediation, material sciences, etc. From an economical point of view, the so called "nanoproducts" industry can rapidly compete with microelectronics or automotive in terms of annual turnover.

At the same time, the potential impact of these new materials on human health and the environment is viewed with apprehension by citizens. A growing body of scientific evidence indicates that exposure to certain types of nanoparticles, *e.g.* carbon nanotubes, can lead to harmful effects. Therefore, in the frame of a responsible development, the industry have to introduce nanoparticles in their materials 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 very reach polymorphism of nanoparticles together with the multitude of sizes, surface charges, etc. it will probably take a very long time to identify which nanoparticles present an acceptable risk compared to the benefit of their use. To be able to use safely nanoparticles in advanced materials before decades, we have to remind that 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. Therefore, the only pragmatic way to introduce on the market safe nanomaterials in a reasonable delay consists in reducing the exposure to nanoparticles of the potentially exposed workers, the consumers and the environment close to zero.

So, it is of prime importance to know how to characterize the release of single nanoparticles, aggregates or nanoparticles embedded in a bigger piece of the matrix during usage solicitations such as mechanical, thermal, UV degradation, shocks, etc.

It is now well recognised that the most dangerous route of entry for nanoparticles in human body is aerosols entering the respiratory track. The authors already presented different works dealing with the measurement of the release ability of nanofillers by abrasion using a standardised Taber equipment [1, 2]. 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.

Finally, for the majority of the pre-industrial nanomaterials tested for industrial partners with this abrasion solicitation -even with our successively optimised generations of test bench in terms of sensitivity- it was almost impossible to detect, any release of single nanoparticles. This is probably good news but the question still pending is: does any other non-standardised method able to reproduce a particularly efficient solicitation close to what can occur actually in usage exist?

In this paper, we go back to basics by fist trying to determine the most efficient -but still realistic- solicitations in usage able to aerosolise the easiest nanoparticles to remove from the nanomaterials: the ones just maintained at the top surface of the material by van der Waals forces (nanoparticles not partially embedded in the matrix nor linked by any covalent bonds).

2 EXPERIMENTAL SETUP AND METHODS

Different samples such as paper, PA6, nylon fabrics (clean room suit) and glass are prepared by dropping 10 μL of commercial solutions of PSL nanoparticles (25 g/L) and uniformly manually spread on a surface of approximately 2 cm^2. Then the solution is dried by natural air. PSL particle contained in the solutions are initially measured by a SMPS (electrostatic classifier 3080 + DMA 308100 + CPC 3075) from TSI in terms of electrical mobility diameters, by using a sprayer 3076 from TSI: the measured particle distributions are centred on 188, 122, 96, 88 and 50 nm. The aerosolised PSL particle distribution curves are reported in green lines in the Figures 3, 4, 5 & 6 as references.

As represented in Figure 1, the tested solicitation tools are: a vibrating engraver tool from Dremel with a round tip, a home made stainless steel rake and a metallic brush. The friction Taber test bench has been described in reference [1].

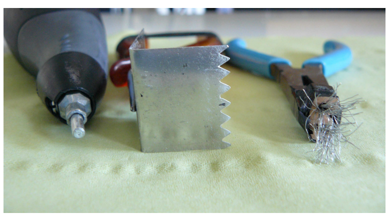

Figure 1: Solicitation tools used in this work: a vibrating engraver, a stainless steel rake and a metallic brush (after hard use!).

As seen in Figure 2, the sample is disposed in a clean glove box using a light air flow filtered with an H14 HEPA filter leading to a very low background level of nanoparticles (5-10 $/cm^3$). The different tools are used manually (except the abrasion solicitation) thanks to the gloves of the glove box. The collecting device is a simple antistatic tube located at about 1 cm of the sample; it is connected to a pump of 10 L/min. The measurement of the expected released nanoparticles is performed by the same SMPS presenting a flow rate of 6 L/min and connected to the aspiration line.

The operator is using a new sample each time and is making carefully the most possible repeatable movement with the tool, during all the SMPS measurement (2 min). For the Taber test, 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.

A first test on each sample types without any deposited nanoparticles is initially performed to adjust the strength of the solicitation in order not to generate an important level of background.

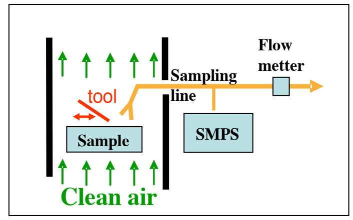

Figure 2: Schematic of the bench test and a picture of the equipment (at this time using the Taber device).

3 THEORETICAL CONSIDERATIONS AND VALIDATION OF THE FORCES ABLE TO REMOVE DEPOSITED NANOPARTICLES

As already depicted by Tardif et al [3], the four main forces which drive particle adhesion/removal mechanisms at the nano scale (1-100 nm) are electrostatic, van der Waals, capillary and drag forces in liquids; gravitational, Archimedes and hydrostatic forces being totally negligible. In the air, only 2 forces are dominating: van der Waals and electrostatic forces. In order to have a chance to remove nanoparticles deposited on a surface, it is first necessary to overcome the van der Waals forces, electrostatic particle/substrate repulsion will then help to hold the nanoparticles off.

The usage-like solicitations able to remove the particles of the substrate surface in air could be among abrasion already investigated: shocks, vibration, scratches, etc. Finally, theses solicitations have to produce a strong acceleration leading to the only force able to compete with van der Waals forces.

$$F_{vdW} = \frac{AR}{6h^2} \qquad (1)$$

With:

R: Particle radius (spherical particles)

h: Particle-substrate distance: minimum equal to the Lennard-Jones distance of h_0 = 0.4 nm for the considered materials.

A: Hamaker constant (depends on the particle, substrate materials and on the nature of the media: interaction transmission).

The counter force generated by an acceleration γ acting on the particle is given by:

$$F_\gamma = m \cdot \gamma \qquad (2)$$

With:

m: Particle mass

γ: Acceleration given to the particles

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Table 1 gives the calculated accelerations necessary to overcome the van der Waals forces for different spherical particles deposited on glass. One can easily see that gigantesque accelerations are necessary to remove so small particles and even higher accelerations are requested for smaller particles (as a function of $1/R^2$). Another conclusion is that the different nanoparticles present Hamaker constants in the same order of magnitude: results obtained with PSL spheres are therefore quite generic.

		Al2O3/SiO2	SiO2/SiO2	PSL/SiO2
Size (nm)	Hamaker (J)	9,60E-20	6,30E-20	7,50E-20
200	FvdW (N)	1,00E-08	6,56E-09	7,81E-09
200	**Acceleration (m/s2)**	**5,97E+08**	**7,84E+08**	**1,87E+09**
100	FvdW (N)	5,00E-09	3,28E-09	3,91E-09
100	**Acceleration (m/s2)**	**2,39E+09**	**3,13E+09**	**7,46E+09**
50	FvdW (N)	2,50E-09	1,64E-09	1,95E-09
50	**Acceleration (m/s2)**	**9,55E+09**	**1,25E+10**	**2,99E+10**

Table 1: Accelerations necessary to overcome van der Waals forces, the Hamaker constants are calculated from reference [4].

The necessary accelerations cannot bee supplied by conventional vibrations but by an instantaneous shock on the particle (like a football kick-out), or for example by a sudden dilatation of the substrate under a laser beam as demonstrated by Wu and co-workers (2000). This was confirmed by a first test consisting in the deposition of 200 nm PSL particles on a membrane of a loudspeaker installed in our clean test bench. No particle release was detected whatever the frequency (10-10 000 Hz), the power (10 W) and the signal type.

In order to validate the capability of strong shocks to remove deposited nanoparticles, a vibrating mechanical engraver was first used on PSL nanoparticles deposited on glass substrates. First measurements performed by using the engraver just beside the area where the particles are deposited confirmed the loud speaker experiment. On the other hand, when the engraver is applied directly on the deposited particle area, the 188, 122, until 88 nm deposited nanoparticles are removed: see Figure 3 & 4. The shocks generated by the engraver are not sufficient to remove the smallest particles: 50 nm, see Figure 5.

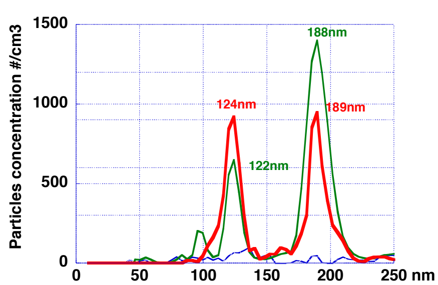

Figure 3: Removal of 188 and 122 nm PSL particles deposited on glass using a vibrating engraver (the green curve corresponds to the initial particle distribution contained in the liquid samples. The blue curve corresponds to the same sample without any deposited nanoparticles).

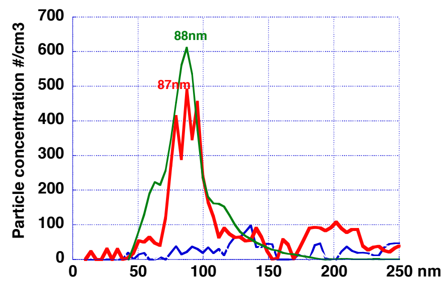

Figure 4: Removal of 88 nm PSL particles deposited on glass using a vibrating engraver.

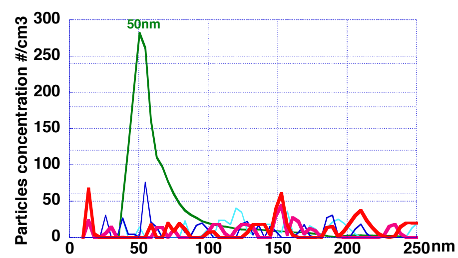

Figure 5: Removal of 50 nm PSL particles deposited on glass using a vibrating engraver.

These results confirm the ability of direct shocks to remove nanoparticles from surfaces until particles as small as 88 nm. Then different test tools more able to mimic actual usage solicitations and susceptible to generate micro shocks are designed, tested and there removal efficiency are compared.

4 COMPARISON OF THE REMOVAL EFFIENCY OF DIFFERENT TOOLS ABLE TO INDUCE SHOCKS ON THE PARTICLES

Different tools were tested on the fabric sample with deposited PSL particles. The operator using the brush and the rake on a textile feels clearly the vibrations induced by the discontinuous progression of the teeth of the rake and the hairs of the brush in the wires of the fabric. This discontinuous movement is expected to induce at the microscopic scale instantaneous local shocks on the particles or/and on the substrate.

Figure 6 shows as an example the results obtained on the bigger PSL particles which confirms the shock effects induced by the brush. Same is observed for the metallic rake.

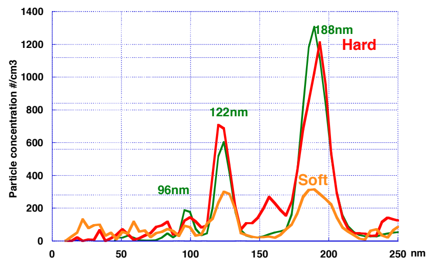

Figure 6: Removal of 188, 122 and 96 nm PSL particles deposited on fabrics using a metallic brush. The harder the brush sollicitation and the higher the removal efficiency.

Figure 7 summarizes the different particle removal efficiencies of the rake, the brush and the abrasion by Taber method in terms of the ratio: particle concentration released by the substrate with deposited particles/particle concentration released by the same substrate with no deposited particles.

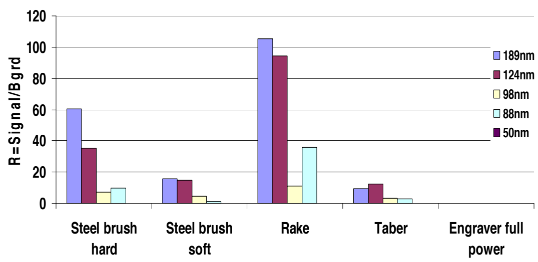

Figure 7: Compared performances of the different particle removal methods used in this work, on fabric substrates.

We verify that in agreement with the forces calculated in Table 1, smaller particles are generally more difficult to remove than bigger particles. For the different tools used even hardly, the forces induced by the shocks are not sufficient to remove particles smaller than 50 nm. The engraver has no removal effect on soft materials.

Finally the most efficient tool on fabrics is the rake. The rake solicitation which mimics scratches is about 10 times more efficient than the standardised Taber method used in our previous works.

Is the rake able to remove the nanoparticles on surfaces whatever the substrate type?

5 RAKE REMOVAL EFFICIENCY ON DIFFERENT MEDIA

Figure 8 shows the different results of PSL particle removal obtained on different substrates: paper, PA6, glass and fabrics.

Acknowledgements

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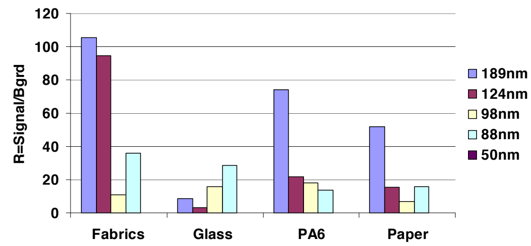

Figure 8: Compared results of PSL particle removal on paper, PA6, glass and fabrics by the rake tool.

The operator feels the vibration induced by the rake on all the substrate types even on PA6 and glass with an increasing frequency when the material is harder. Finally, the rake is able to remove the nanoparticles on both hard and soft surfaces. The higher efficiency is obtained on fabrics. Again, none of the tested solicitation tools are able to remove the 50 nm particles.

6 CONCLUSION

To be able to remove nanofillers from nanomaterials, a usage solicitation has to first be able to remove particles just deposited on the top surface. Due to the tiny mass of the nanoparticles, very huge accelerations are necessary to generate forces able to compete with van der Waals forces. These accelerations can originate from instantaneous shocks only (like a micro football kick out). A metallic rake or a steel brush moved hardly, both simulating rough but still realistic usage solicitations are generating a succession of shocks on the particles leading to removal efficiencies much higher than the standardized Taber method. As expected, the smaller particles were the most difficult to remove, no solicitation tested in this work was able to remove nanoparticles smaller than 50 nm which are literally trapped on the surface by van der Waals forces. A metallic rake moved roughly on the nanomaterial surface removes efficiently the nanoparticles deposited on both soft and hard materials.

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