Nanoparticle release from nano-containing product, introduction to an energetic approach

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ABSTRACT

The use of nanoparticles in manufactured products becomes more and more frequent and could lead to new potential risks for the workers, the consumers and the environment. This study focused on the R&D process of a nano-structured part; the stress operated during this process was reproduced into a nanosecurised facility, in order to characterize possible release of nanoparticles from the product. It appears that the release of nanoparticle is proportional to the energy applied on the surface. The particle release have been studied for three energy levels. The maximum particle concentration was around 10 p/cc for scratching operation, 380 p/cc while sawing and above 100.000 p/cc while sanding. Stress tests operated on a non nanostructured part induce also a release of nanoparticles.

Keywords: energy, abrasion, coating, nanoparticle, release

1 INTRODUCTION

Nowadays, with nanotechnology, consumer products become self-cleaning, antibacterial, UV-resistant... The effects of nanoparticles are not well known and represent a possible risk for people and the environment. The mechanical behaviour of nano-containing products has to be studied during their whole life-cycle. For this, INERIS develops new methods and tools allowing the characterization of the nanoparticles released into the air from the product.

A first study demonstrates the release of nanoparticules from both nanocomposite and standard material while drilling and sanding [1]. Abrasive wear is a very common wear mechanism. Taber-based tests, reproducing daily-life stress, have also been applied on polymer coatings containing nanoclay [2] and nanometric zinc oxide [3]. The concentration level of released nanoparticle from these products is very low and the particles remain embedded in the polymer matrix. Effects of sanding on nano-enabled paints have also been studied [4].

In this context, car manufacturer RENAULT is investigating the mechanical properties of nanomaterials, in the frame of the FOREMOST European Project. The company asked INERIS to determine whether there are nanoparticle releases from a nanostructured part during the R&D process. This metallic part, coated with inorganic fullerene, was designed for lowering the friction coefficient to reduce vehicle fuel consumption. The aim of this study is to reproduce representative operations of the process that are: unpacking, handling, roughness measurement and fracturing for microscopy observation. Accidental scenarios such as surface rubbing or the falling of the part have been considered.

2 TOOLS & METHODS

The stress tests have been operated sequentially, in order to evaluate a potential impact of each operation, in term of particle concentration. After a stress, the stabilization of the level of particle concentration was necessary to separate a possible input for the next test.

A first attempt was done on a nanostructured sample part to optimize and validate the whole experimental protocol. The main testing was led on three nanostructured sample parts, which are supposed to be the same, to evaluate the reliability of the results. Two standard parts, which are not coated with the nanostructured layer, have also been tested for particle release comparison.

2.1 Instrumentation

The choice of the devices allows informing about total concentration in number, on a range of time as short as possible to detect brief emissions, and about size distribution from 10 nm up to 20 μm.

Instruments are SMPS with long DMA (TSI 3080 coupled to 3031) and an optical counter (Grimm 1.108) for size distribution. The use in parallel of two CPC (TSI 3785 and Grimm 5.400) gives more reliability to the results when measuring low-level concentrations.

Device	Range	Sampling time
TSI 3080+3031	[10 nm ; 500 nm]	235 s
TSI 3785	[4 nm ; 1 μm]	1 s
Grimm 5.400	[4 nm ; 1 μm]	6 s
Grimm 1.108	[0.3 μm ; 20 μm]	6 s

Table 1 : Range and sampling time of the devices

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2.2 Nano-safety

Throughout testing, the following security principles have been followed: the stress was applied in a nanosecurised facility which consists in a double-containment of the controlled atmosphere, by putting a glove-box within a venting hood. When they are outside of the nanosecurised facility, sample parts were systematically contained in two plastic bags, in order to avoid nanoparticle release into the ambient air.

2.3 Experiment

At the end of each experiment, the glove-box and every tool within were cleaned with a dust repellent spray. The controlled atmosphere was recycled, to reach a background noise level lower than 1 p/cc.

The tools used during the experiment were: a hand saw, a vise and a needle. Concerning the inlet flow rate, its value was equal to the devices flow consumption, which was around 4.5 lpm. A sampling point was set above the nanostructured surface to exhaust the maximum of particles released into the air. The description of each test is given in the following table.

#	Description	Aim
1	Extraction from the safety bag	Is there any nanoparticle release when handling the part?
2	Plastic bag agitation	
3	Part extraction from plastic bag	
4	Part moves in 3 dimensions + shock test	
5	Surface rubbing with glove	Accidental scenario #1
6	Falling from a height of 20 cm	Accidental scenario #2
7	Surface scratching (3 directions)	Is there any nanoparticle release during roughness measurement?
8	Surface sawing	Is there any nanoparticle release during sample preparation for microscopy?
9	Surface sanding	Extreme stress

Table 2 : Description and aim of the stress tests.

3 RESULTS

3.1 Nanostructured part

Stress tests 1 to 7 generate emission peaks that are around 10 p/cc. While sawing, emission peaks in a range from 50 to 1,000 p/cc are measured (see Fig. 1).

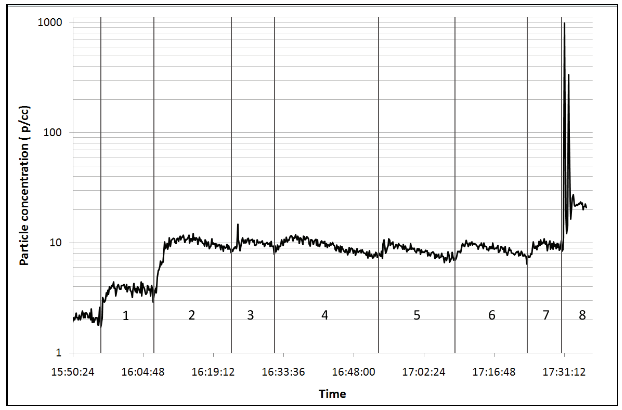

Figure 1 : Particle concentration through time while testing a single nanostructured part (except sanding).

3.2 Comparison with standard part

The same tests as those described in table 2 were applied on a standard part which does not contain nanoparticles. The particle concentration during tests 1 to 6 is in a range from 4 to 12 p/cc. In comparison with a nanostructured part (see Tab. 3), no specific emission –that is the difference between the emission peak and the background noise– was detected during the scratch test. Also, no scratch was observed on the standard part while the nanostructured layer is damaged and thus involves a particle emission. The nanostructured layer is less wear-resistant than the non nanostructured surface. Sanding results are not representative while testing the standard part because the surface was too hard for the abrasive wheel.

#	Test	Nanostructured part	Standard part
1	Extraction bag #1	+	+
2	Bag agitation	+	+
3	Part extraction	+	+
4	Handling + shock	+	+
5	Surface rubbing	+	+
6	Part falling	+	+
7	Surface scratching	+	< 1
8	Surface sawing	++	++
9	Surface sanding	++++	

Table 3 : Comparison of particle emissions between nanostructured and standard parts.

3.3 Surface sanding

A Dremel 400 DIGITAL has been used to force particle release by sanding the surface, even if this stress does not appear during the R&D process. Velocity of rotation was 19,000 rpm, using an aluminum oxide abrasive wheel. The machine engine is located outside of the glove-box, to avoid nanoparticle release from the brushes.

The surface sanding generates higher particle emissions than that observed during the previous stress tests. The particle concentration is above 100,000 p/cc and depends on the worn surface area.

Size distribution is unimodal with a mode included between 30 and 40 nm. Also, 95% of the measured particles have a diameter range which is 10 nm to 100 nm (see Fig. 2).

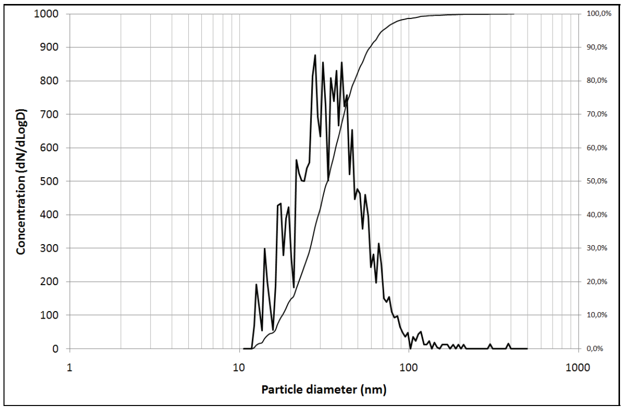

Figure 2 : Particle size distribution while sanding.

4 DISCUSSION

When handling the part, either nanostructured or not, the devices measured particle emissions in a range from 4 nm to 1 μm. In the both cases, the particle concentration level was very low. The situation is different while sawing or sanding the surface. The emission induced by the sawing test remains short-time emissions while the sanding test generates a high concentration. A comparison is made between three stress tests: scratching, sawing and sanding (Fig. 3). The maximum particle concentration is the mean value of the highest emission peak measured with CPC while testing the three nanostructured parts.

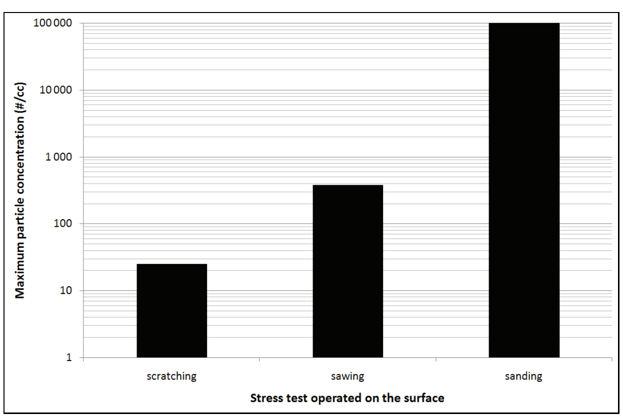

Figure 3 : Maximum particle concentration for three stress test.

The maximum particle concentration is clearly due to the brutality of the stress. Scratching, sawing and sanding represent low, medium and high energy mechanical processes respectively.

Figure 3 suggests that there is a relationship between the maximum particle concentration and the energy applied on the surface. Because of this, an estimation of the energy loss by friction, to determine an order of magnitude of these processes, is made (see table 4) with the following equations [5]:

- For scratching and sanding :

$$E_d = \mu \times F_N \times d \tag{1}$$

- For sanding :

$$E_d = \mu \times F_N \times r \times \omega \times t \tag{2}$$

With E_d the energy loss (J), F_N the normal load (N), d the crossed distance (m), μ the friction coefficient, r the radius of the abrasive wheel (m), ω the velocity of rotation (rad.s^{-1}) ant t the stress duration (s).

Process	Energy loss (J)
Scratching	0.01
Sawing	0.4
Sanding	2.0

Table 4 : Estimation of the energy loss.

Figure 4 represents the relationships that can be established between the maximum particle concentration and the energy loss.

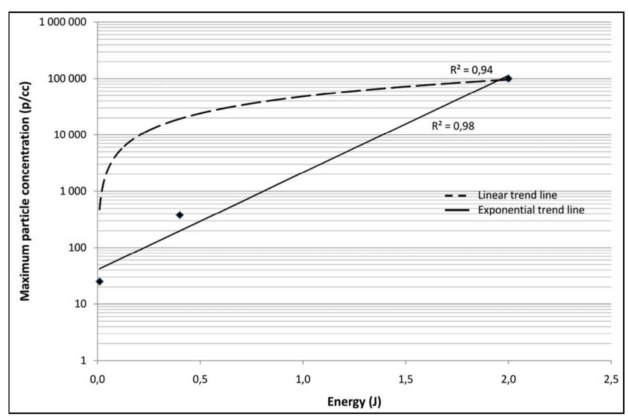

Figure 4 : Relationship between maximum particle emission and energy loss.

As a first approach, two trend lines can be defined : a linear and an exponential functions, both of them with a correlation coefficient R^2 higher than 0,90. It clearly

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appears that a strong correlation exists between the particle release and the energy applied on the coating.

More data are required, in order to determine which trend line is the more suitable to describe the relationship between the maximum particle concentration and the energy loss.

5 CONCLUSION

The objective of this study was to evaluate a possible nanoparticle release into the air from a metallic part coated with inorganic fullerene, during the R&D process in Renault laboratories.

The stress operated on the nanostructured parts during this process have been reproduced successfully into a controlled atmosphere. The impact of each action on the surface has been identified. Even in the case of low-level emissions, the devices made possible to detect some particle release.

When comparing with a standard part, emissions due to the nanostructured layer were identified. The nano-coating starts to be damaged while scratching whereas the standard part remains intact, due to the differences of hardness between the nanostructured coating and the standard surface. During sawing process, nanoparticle emissions duration stills short, independently of the maximum particle concentration. The surface sanding generates an aerosol which size mode is centered around 30-40 nm with a distribution width from 10 to 100 nm. However, for a normal use, the particle release is under 10 particles per stress, whereas the total particle concentration into the ambient air is above 10,000 p/cc.

A relationship between the maximum particle concentration and the energy loss during the stress test has been approximated, meaning that threshold values can be defined to forecast the mechanical behavior of the layer during specific uses. More stress tests, with different levels of energy, are required to refine the relationship between the energy loss and the maximum particle concentration.

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