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Measurement of Nanoparticles Release during Drilling of Polymer Nanocomposites

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Abstract. Nanomaterials are one of the promising technologies of this century. The Project on Emerging Nanotechnologies [1] reports more than 1600 consumer products based on nanotechnology that are currently on the market and advantages link to the reinforcement of polymeric materials using nano-fillers are not to demonstrate anymore. However, the concerns about safety and its consumer perception can slow down the acceptance of nanocomposites. Indeed, during its life-cycle, a nanotechnology-based product can release nano-sized particles exposing workers, consumers and environment and the risk involved in the use and disposal of such particles is not well known. The current legislation concerning chemicals and environment protection doesn't explicitly cover nanomaterials and changes undergone by nanoparticles during the products' life cycle. Also, the possible physio-chemical changes that the nanoparticles may undergo during its life cycle are unknown. Industries need a standard method to evaluate nanoparticles release during products' life cycle in order to improve the knowledge in nanomaterials risk assessment and the legislation, and to inform customers about the safety of nanomaterials and nanoproducts. This work aims to propose a replicable method in order to assess the release of nanoparticles during the machining of nanocomposites in a controlled environment. For this purpose, a new experimental set-up was implemented and issues observed in previous methods (background noise due to uncontrolled ambient environment and the process itself, unrepeatable machining parameters) were solved. A characterisation and validation of the chamber used is presented in this paper. Also, preliminary testing on drilling of polymer-based nanocomposites (Polyamide-6/Glass Fibre reinforced with nano-SiO₂) manufactured by extrusion and injection moulding were achieved.

1. Introduction

Nanomaterials are one of the most promising technologies of this century. They are defined as materials composed of several phases one of which has at least one dimension of less than 100 nanometers [2]. Usually, a nanocomposite is a matrix (like ceramic, metal or polymer) with an addition of nanofillers of varying shapes, like spheres, fibres, platelets, particles, or tubes, and of different chemical compositions.

Nowadays, industrial sectors, such as automotive or aerospace industry, include more and more nanocomposites materials in their products. In fact polymer-matrix nanocomposites seem to be a good alternative to replace metallic parts. They allow a considerable weight and cost reduction, and the use of nanofillers presents some advantages compared to traditional macro or microfillers: good



mechanical properties, high energy absorption capability, recyclability, resistance to corrosion and chemical attack, high heat-distortion temperature, etc [3]–[5]. Compared to the traditional reinforcement, the addition of nanofillers in polymer implies a minor increase in the cost but reduces the weight. Actually, it is known that an addition of only 5wt.% of inorganic nano-particles in polymers is enough for a considerable improvement of the material's behaviour and properties compare to 20wt.% for a micro filler [6]–[10]. These improvements can be explained by the fact that fillers in nano-size allow a high volume-to-surface ratio of the nanoparticles, and so an increase of the contact surface between matrix and fibre [11]. It also allows a low inter-particles distance compare to microsize fillers and reduces stress concentrations around the fillers.

However, the risk involved in the use and disposal of such particles is not well known. The current legislation concerning chemicals and environment protection doesn't cover nanomaterials. Nevertheless the release of nano-sized particles from nanotechnology part can be a risk for human health and environment, and especially the physio-chemical properties of the nanoparticles embedded into the polymeric-matrix are unknown along the whole life cycle of the nanomaterials. Industries need a standard method to evaluate nanoparticles release during products' life cycle in order to improve the knowledge in nanomaterials risk assessment and the legislation, and to inform customers about the safety of nanomaterials and nanoproducts. It is safe to say that, given the explosive R&D and commercial uptake of nanomaterials (for example, the number of submissions per year to the Journal of Nanoparticle Research increased every year and reached 2149 in 2013 [12]), unsurprisingly, the regulations governing the use and disposal of nanomaterials during its life cycle is behind the curve. The wide acceptance of nanotechnology by the consumers depends on alleviating the perceived safety related concerns. In this context, many projects, aiming to understand the effects of nanomaterials usage on human health and environment, were and still are funded by the European Commission. Project Nanopolytox studied the "toxicological impact of nanomaterials derived from processing, weathering and recycling from polymer nanocomposites used in various industrial applications" [13], and SIRENA the SIMulation of the RElease of NANomaterials from consumer products for environmental exposure assessment, which is funding this study. We can also cite MARINA (Managing Risks of Nanomaterials) and NanoValid (Developing References Methods for Nanomaterials).

The SIRENA project aims to demonstrate and validate a methodology to simulate the unintended release of nanomaterials from consumer products by replicating different life cycle scenarios to be adopted by a wide number of industrial sectors in order to get the necessary information for exposure assessment [2]. In order to replicate different stages of products' life cycle, two types of experiments will be conducted: crashing (to simulate accidental or intended fractures), and drilling (which is a common procedure in different stages of product's usage phase). During these experiments, nanoparticles released have to be collected, sampled and characterised (chemical composition, shape, size, quantity, size distribution), in order to know if they present a risk to human health and environment. The main motivations of this work are:

- Provide different industrial sectors with a standard method to evaluate the release of nanoparticles from nanoproducts during their life-cycle, and so link to the potential risk on human health and environment.
- Increase and improve actual knowledge in nanomaterials risk assessment, in order to implement EU legislation in relation to chemicals and environmental protection.
- Inform consumers and general public about the safety of nanomaterials and nanoproducts, in order to allow a successful penetration into market and sustainability of Nanotechnology.

The work presented in this paper is part of the SIRENA project and aims to assess the release of nanoparticles during the machining of nanocomposites. The protocol developed in NEPHH project for the simulation of the release of nanoparticles was replicated and tested for this purpose. The results and deficiencies observed with this protocol led to the implementation of a new experimental set-up. A characterisation and validation of the chamber used for this work was done in order to assess the controllability of the environment and the replicability of the experiments. Also, preliminary testing on

drilling of polymer-based nanocomposites (Polyamide-6/Glass Fibre reinforced by nano-SiO₂) manufactured by extrusion and injection moulding were achieved.

2. Replication and assessment of the NEPHH protocol

The first step of this work was to assess the NEPHH protocol [14]. For this, we replicate the experiments with a similar method. The analysis of the results highlighted several deficiencies that are presented in the following part.

2.1. Replication of the NEPHH protocol: Materials & Methods

2.1.1. Materials. The materials used for the replication of the NEPHH protocol are flat donut-shape rings of 4mm thick. The dimensions of the samples were 160mm for the external diameter and 100mm for the internal one. The materials studied were three-phase polymer matrix nanocomposites: Polyamide-6 (Durethan B30) reinforced by 30wt.% of Glass fiber (ThermoFlow 672) and different percentage of either nano-SiO₂ (Aerosil R 974) or organically modified Montmorillonite (OMMT, Dellite 43B). The nanocomposites were prepared at Fraunhofer – Institute of Chemical Technology (Germany), by direct melting extrusion in a twin-screw extruder at a maximum temperature of 280°C. The product was cooled in a water bath, pelletized and dried. The samples were injected moulded from the pellets produced. The composition of the different grades can be found *Table 1*.

Table 1: Composition of the studied materials

	Type of Matrix	wt.% of PA6	Type of Glass Fibre	wt.% of GF	Type of filler	wt.% of filler
PA/GF/OMMT 5wt.%	Durethan B30	65	ThermoFlow 672	30	Dellite 43B	5
PA/GF/OMMT 7.5wt.%	Durethan B30	62.5	ThermoFlow 672	30	Dellite 43B	7.5
PA/GF/OMMT 10wt.%	Durethan B30	60	ThermoFlow 672	30	Dellite 43B	10
PA/GF/SiO ₂ 0.5wt.%	Durethan B30	69.5	ThermoFlow 672	30	Aerosil R 974	0.5
PA/GF/SiO ₂ 1wt.%	Durethan B30	69	ThermoFlow 672	30	Aerosil R 974	1
PA/GF/SiO ₂ 1.5wt.%	Durethan B30	68.5	ThermoFlow 672	30	Aerosil R 974	1.5
PA/GF/SiO ₂ 3wt.%	Durethan B30	67	ThermoFlow 673	30	Aerosil R 974	3

2.1.2. Methods. The method used replicated the protocol defined during the NEPHH project [15]. The generation of particles by drilling was carried out in a closed chamber, with the following dimensions: width of 690mm, depth of 330mm and height of 560mm. The samples were fixed into the chamber and the angle drill (Makita BDA351Z 18V LXT Angle Drill) was totally enclosed into the chamber during all the measurement cycle. The emissions of nano-particles released were measured with a portable aerosol sizer and counter SMPS+C (Grimm Aerosol) composed by a Condensation Particle Counter (CPC) model 5.403 with a classifier type Vienna, long U-DMA. It allows a particle size resolution of 44 channels over a size range of 11.1-1083.8nm. The SMPS+C was connected to the chamber by an antistatic hose. An overview of the installation can be found in Figure 1 and Figure 2.

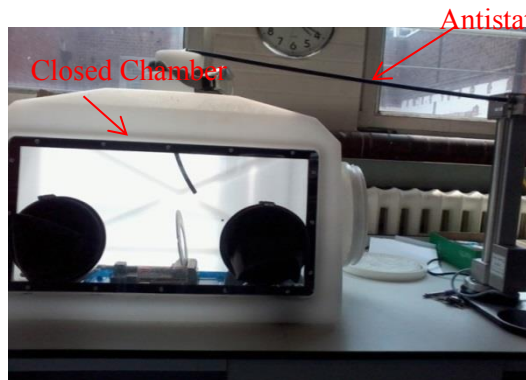


Figure 2: chamber connected to the

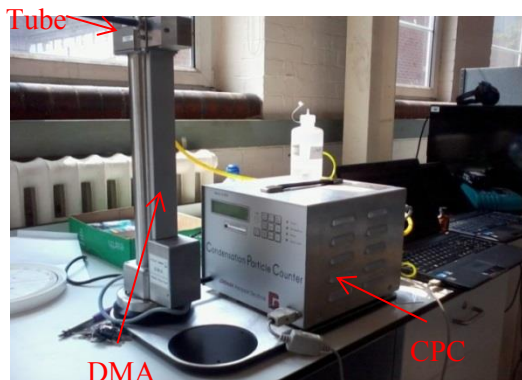


Figure 1: SMPS+C

The measurement cycle includes 20 minutes with the chamber open in order to purge it with lab air before the measurements. After, the chamber was closed and the measurements start with 30 minutes of record of the background noise, then a plate is drilled during 7 minutes, and the cycle finish with 60 minutes measurement of post-drilling.

The angle drill was used at its maximum speed: 1800 rpm; and two different sizes of drill bit were studied: 5 and 8 mm diameter. The experiment was repeated 3 times for each material composition and drill bit size. In addition, every morning one measurement cycle was conducted in order to record the noise of the drill itself.

2.2. Replication of the NEPHH protocol: Results and Identification of the Deficiencies

Results concerning the number concentration of particles along the time during the drilling of the different nanocomposites with a 5mm diameter drill bit are presented Figure 3. The background noise in the chamber recorded previous to drilling was around 10000 cm^{-3} . The concentration of particles was in every case at its maximum at the end of the 7 minutes of active drilling. Maximum airborne particles were comprised between 120000 cm^{-3} to 520000 cm^{-3} .

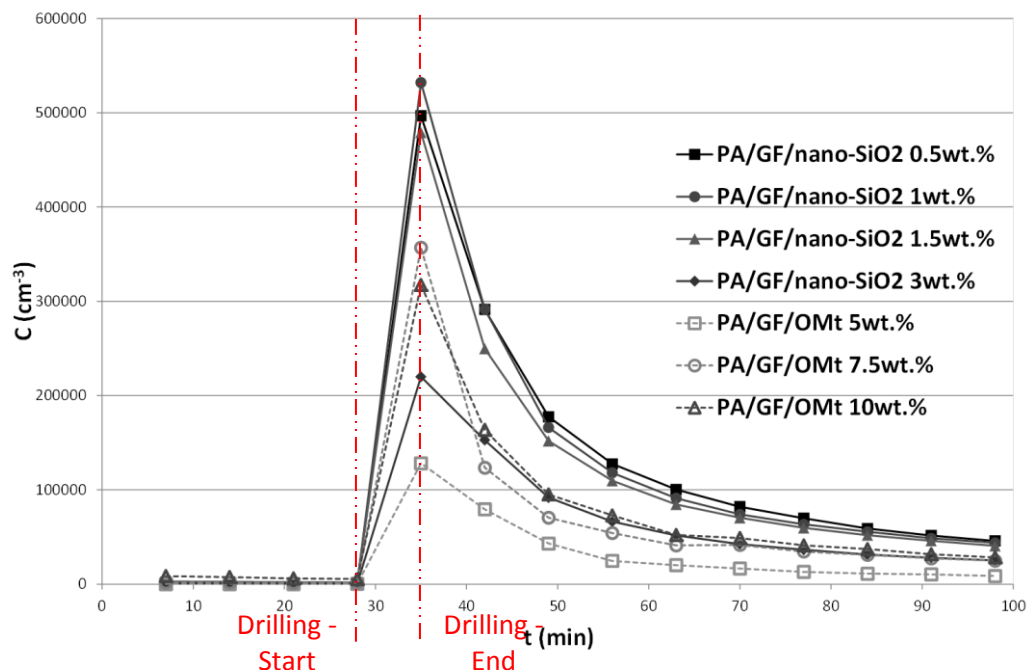


Figure 3: Number concentration of particles (C) vs time during the replication of NEPHH protocol for the 5mmØ drill bit

The replication of the experiments, these results and the analyses of several parameters showed some deficiencies of this protocol. The two main problems are the following:

- Variability of the process parameters: the spindle speed is controlled by an analogue switch with manual pressure. The speed is then only known when the pressure is maximal and cannot be controlled precisely. Also, the feed rate is determined by the pressure given by the operator on the manual drill. It is then dependant of the operator itself and totally variable during the experiment and not replicable. Figure 4 shows the difference in the particle size distribution between a manual pressure pushed around 4mm/min (corresponding to 7holes drilled in 7 minutes), and a manual pressure pushed around 1.14 mm/min (corresponding to 2 holes drilled in 7 minutes). The difference is significant and so the feed rate is a non-negligible parameters influencing the release of nanoparticles and needs to be controlled to insure replicable data.

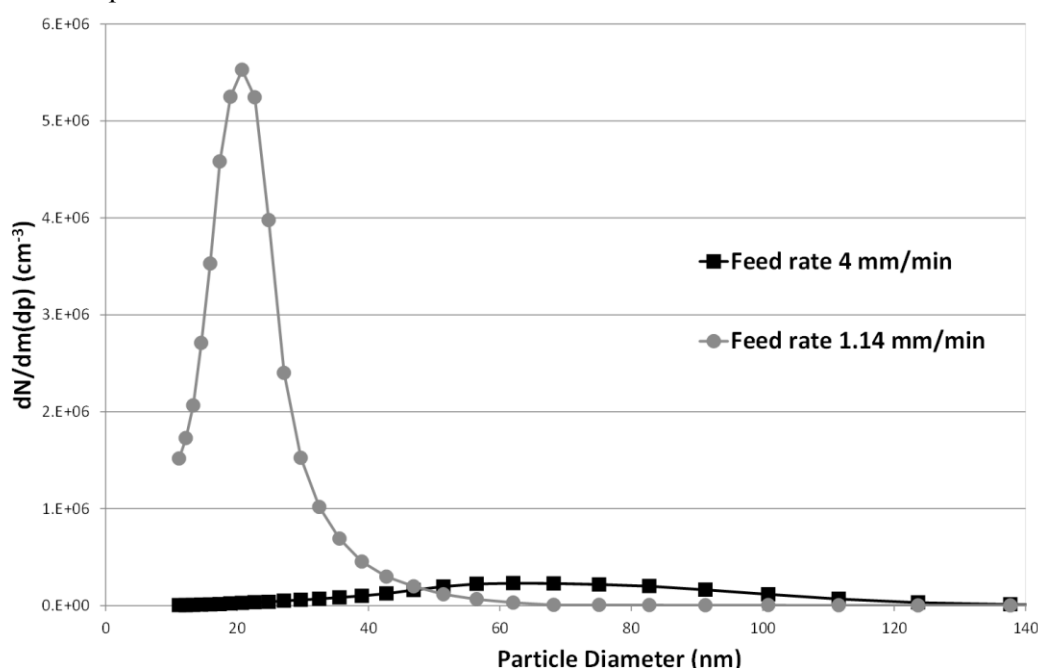


Figure 4: Normalised particle size distribution (dN/dm(dp)) inside the chamber at time 35 minutes - Study of the feed rate influence

- Influence of the background noises: first of all, in NEPHH protocol the chamber is purged with lab air during 20 minutes prior to drilling. The environment is dependant of the quality of the air in the lab and of the activities carried out in the same room. Also, every day, a blank test was done recording the level of particles when the manual angle drill was on, but no materials were drilled. Figure 5 presents the results of these tests for different day. It is clear that the manual angle drill itself is producing a significant level of particles (up to 700000 cm⁻³). Also, the level of particles generated by the drill is variable according to the day. Again, these tests show that the protocol used is not replicable, and the results of these experiments are not exploitable.

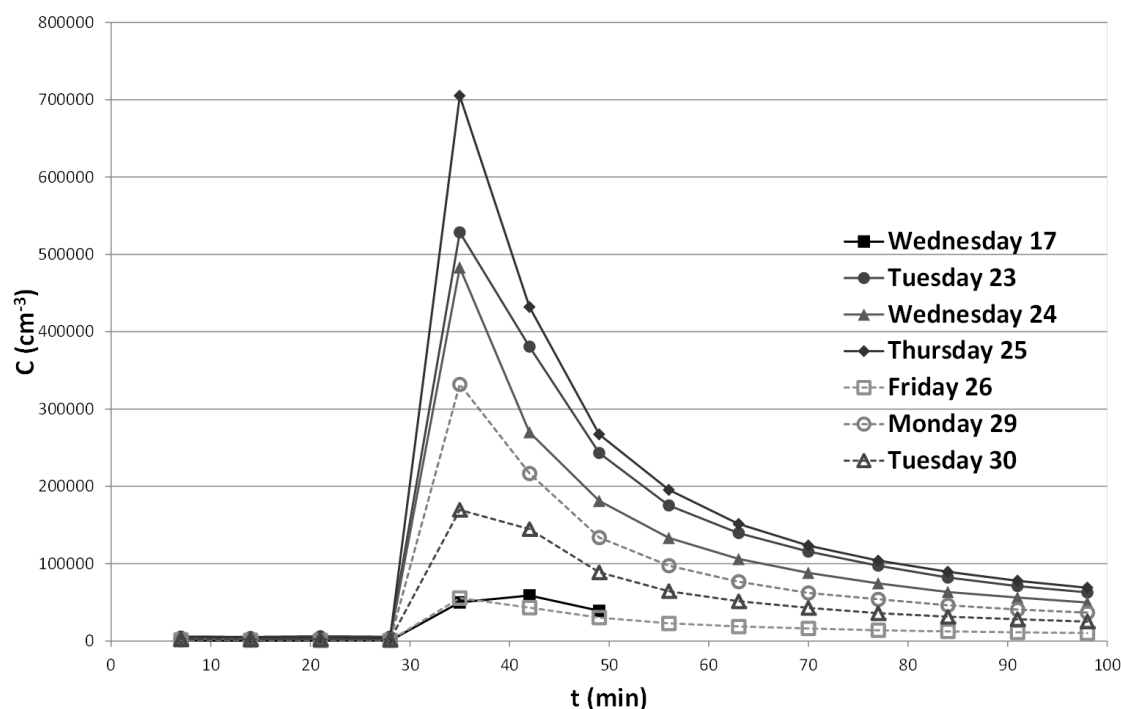


Figure 5: Number concentration of particles (C) versus time (t) for the particles released by the manual drill without sampling in different days (Blank tests)

3. Presentation and validation of the new protocol

3.1. Presentation of the prototype

Following the previous results, it was decided to implement a new system, presented Figure 6, in order to address these deficiencies and propose a robust and replicable method to assess the nanoparticle release during the machining of nanocomposites. The main features and elements of this system are:

- *Environmental control:* The environmental control system comprising of a sealed chamber with a fan, BenchVent I100-4, has been implemented. In addition, a pre-filter and HEPA filter (category H14) are used to clean the air inside the chamber. An air recirculation system was also implemented in order to reduce the amount of 'dirty' air from the room to enter the chamber. Also, the chamber was transformed into a glove box in order to reduce the time between the opening and closing of the chamber. This configuration ensures a good control of the environment inside the chamber, as well as protection for the operator

- *Automatic machining system:* A CNC machine was designed and built at Cranfield University (not off-the-shelf), which allows the precise control of drilling parameters (feed rate, spindle speed, etc.). This system makes it possible to have reproducible and repeatable experiments in a controlled environment. Additionally, a water cooled spindle drill is used in order to avoid background noise or particles produced by the motor, as the motor is totally sealed

- *Dust collection system:* A fixture system composed of a base plate made of antistatic polymer (Teflon HDPE), with a pattern to drill the holes in the samples was implemented. In addition, a Petri dish with lid, adapted for the drilling process, will be located on the surface of the sample. Therefore, the deposited fraction of particles could be easily collected into the Petri dish and will not be blown away because of the fan. Furthermore, the Petri dish will be sealed and used as a container. This way, the collection and storage of generated dust will be reduced to a single step

- *Instrumentation:* The scanning mobility particle sizer plus particle counter ('SMPS+C') from Grimm Aerosol was used to monitor the nanoparticles released. The 'SMPS+C'

comprises of a Condensation Particle Counter (CPC) model 5.403 with a classifier type Vienna, long U-DMA, for the measurement of the airborne particles. This equipment is connected to the chamber using antistatic hoses. The particle size range measured is from 11.1 to 1083.8nm distributed in 44 channels

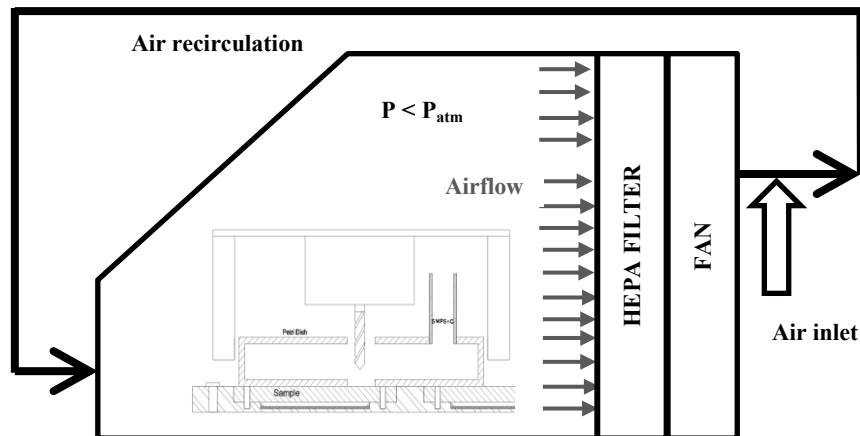


Figure 6: Scheme of the new configuration for the drilling prototype

3.2. Validation of the new protocol: Characterisation of the environmental background in the chamber

A baseline experiment was conducted in order to characterise the air inside the chamber. Results are presented Figure 7. We can see that the air in the room is usually around 6000 cm^{-3} . Then, when the fan is on, and the air recirculated, it takes around 2 hours to reach an acceptable level of particles inside the chamber under 1000 cm^{-3} . The environment is then stabilized and the average number of particles inside the chamber is 312 cm^{-3} , which is a first improvement compared to the chamber used previously.

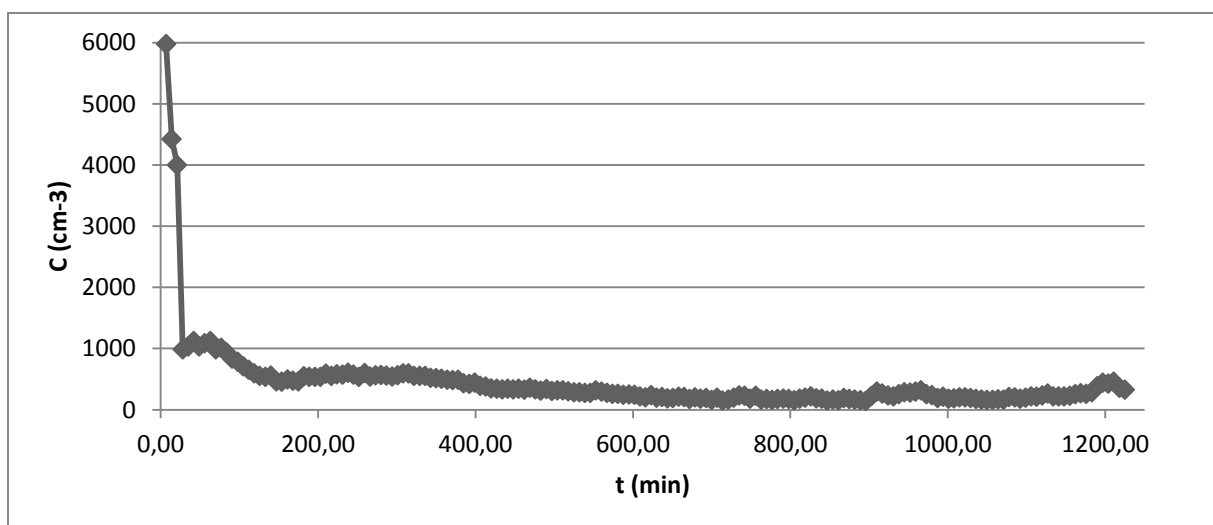


Figure 7: Baseline test of the air inside the chamber prior to cutting or drilling activities

3.3. Validation of the new protocol: Comparison between a manual angle drill and the CNC drill

In order to compare the new protocol with the protocol developed in NEPHH, the manual drill, used in the NEPHH experiments, was monitored. The manual drill was placed completely inside the chamber with the air recirculation system working (“fan on”). The manual drill was working for 7 minutes with a drill bit of 8 mmØ at maximum speed (1400 rpm). But no sample was machined. The air inside the chamber was monitored before using the manual drill and the airborne particles released by the drill (Figure 8). The hose for air inlet to the ‘SMPS+C’ was placed near the drill bit.

Inside the chamber, the average of C was about $590 \pm 75 \text{ cm}^{-3}$. In case of the manual drill, it was switch on for 7 minutes in 3 occasions, but drilling no sample. These occasions correspond to scans 9, 13 and 21, in which, C increased to 8688, 8066 and 4609 cm^{-3} respectively. Under similar operating conditions (7 minutes working but drilling no sample), for the CNC machine (scan 32) C increased only to 905 cm^{-3} . This experiment proved that, unlike the manual drill from NEPHH protocol, the CNC machine was not a contamination source. These particles are probably metallic ones produced by the engine of the manual drill which are metal brushes.

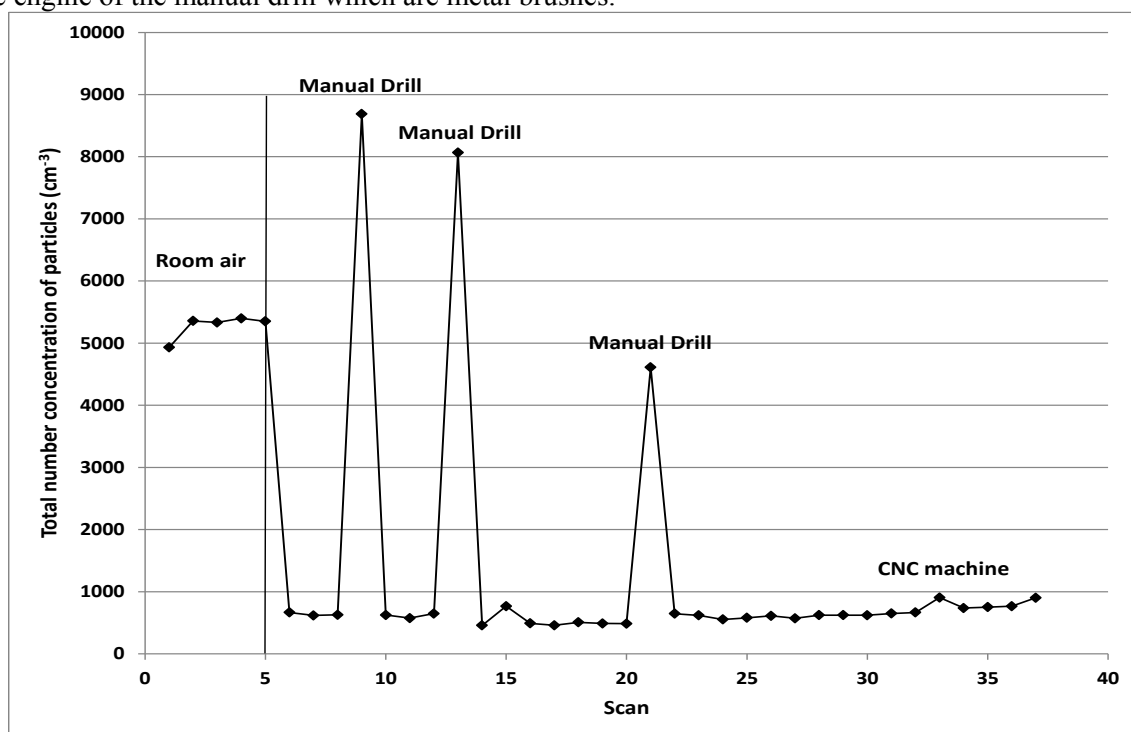


Figure 8: Characterisation of the release of particles from the Manual Drill and from the CNC machine. In scans 1 to 5 the room air is measured. Scans 5 to 38 measure the air inside the chamber. Manual drill on in scans 9, 13 and 21; and CNC machine on in scan 32

4. Preliminary testing on drilling of polymer-nanocomposites

After assessing the level of particles inside the chamber as background noise, first drilling experiments were conducted in order to validate the method for dust collection.

4.1. Preliminary Testing: Materials & Methods

Three holes were drilled in a Polyamide-6/Glass Fiber/3wt.% nano-SiO₂ at three different feed rate: 2mm/min; 20mm/min and 200mm/min. Every hole was drilled using a different Petri dish, which was sealed following the drilling. The spindle speed was set to 10000 rpm according to industrial guidelines.

4.2. Preliminary Testing: Results & Discussions

Pictures of the deposited particles collected in the three cases are available in Figure 9. Differences in shape and size could be noticed. From the hole drilled at 2mm/min, the particles were long and thin as filament, around 200 μ m diameter and 5mm long and several (around 30) particles could be found in the Petri dish. At a higher speed, 20mm/min, particles were fewer (less than 10) but bigger in size, 1mm large and few mm long. Size was more difficult to assess as the particles were shaped as remaining from a pencil sharpener. Finally, at high speed drilling, 200 mm/min, only one big piece of material was remaining after drilling.

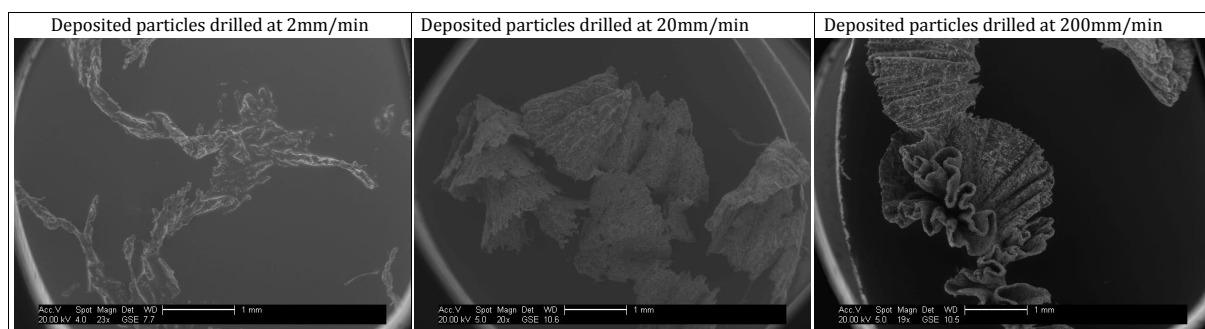


Figure 9: SEM pictures of the deposited particles at a micro scale

SEM images of the deposited particles generated by drilling at a nano scale can be found Figure 10. Nano-SiO₂ particles are provided as spherical particles with a diameter from 7nm to 50 μ m for the agglomerates. On the three images, spherical nanoparticles with a diameter under 100nm can be found. It is noticeable that more particles can be found at the surface of the deposited dust generated by drilling at higher feed rate. This can probably be explain by the fact than drilling at high speed produced big bites but accompanied with a large quantity of nanoparticles, as at lower speed, large amount of small micro-sized particles are produced but only a few quantity of nanoparticles is released from this mechanism. These assumption need to be correlated with a record of the airborne nanoparticles released during the experiments.

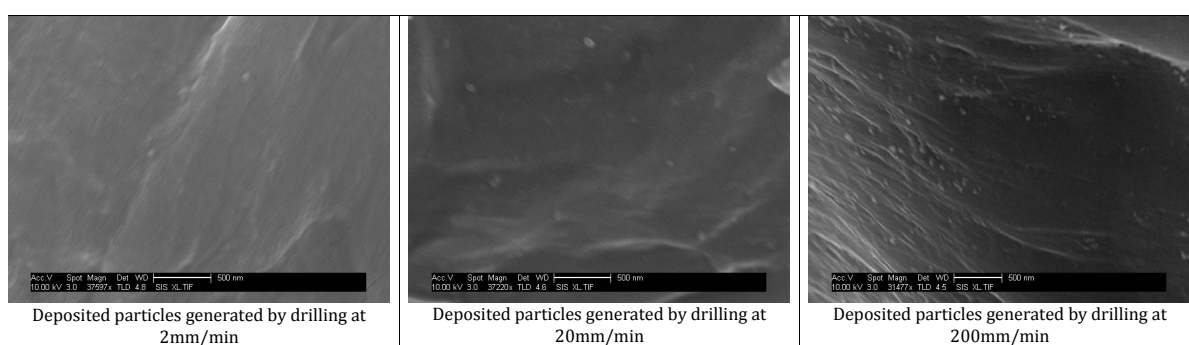


Figure 10: SEM pictures of the deposited particles at a nano scale

5. Conclusions

A new prototype and protocol have been developed to assess the release of nanoparticles from nanocomposites. An automated system controls the process parameters and there is precise control over the environment in the chamber where the experiments take place. In addition, safety

measurements are considered to protect the operator. In general, it can be concluded that the new prototype provides reproducibility and reliability, overcoming issues in the previous protocol like contamination from the manual drill, precise control of process parameters and reduction of the contamination from background.

Aknoledgment

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