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Environmental Particle Emissions due to Automated Drilling of Polypropylene Composites and Nanocomposites Reinforced with Talc, Montmorillonite and Wollastonite

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Abstract. In this study, the effect on nanoparticle emissions due to drilling on Polypropylene (PP) reinforced with 20% talc, 5% montmorillonite (MMT) and 5% Wollastonite (WO) is investigated. The study is the first to explore the nanoparticle release from WO and talc reinforced composites and compares the results to previously researched MMT. With 5% WO, equivalent tensile properties with a 10 % weight reduction were obtained relative to the reference 20% talc sample. The materials were fabricated through injection moulding. The nanorelease studies were undertaken using the controlled drilling methodology for nanoparticle exposure assessment developed within the European Commission funded SIRENA Life 11 ENV/ES/506 project. Measurements were taken using CPC and DMS50 equipment for real-time characterization and measurements. The particle number concentration (of particles <1000nm) and particle size distribution (4.87nm – 562.34nm) of the particles emitted during drilling were evaluated to investigate the effect of the silicate fillers on the particles released. The nano-filled samples exhibited a 33% decrease (MMT sample) or a 30% increase (WO sample) on the average particle number concentration released in comparison to the neat polypropylene sample. The size distribution data displayed a substantial percentage of the particles released from the PP, PP/WO and PP/MMT samples to be between 5-20nm, whereas the PP/talc sample emitted larger particle diameters.

1. Introduction

The use of sillicate nanofillers as mechanical reinforcements in polymers is increasingly being well established throughout literature. This has generated an influx into various high performance lightweight-material commercial industries such as the automotive industry [1]. To continue to improve performance and economical costs, industries are using nano-fillers to reinforce the composite materials. talc [2], montmorillonite (MMT) [3] and Wollastonite (WO) [4] are commercially available fillers increasingly being researched and introduced in the automotive industry. These micro and nano-sized fillers have however also shown potential cytotoxicity if exposed and inhaled [5-7]. However, there is still an insufficient understanding on how these fillers effect the release of nanoparticles to evaluate and

quantify the full risks associated to the emissions and nanoparticle exposure into the environment [8,9]. The results demonstrated within this paper are part of an ongoing study looking into the release and exposure of nanocomposite materials when under a simulated and controlled life cycle scenario: drilling process. This paper reveals some of the findings from PP-based nanocomposite materials reinforced with talc, MMT and WO. As to validate the improved properties and to support the link between mechanical performance and the nanoparticle release of the materials, the samples underwent a tensile test in accordance to ISO 527 [15] at a 2mm/min standard. The PP/WO sample demonstrated the same mechanical performance of the reference sample (PP/talc) with a 10% density decrease.

2. Experiments

2.1. Materials and Fabrication

A commercially available Polypropylene homopolymer was purchased from Lyondell Basell Industries (Moplen HP648T). A 20% talc filled polypropylene copolymer (Holstacom XM 2416) was also chosen from Lydonell Basell Industries as another reference material. The reinforcements and concentrations chosen were 5 wt. % Wollastonite (WO) from Nordkalk (Harwoll 7ST5) and 5 wt. % of montmorillonite (MMT) from Nanocor Corporation (Nanomer I30T).

The Coperion ZSK 26 MEGAcompounder twin-screw extruder was used for homogenization of the nanocomposites. The extruded pellets of the materials were moulded by injection process by means of an Arburg All Rounder 270C-300-100 Injection Machine. Due to the diverse polarity nature of the polypropylene and the MMT and WO, a coupling agent (POLYBOND 3200 from ADDIVANT) was used to ensure adhesion between the nanofillers and the polymer. Therefore, four sets of samples were fabricated: neat PP, PP with 20% talc, PP with 5wt. % MMT and 2 wt. % coupling agent, and PP with 5wt. % WO with 2 wt. % coupling agent. A common sample size of 70x45x5mm were prepared for the drilling investigations. The corresponding dog-bone standard sample was fabricated for the polymer reference standard ISO 527 tensile test [15].

2.2. Automated Drilling Procedure

The materials were tested using a purpose built controlled test chamber that allows direct measurement of nanoparticles emitted during drilling. The process is developed and initiated by the SIRENA Life project –an acronym for Simulation of the Release of Nanomaterials from Consumer Products for Environmental Exposure Assessment. This process is designed to simulate mechanical drilling on nanocomposite materials and is continued work from a previous European Commission funded NEPHH project titled 'Nanomaterials related Environmental Pollution and Health Hazards throughout their life cycle' (NEPHH, Project No. 228536) delivered by the same team of researchers [10]. The methodology allows for a categorical representation of the nanoparticles released from the material without any background interference and in higher accuracy than reported in the literature.

Based on industrial specifications and previous studies carried out on nanocomposite drilling, a standard Dremel 4000 drilling tool with an industrial standard stainless steel 3.5mm twist drill bit was used at 10000 rpm with a feed rate of 78mm/min [10-13]. The setup uses an automated drilling assembly operated externally to the chamber to permit a repeatable and controlled environment within the chamber as shown in Figure 1.

The closed steel chamber has dimensions of 740 mm x 550 mm x 590mm, and therefore a total inner volume of 0.240m^3. It is designed to assure a closed environment to simulate an appropriate volume around the drill and minimising electrostatic attraction to the surfaces. To quantify only the particles released from the sample, the chamber was initially cleared of particles through an inflow of clean air with the use of TSI 99.97% retention HEPA Capsule Filters. A separate capsule was constructed around the drill with separate air flow to avoid any interference of the drilling fumes on the particle number concentration within the capsule. The clean air system using the HEPA Capsule filters was capable of producing a particle number concentration reading within the chamber of 0 #/cm^3 as measured using a Condensation Particle Counter, CPC model 3783 at a flow rate of 0.6 litres per minute (lpm).

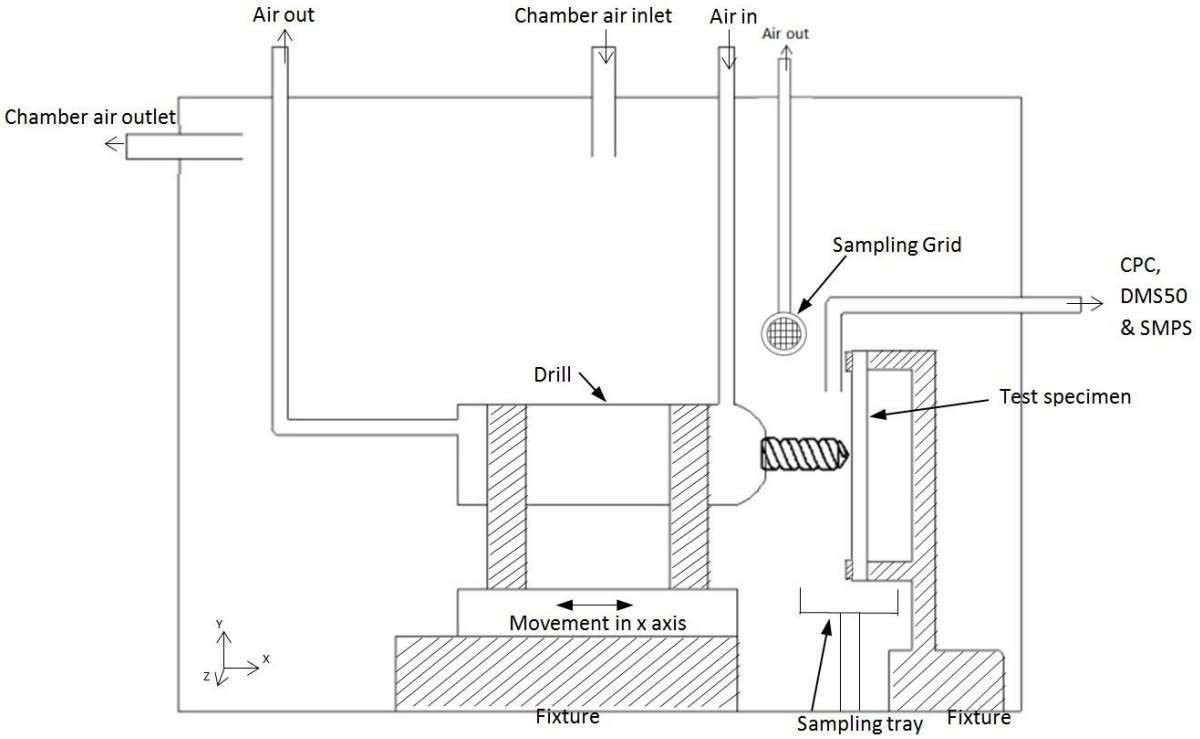

Figure 1: Schematic of automated drilling process setup within test chamber to remove background interfering particles and allow for a repeatable and controllable test procedure

An outlet channel is placed adjacent to the test specimen for the nanoparticle release equipment readings. A sampling grid for post-test analysis and characterization of the airborne particles was placed next the test specimen with a slight suction to attract and prevent particles from detaching away from the grid. An additional sampling tray was positioned below the test specimen for collection of the deposited particles for further post-test analysis.

A Cambustion DMS50 Fast Particle Size Spectrometer with a 1 second sampling period, inlet flow rate of 6lpm, with 34 distinct particle diameters of size range between 4.87nm – 562.34nm was used for the particle size distribution. This allowed for a size distribution every second compared to an SMPS of 55s and therefore an accurate representation of the particles being released from the sample in a given time. Particles released from the drilling were sampled as shown in Figure 1 to be analysed with an SEM, EDX and XRF were used but are beyond the scope of this paper.

3. Results and Discussion

3.1. Filler Effect on Particle Number Concentration

The polypropylene based nanocomposite samples underwent the automated drilling procedure described. Each test consisted of drilling eight holes within 3 minutes followed by 1 minute of no drilling. This methodology allows for both an investigation into the particles released at the instant of drilling and the remaining emissions airborne post drilling. Using the CPC, the particle number concentration was quantified in situ with a sampling rate of 1 second. An average of the repeated test for each sample is displayed in Figure 2.

The peaks observed in Figure 2 clearly exemplifies the eight holes drilled within the 3 minutes for the four PP based samples. On most of the peaks, the movement of the drill going in and out of the sample can also be seen from peaks being faintly divided into two peaks. When the drill is out of the sample, the particle number concentration is seen to drop between each hole being drilled. The particle number concentration can be perceived to then relatively stabilize during the 1 minute after the drilling has ended, but does not drop back to the initial 0 #/cm^3. Thus, the particles produced from the drilling remain airborne within the chamber environment.

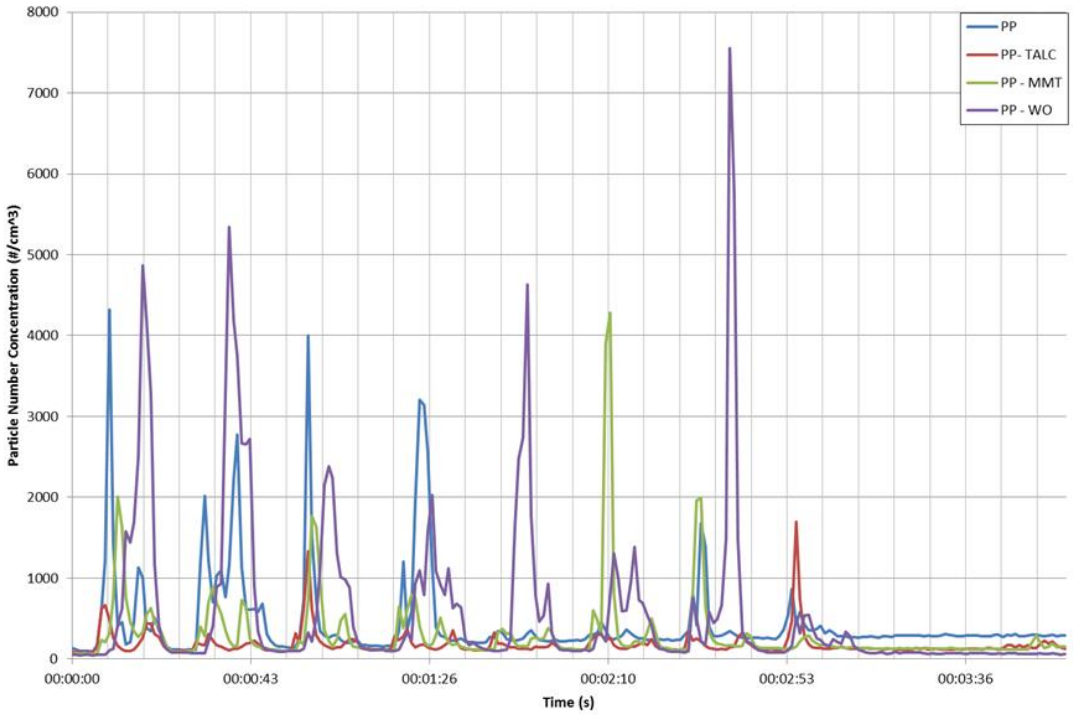

Figure 2: Particle number concentration of PP based nanocomposite samples during eight holes drilled within 3 minutes followed by 1 minute of no drilling

The PP/WO sample demonstrated the largest average peaks across the eight holes drilled when compared to the PP, PP/talc and PP/MMT. The PP and PP/MMT sample displayed similar size peaks during the drilling, whereas the PP/talc sample indicated the lowest peaks of all the samples. However, the PP/WO sample demonstrated to have the lowest particle number concentration at the end of the four-minute sampling period, and in contrast, the PP sample displayed the highest particle number concentration. Although, the PP/WO sample illustrated to have the highest peak value, peak average and total average over the entire four-minute sampling period, the sample presented the least particle number concentration at the end of the four minutes. The PP/WO released particles are therefore, perceived to deposit quicker than the three other samples. This conflicts with the nano-reinforced samples having a lower density to the PP or PP/talc sample. The lower particle number concentration after drilling is beneficial in relation to nanosafety and if considering materials safer by design, but the cause is ambiguous. The particles suggest being more reactive and either attracted to components within the chamber or agglomerating to larger particles the CPC is unable to pick up.
In relation to the average particle number concentration over the sampling period, PP/WO is the only sample that produced an increase in particles over the PP sample, with a 30% increase, compared to the decrease of 59% and 33% from the PP/talc and PP/MMT samples respectively. The nano-filled samples therefore, exhibited a converse 33% decrease (PP/MMT) or a 30% increase (PP/WO) on the particle number concentration released over the PP sample. However, these sets of results prominently indicate that the matrix has a substantial contributing factor on the particle number concentration when comparing the PP samples with other polymers. A similar trend with a silicate nanofiller producing the most particles during drilling and the influencing factor of the PP is observed in the NEPHH project reported in Irfan et al 2013 [14].

3.2. Filler Effect on Particle Size Distribution

Simultaneous to the data gathered for the particle number concentration, the particle size distribution was quantified in situ using a DMS50. This provides a better understanding of the size of the particles number concentration seen in the Figure 2. Additional to the DMS50, an SMPS was also utilised to evaluate the size distribution (not reported). In comparison to the SMPS which has a sampling period of

1 minute, the DMS50 generates a size distribution every second. This provides a more live visual of the nanoparticles as they are being released from the material before the particles are dispersed within the chamber.

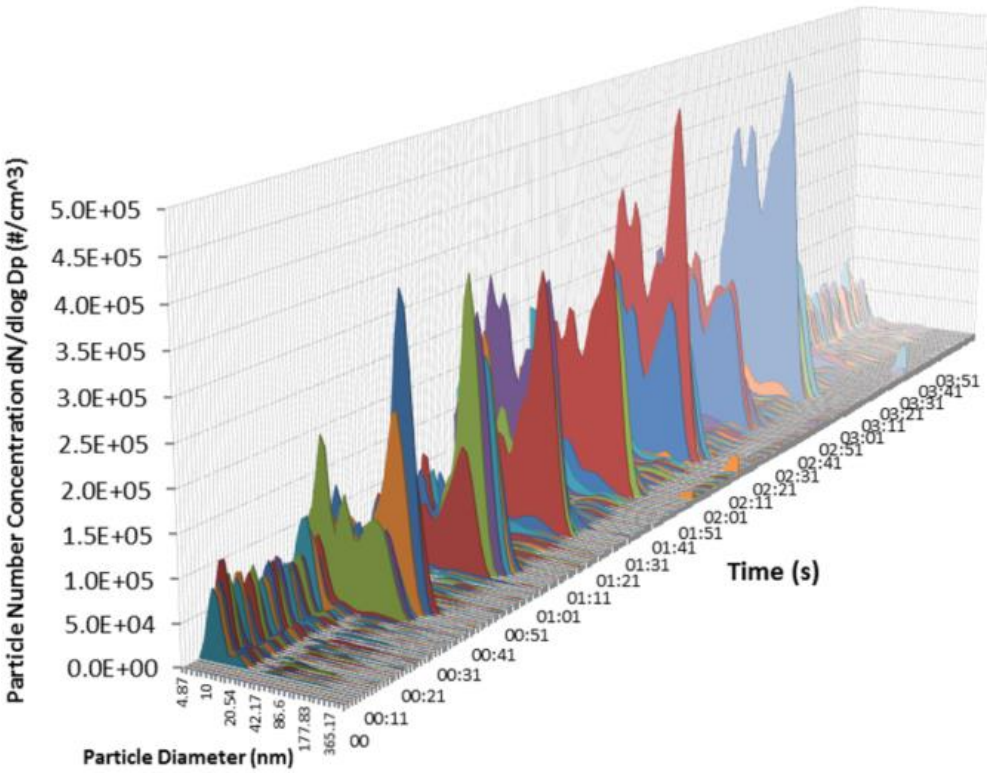

Figure 3: Particle size distribution over four minutes of PP/talc sample as measured on the DMS50

Since a size distribution is generated every second, Figure 3 illustrates the combination of the particle number concentration and its corresponding size distribution in a three-dimensional plot over the 4-minute sampling period. The drilling of the eight holes is perceivable with an initial introduction of particles for the first hole followed by 7 substantial peak concentration of particles emitted for the remaining holes. The size distributions between peaks and after drilling are less visible due to the high concentrations from the peaks. As indicated on the CPC data displayed in Figure 2, this highlights the vast particle concentrations produced at the time of drilling before the emissions disperse within the chamber and stabilise. Although the particles do stabilise and reduce in particle number concentration, a small percentage (<400#/cm^3) still remain airborne within the chamber environment. Figure 3 also demonstrates that the peaks of particles generated due to the drilling across the eight holes are relatively consistent in particle diameter. It is important to note that the data is taken from a separate run to the CPC and SMPS data due to the required increased inflow rate (6 lpm for the DMS50 compared to 0.6 lpm for the CPC) which is the probable cause for the increase in particle number concentrations relative to the CPC data represented in Figure 2.

Similar three-dimensional plots as illustrated in Figure 3 were generated for the four samples. In order to allow for a comprehensible comparison between the samples, a two-dimensional plot of the size distribution taken from the highest peak for each sample is displayed in Figure 4. The PP, PP/WO and PP/MMT samples revealed a substantial percentage of their particles between 5-20 nm particle diameter range. Therefore, the PP, PP/WO and PP/MMT appeared to release a greater proportion of particles with smaller diameters compared to the PP/talc sample. Despite exhibiting a peak at a greater particle diameter, it must be noted that the PP/talc sample released a high peak concentration of particles within the same diameters of other three PP-based samples. The data therefore suggests that the WO and MMT nano-sized reinforcements have little effect on the particle size distribution. The increase in particle number concentration seen in Figure 2 could be due to larger particle diameters as the CPC has a size range between 7-1000nm.

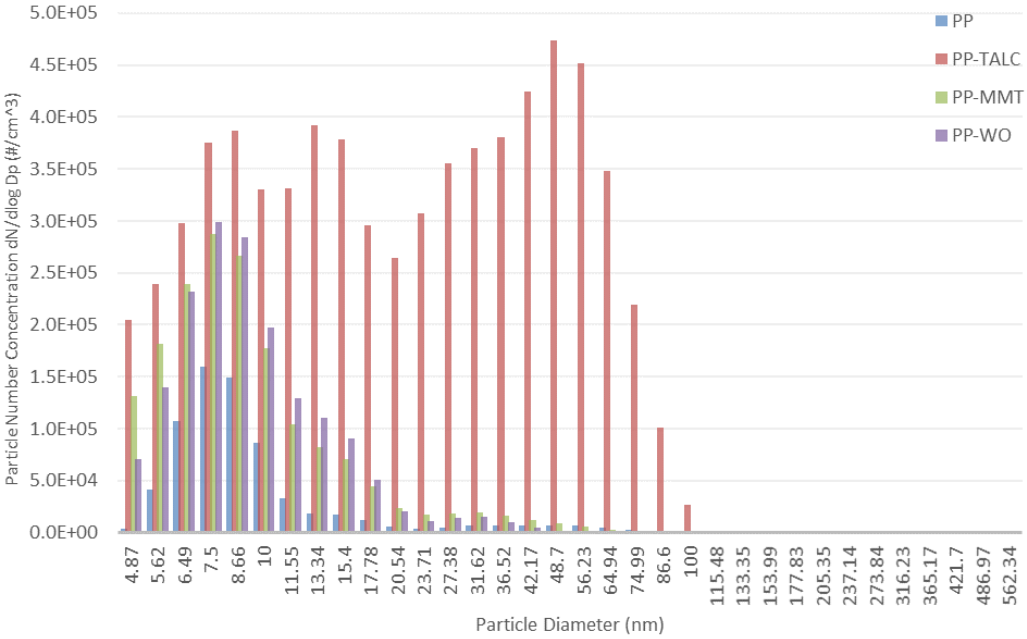

Figure 4: Particle size distribution of peak number concentrations during 4-minute sampling period for PP based nanocomposite samples recorded on DMS50

Figure 4 demonstrates that all samples released nanoparticles during the 4-minute sampling period, including the neat PP sample. None of the samples released particles between 115-562nm. The data from the particle size distribution reveals that the particles released are highly influenced by the PP matrix. The nano-reinforcements of WO and MMT did not demonstrate any additional nano-sized peaks in the DMS50 or the SMPS results, and must therefore be agglomerating or adhering to the matrix. The talcum reinforcement is the only filler showing an effect on the particle size distribution. This could also be due to the higher percentage of filler concentration. A further investigation is required to understand the nature of the larger particle diameter introduced by the PP/talc sample.

4. Conclusion

The automated drilling process validates a nanoparticle release testing methodology permitting a direct measurement of nanoparticle emissions into a clean chamber environment without any background interference. Talc and WO reinforced composites have both demonstrated nanoparticle release for the first time and compared to MMT. The initial data presented reveals minor difference in nanoparticle release between the four PP-based samples. All four samples exposed a concentration of nanoparticles introduced due to the drilling into the chamber environment. The nanofillers (WO and MMT) demonstrated both an increase and decrease in nanoparticle release, but no visible difference in particle size distribution. The higher concentration of talc as a filler had the biggest effect on particle size distribution compared to the other PP-based samples. The data presented is part of an ongoing study which will further investigate the initial findings and understand the causality of the results.

5. Acknowledgments

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6. References

[1] Njuguna J, Pielichowski K, Desai S. Nanofiller-reinforced polymer nanocomposites. *Polym Adv Technol* 2008;**19**(8):947-959.

[2] Lapcik Jr L, Jindrova P, Lapcikova B. Effect of Talc Filler Content on Poly (Propylene) Composite Mechanical Properties. *Engineering Against Fracture*: Springer; 2009. p. 73-80.

[3] Selvakumar V, Palanikumar K, Palanivelu K. Studies on mechanical characterization of polypropylene/Na -MMT nanocomposites. Journal of Minerals and Materials Characterization and Engineering 2010;**9**(08):671.

[4] Luyt A, Dramićanin M, Antić Ž, Djoković V. Morphology, mechanical and thermal properties of composites of polypropylene and nanostructured wollastonite filler. *Polym Test* 2009;**28**(3):348-356.

[5] Akhtar MJ, Ahamed M, Khan M, Alrokayan SA, Ahmad I, Kumar S. Cytotoxicity and apoptosis induction by nanoscale talc particles from two different geographical regions in human lung epithelial cells. *Environ Toxicol* 2014;**29**(4):394-406.

[6] Lordan S, Kennedy JE, Higginbotham CL. Cytotoxic effects induced by unmodified and organically modified nanoclays in the human hepatic HepG2 cell line. *Journal of applied toxicology* 2011;**31**(1):27-35.

[7] Maxim LD, McConnell E. A review of the toxicology and epidemiology of wollastonite. *Inhal Toxicol* 2005;**17**(9):451-466.

[8] Njuguna J, Pielichowski K, Zhu H. Health and Environmental Safety of Nanomaterials: Polymer Nancomposites and Other Materials Containing Nanoparticles. : Elsevier; 2014.

[9] Gendre L, Marchante V, Abhyankar HA, Blackburn K, Temple C, Brighton JL. Development of CNC prototype for the characterization of the nanoparticle release during physical manipulation of nanocomposites. *Journal of Environmental Science and Health*, Part A 2016;**51**(6):495-501.

[10] Sachse S, Silva F, Zhu H, Irfan A, Leszczyńska A, Pielichowski K, et al. The effect of nanoclay on dust generation during drilling of PA6 nanocomposites. *Journal of Nanomaterials* 2012;**2012**:26.

[11] Bello D, Wardle BL, Zhang J, Yamamoto N, Santeufemio C, Hallock M, et al. Characterization of exposures to nanoscale particles and fibers during solid core drilling of hybrid carbon nanotube advanced composites. *International journal of occupational and environmental health* 2013.

[12] Starost K, Njuguna J. A review on the effect of mechanical drilling on polymer nanocomposites. In *IOP Conference Series: Materials Science and Engineering* 2014 (Vol. **64**, No. 1, p. 012031). IOP Publishing.

[13] Starost K, Frijns E, Laer JV, Faisal N, Egizabal A, Elizextea C, Blazquez M, Njuguna J. The Effect of Drilling on Nanoparticles Release from Silica and Alumina Reinforced Polyester Nanocomposites. 7th International Symposium on Nanotechnology, Occupational and Environmental Health; 2015.

[14] Irfan A, Sachse S, Njuguna J, Pielichowski K, Silva F, Zhu H. Assessment of nanoparticle release from polyamide 6-and polypropylene-silicon composites and cytotoxicity in human lung A549 cells. *Journal of Inorganic and Organometallic Polymers and Materials* 2013;**23**(4):861-870.

[15] ISO B. 527-2: 1996. Plastics—determination of tensile properties—part 2: test conditions for moulding and extrusion plastics. *British Standards Institution*. 1996 Jul:1-4.