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Nano-sized Particles Emission during Drilling and Low Velocity
Impact of Silica-based Thermoplastic Nanocomposites

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PhD Thesis

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Abstract

During the past decade, polymer nanocomposites have emerged as a novel and rapidly developing class of materials and attracted considerable investment in research and development worldwide. Driven by the certainty that by the integration of low nanofiller amounts, existing material properties can be improved and moreover new material properties can be developed. Despite the clear benefit and therefore, increasing research, production and utilisation of nanomaterials, little is known about how nanocomposites will perform over their whole life cycle, especially in the usage and end of life phase. Under the influence of environmental factors such as ultraviolet light, moisture, temperature and mechanical actions, nano-sized particles can be potentially released from nanocomposites and thus may have negative effects on the human health and the environment.

Within the scope of this work an extensive literature review has been conducted in which polymer nanocomposites are briefly introduced and release scenarios of engineered nano-sized particles from nanocomposites during their life cycle are discussed. In the experimental part of this work silica based polypropylene, polyamide and polyurethane composites were manufactured and particle exposure mechanism during mechanical processing and testing were monitored and analysed. A series of comprehensive physical characterisation techniques were utilised to assess particle size distribution, shape, and concentration in different mediums, once emitted by the solid composite materials.

It was observed that during drilling of PA6 composites, the airborne particle emis-

sion rates were 10 times higher than those for the PP based composites. However, the characterisation of deposited particles showed exactly the opposite behaviour, were the total number of particles emitted by the PP based composites was 10-100 times higher than those of the PA6 based composites. To the best of our knowledge, this is the first time such work has been reported in the literature.

Further, the addition of secondary filler into a polymer/glass-fibre composites changed the micro-mechanism during crash testing and therefore controlled the energy absorption characteristics of the composites. However, it was shown that once subjected to higher impact energies the geometric particle size of the released particles increased from approx. 25 nm for the 530 J to approx. 60 nm for the 1560 J impact. Additionally, the tensile modulus increased by 0.31 GPa and the specific energy absorbed during impact test increased from 20.7 kJ to 22.6 kJ by using nano-SiO₂ alternative to micro-SiO₂ particles in PP/glass-fibre matrix. Even though a respective enhancement in mechanical properties were observed by using nanofillers over microfillers, no significant difference in particle emission during impact test were measured.

Further, it could be shown that during drilling and testing, nano-sized particles were released from all materials studied, regardless of whether they had nanoparticles integrated or not. In one particular case, the neat polymer matrix generated more nano-sized particles during drilling than the exfoliated PA6/nanoclay nanocomposite. Hence, the addition of nanoclay can have beneficial impact in terms of controlled particle release. However, in general the addition of nanofillers increased the particle emission rates during drilling and impact testing of the nanocomposites. Further, the emitted nano-sized particles were not all free engineered pristine nanoparticles but also hybrid particles consisting of matrix/nanofiller material. A significant set of data was obtained during this study and hence the outcomes sets an excellent foundation for risk assessment and life cycle analysis of silica based polypropylene, polyamide and polyurethane nanocomposites.

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Nomenclature

Latin symbols

C	Concentration
d_{001}	Crystallographic direction [001]
E	Elasticity modulus
e	Euler's number
H	Hight
H_c	Enthalpy of crystallisation
H_f	Heat of fusion
k	Removal rate
k_B	Boltzmann constant
P	Emission rate

R	Radius
r^2	Coefficient of determination
r_h	Hydrodynamic radius
t	Time
T_m	Melting temperature
V	Volume
$(x, \bar{y})^2$	Mean-squared speed

Greek symbols

α	Aspect ratio
η	Viscosity
θ	Diffraction angle
λ	Wave length
μ	Micro
π	Mathematical constant

χ Percentage of crystallinity

Acronyms

AFM Atomic force microscopy

APS Aerodynamic particle sizer

BAS Button aerosol sampler

CNT Carbon nanotube

CPC Condensation particle counter

DAQ Data acquisition system

DLS Dynamic light scattering

DMA Differential mobility Analyser

DSC Differential scanning calorimetry

EDX Energy-dispersive X-ray spectroscopy

ELPI Electrical low pressure impactor

ENP Engineered nanoparticles

<i>ESP</i>	Electrostatic precipitator
<i>FMPS</i>	Fast scanning mobility particle sizer
<i>FGC</i>	Foam-glass crystal material
<i>FTIR</i>	Fourier transformation infrared spectroscopy
<i>GF</i>	Glass fibres
<i>ln</i>	Natural logarithm
<i>LPI</i>	Low pressure impactor
<i>MMT</i>	Montmorillonite
<i>MWCNT</i>	Multi-wall carbon nanotube
<i>NAS</i>	Nanometer aerosol sampler
<i>NC</i>	Nanocomposite
<i>NP</i>	Nanoparticles
<i>NTA</i>	Nanoscale particle tracking analysis
<i>OMMT</i>	Organically modified montmorillonite

<i>PA</i>	Polyamide
<i>POM</i>	Polyoxymethylene
<i>PP</i>	Polypropylene
<i>PU</i>	Polyurethane
<i>PVC</i>	Polyvinyl chloride
<i>SAXD</i>	Small angle X-ray diffraction
<i>SEM</i>	Scanning electron microscopy
<i>SMPS</i>	Scanning mobility particle sizer
<i>SPI</i>	Silicon chip substrate
<i>SWCNT</i>	Single wall carbon nanotube
<i>TG</i>	Thermogravimetry
<i>TEOM</i>	Tapered element oscillating microbalance
<i>tan</i>	Tangents
<i>USD</i>	United States of America

USD United States dollar

UV Ultraviolet

WAXD Wide angle X-ray diffraction

wt. Weight

XRD X-ray diffraction

Chemical symbols and compounds

Al₂O₃ Aluminium oxide

Am Americium

COOH Carboxylic acid

Fe₂O₃ Iron(III) oxide

Kr Krypton

N Nitrogen

NaCl Sodium chloride

NO Nitric oxide

O	Oxygen
OH	Hydroxide
SiO_2	Silicon dioxide
TiO_2	Titanium dioxide
ZnO	Zinc oxide

Units

A	Ampere
$\text{\AA}$	Angstrom
$^{\circ}C$	degree Celsius
cm	Centimetre
kH	Kilohertz
K	Kelvin
kg	Kilogram
J	Joules

<i>l</i>	Litre
<i>m</i>	Meter
<i>min</i>	Minute
<i>mg</i>	Milligram
<i>ml</i>	Millilitre
<i>nm</i>	Nanometer
<i>Pa</i>	Pascal
<i>s</i>	Second
<i>V</i>	Volt
%	Percentage

Contents

1	Introduction	1
1.1	General Introduction	1
1.2	Motivation	4
1.3	Aims and Objectives	6
1.4	Thesis approach	8
1.5	Thesis Structure	9
2	Literature Review	11
2.1	Introduction	11
2.2	Polymer nanocomposites	12
2.2.1	Nanocomposites filled with nanoplates	13
2.2.2	Nanocomposites filled with nanoparticles	17
2.2.3	Impact behaviour of nanocomposites	19
2.3	Identification of release scenarios of nano-sized particles from nanocomposites	24
2.3.1	Nano-sized particles released from surface coating	27
2.3.2	Nano-sized particles released from nanocomposites	31
2.4	Measurement of airborne nano-sized particles	32
2.4.1	Scanning Mobility Particle Sizer (SMPS)	34
2.4.2	Fast Mobility Particle Sizer (FMPS)	36
2.4.3	Electrical Low Pressure Impactor (ELPI)	37

2.4.4	Tapered Element Oscillating Microbalance (TEOM)	37
2.4.5	Comparison of devices for measuring airborne nano-sized particles	39
2.4.6	Collection of airborne particles	42
2.4.7	Deficiencies of devices for measuring airborne nano-sized par- ticles	44
2.5	Conclusion	46
3	Physical characteristics of nano-sized particles emitted during drilling of polypropylene and polyamide 6 nanocomposites	51
3.1	Introduction	51
3.2	Experiments	53
3.2.1	Preparation of nanofillers	53
3.2.2	Preparation of polymer nanocomposites	55
3.2.3	Characterisation	56
3.2.4	Measurement of airborne particles concentration and size distribution	57
3.2.5	Sampling and characterisation of deposited particles	60
3.3	Results and Discussion	62
3.3.1	Nanofillers	62
3.3.2	Structure and morphology analysis of nanocomposites	66
3.3.3	Thermal properties of manufactured nanocomposites	75
3.3.4	Airborne Particle	79
3.3.5	Deposited particles	95
3.4	Conclusion	112
4	The effect of low velocity impacts on the emission of nano-sized particles from polypropylene and polyamide 6 nanocomposites	115
4.1	Introduction	115

4.2	Experiments	117
4.2.1	Material selection and preparation of test samples	117
4.2.2	Characterisation	119
4.2.3	Mechanical testing	119
4.2.4	Measurement of airborne particle number concentration and size distribution	121
4.3	Results and Discussion	122
4.3.1	Morphology of nano and micro composites	122
4.3.2	Quasi-static tensile test	127
4.3.3	Impact behaviour	127
4.3.4	Airborne particle emission during low velocity impact tests .	130
4.4	Conclusion	133
5	Influence of fracture at low velocity impacts on the nano-sized particle emission of sandwich structures with nanofilled foam cores	145
5.1	Introduction	145
5.2	Experiments	147
5.2.1	Synthesis of OMMT filled polyurethane foams	147
5.2.2	Fabrication of face sheet panels	147
5.2.3	Fabrication of sandwich structures	148
5.2.4	Foam characterisation	149
5.2.5	Quasi-static compression	149
5.2.6	Low energy impact testing	149
5.2.7	Characterisation of emitted dust particles	151
5.3	Results and Discussion	151
5.3.1	Morphology	151
5.3.2	FTIR and WAXS analysis of PU modified with OMMT . . .	153
5.3.3	Thermal stability	154

5.3.4	Quasi-static compression behaviour	156
5.3.5	Low energy impact behaviour	157
5.3.6	Dust emitted from PU/OMMT foam cores	171
5.4	Conclusion	177
6	Overall discussion	179
6.1	Experimental evidence of effects influencing particle emission during different release scenario	179
6.1.1	Effect of matrix type on particle emission	180
6.1.2	Effect of nanofiller type on particle emission	184
6.1.3	Effect of filler size on particle emission	185
6.2	Summary and recommendations	188
7	Conclusion and future work	191
A	Air monitoring instruments	227
B	Extrusion and injection moulding parameters	233
B.1	Recipes used for compounding of nanogranulates	233
B.2	Injection moulding parameters	235
C	EDX results	239
D	Injection moulding plates	243
E	NEPHH- Deliveable 1.3 Sampling Protocol	245

List of Figures

1.1	Application of nanocomposites in the automotive industry	3
1.2	Current state of the art and gap in knowledge	6
1.3	Definition of nanomaterials according to the recommendation of the European Commission	7
1.4	Work flow chart for thesis approach	9
2.1	Logarithmic isolines of interfacial (surface) area / volume of par- ticles ($\mu\text{m}^1 = \text{m}^2/\text{ml}$) with respect to the aspect ratio, $\alpha = \text{H}/\text{R}$, and largest dimension of particle ($\text{R} = \text{radius}$, $\text{H} = \text{height}$, length) based on approximating particles as cylinders ($\text{area}/\text{volume} = 1/\text{H}$ $+ 1/\text{R}$).	12
2.2	Morphology of nano-clay composites: (a) conventional miscible, (b) partially intercalated and exfoliated, (c) fully intercalated and dis- persed and (d) fully exfoliated and dispersed	14
2.3	Schematic diagram showing the in situ polymerisation process . . .	15
2.4	Release of NP from products and (intended or unintended) applica- tions: (a) release of functionalized NP, (b) release of NP embedded in a matrix, (c) release of aggregates of NP and (d) release of free NP. Environmental factors (e.g. light, microorganisms) result in forma- tion of free NP that can undergo aggregation reactions. Moreover, surface modifications (e.g. coating with natural compounds) can affect the aggregation behavior of the NP.	25

2.5	Number of peer reviewed journal papers related to nanotoxicology and nanoparticle release in the time period of December 2010 to August 2011	27
2.6	Particle number concentration spectra measured during sanding: (a) with sanding machine emissions and (b) corrected for sander emissions.	30
2.7	TEM images of abraded particles. (a) Agglomerated particles from the pure epoxy sample; (b) free-standing individual CNTs	33
2.8	Schematic set up of a DMA and CPC	35
2.9	Schematic set up of a FMPS	37
2.10	Schematic set up of a ELPI	38
2.11	Schematic set up of a TEOM	38
2.12	Average size distributions of indoor particles (A) salt particles (B) measured by the diffusion loss corrected SMPS (SMPS1) and FMPS (FMPS1).	41
2.13	Comparison of ELPI (A) and SMPS (B) distributions of gasoline vehicle PM emissions versus particle diameter and time. C: Transient response of ELPI versus SMPS.	43
3.1	The principal procedure for foam-glass-crystal materials	54
3.2	Apparatus and setup for the experimental measurement of airborne particles concentration and size distribution via SMPS in a closed environment	58
3.3	SMPS on-line measurement of the particle size distribution (difference in the natural logarithm of the particle concentration vs. mean particle size) during drilling; the green line represents the actual measurement and the yellow line represent the previous measurements	59

3.4	Outline of generation, sampling and characterisation processes for deposited particles	61
3.5	WAXD diffractogram of unmodified and OMMT	63
3.6	TEM and SEM micrographs of AEROSIL 200	64
3.7	WAXD diffractograms of nano-SiO ₂ and glass fibres	67
3.8	SEM micrographs (1) surface area (2)(3)pore walls at higher magnifications and EDX spectrum of FGC	68
3.9	Manufactured nanocomposite based on PP matrix a) neat panel, b) OMMT c) Nano-SiO ₂ d) foam-glass-crystal, and e) glass fibres . . .	69
3.10	WAXD diffractograms of manufactured PP nanocomposites	70
3.11	SAXD comparison between PP/OMMT composite and neat OMMT	71
3.12	Manufactured nanocomposite based on PA6 matrix a) neat panel, b) OMMT c) nano-SiO ₂ d) foam-glass-crystal, and e) glass fibres . .	72
3.13	WAXD diffractograms of manufactured PA6 nanocomposites	73
3.14	SAXD comparison between PA6/OMMT composite and neat OMMT	74
3.15	TGA and DTG thermograms of PP and PP nanocomposites	84
3.16	Cooling and heating scan during DSC analysis of PP and PP composites	85
3.17	TGA and DTG thermograms of PA6 and PA6 nanocomposites . . .	86
3.18	Cooling and second heating scan during DSC analysis of PA6 and PA6 nanocomposites	87
3.19	SMPS on-line measurement of the particle size distribution (difference in the natural logarithm of the particle concentration vs. mean particle size) during drilling; the green line represents the actual measurement and the yellow line represent the previous measurements	88

3.20	Sequential alteration of number concentration of a typical sampling cycle, consisting of a 60 min background measurement ($t \leq t_{max}$), the 14 min drilling period ($0 \leq t \leq t_{max}$), and a 120 min post-drilling period ($t \geq t_{max}$, for PA6 and PP panel (drill represents the background noises generated by the drill engine)).	89
3.21	Normalised particle size distributions at time $t_{(max)}$ of PP and PA6 based composites	90
3.22	SEM micrographs of generated particles collected by ESP for each PP based composite	91
3.23	SEM micrographs of generated particles collected by ESP	92
3.24	Emission rates of particles for different PP and PA6 based composites	94
3.25	Set of dry particles sampled from drilling of nanocomposites	95
3.26	Size distribution for particles generated from PP/nano-SiO ₂ and PA6/GF composites during the drilling process	101
3.27	Dependency of particle shape on hydrodynamic diameter	102
3.28	Light ray interaction with a particles	103
3.29	Particle analysis via SEM [particles with 25nm diameter (yellow), particles with 50nm diameter (red), particles with 100nm diameter and above (blue)]	104
3.30	Particle size distribution of PP and PA6 composites emitted during drilling process of bulk composite panels	105
3.31	SEM micrographs of generated particles collected by ESP during the drilling process	106
3.32	SEM micrographs of generated particles collected by ESP during the drilling process	107
3.33	WAXD spectrum of bulk PP composite and spectrum of dust emitted from the bulk composites during drilling process	110

3.34	WAXD spectrum of bulk PA6 composite and spectrum of dust emitted from the bulk composites during drilling process	111
4.1	Three step manufacturing process of test specimen	118
4.2	Manufactured crash cone dimensions form fibre reinforced nanocomposites granulate	119
4.3	Quasi-static tensile and compression test conducted on Instron 5500R electro-mechanical testing machine	120
4.4	Experimental set up during drop tower impact testing of crash cones	121
4.5	Schematic set up of crash chamber for measuring the particle emission from crash cones during impact testing	122
4.6	SEM micrographs of fibre reinforced PP nano and micro composite	124
4.7	SEM micrographs of fibre reinforced PA6 nano and micro composite	125
4.8	WAXD diffractograms of fibre reinforced PP nano- and micro-composite	135
4.9	WAXD diffractograms of fibre reinforced PA6 nano- and micro-composite	136
4.10	Macroscopic comparison of PP based crash cones subjected to 2m impact event	137
4.11	Macroscopic comparison o PA6 based crash cones subjected to 2m impact event	138
4.12	Sequential alteration of number concentration of a typical sampling cycle, consisting of a 20-30 min background measurement ($t \leq t_{max}$), the impact event ($t_0 = 0$), and a 30 min post-impact period ($t_0 \geq t_{max}$) for PA6 and PP glass fibre/OMMT cones for the 1m impact event (dummy represents the background noises generated by the impact event)	139
4.13	Normalised particle size distributions of PP based cones during 1, 2 and 3m impact events	140

4.14	Normalised particle size distributions of PA6 based cones during 1, 2 and 3m impact events	141
4.15	Particles emitted during impact testing at different impact velocities and hight	142
4.16	SEM micrographs of fracture surface of impacted crash cones	143
4.17	SEM micrographs of fractured fibre	144
5.1	Manufactured foam composites	148
5.2	Schematic diagram of designed crash camber for particle collection (left) and drop tower configuration (right)	150
5.3	Cell structure of modified PU/OMMT foamed materials parallel to the direction of foam's growth	159
5.4	Cell structure of modified PU/OMMT foamed materials perpendicular to the direction of foam's growth	160
5.5	SEM micrographs of modified PU/OMMT foamed core materials, for foams neat foams and foams with 10wt.% OMMT and EDX spectra of these foams	161
5.6	FTIR spectrum of PU/OMMT nanocomposites	162
5.7	WAXD diffractogram of PU/OMMT	163
5.8	TG and DTG curves of PU/OMMT composites	164
5.9	Stress-strain relationship for manufactured sandwiches panels during quasi-static compression test	165
5.10	Energy absorption vs. composite loading for manufactured sandwich structures	166
5.11	Energy absorption of neat PP facesheet/PU-OMMT cores with increasing filler loading for 15J point impact	169
5.12	Load-deflection graphs for point load and surface impact of manufactured sandwich structures	170

5.13	Normalized particle size distributions of generated particles during impact of sandwich structures	172
5.14	SEM images of un-filtrated solution of collected particles from the impact event	173
5.15	SEM images of filtrated solution $< 11 \mu\text{m}$ of collected particles from the impact event	174
5.16	SEM images of filtrated solution $< 1 \mu\text{m}$ of collected particles from the impact event	174
5.17	TEM images of filtrated solution $< 1 \mu\text{m}$ of collected particles from the impact event	175
5.18	DLS analyse of suspensions of collected particles from the impact event	176
6.1	Dependency of emission rate on the temperature	181
6.2	Schematic representation of possible sources of particle emission during machining	182
6.3	Difference in fracture behaviour depending of the degree of exfoliation	186
6.4	Comparison plot of nano-SiO ₂ and micro-SiO ₂ fillers on particle emission for PP composites	189
B.1	Extrusion Temperature in different Zones	235
C.1	EDX analysis of PP based nanocomposites	240
C.2	EDX analysis of PA6based nanocomposites	241

List of Tables

2.1	Nanoparticle release scenarios found in open literature between 2009-2012	28
2.2	Summary table of widely used air monitoring instruments	34
2.3	Comparison between different measurement devices for nano-sized particles	40
2.4	Sampling instruments for nano-sized particles	44
3.1	DSC results for PP composites	77
3.2	DSC results for PA6 composites	78
3.3	Monitoring studies for nanoparticles	80
3.4	Sample denotation	96
4.1	Fibre reinforced nano and micro composite composition	123
4.2	Mechanical properties of nano- and microcomposites	128
4.3	Impact properties of nano- and microcomposites	129
5.1	Structural properties of the PU/OMMT foamed nanofoams	153
5.2	Quasi-static properties comparison	156
5.3	Impact performance properties of manufactured sandwich structures	167
B.1	Recipes used for compounding of the final granulate for injection moulding	233
B.2	Extrusion parameter	234

B.3	Injection moulding parameter for crash cones	236
B.4	Injection moulding parameter for tensile bars	237
D.1	Injection moulding parameter for tensile bars	244

Chapter 1

Introduction

1.1 General Introduction

The most established engineering thermoplastic polymer, especially in the automotive industry, are polyamide (PAs) and polypropylene (PP) due to their good mechanical performances, processing properties and low cost^[1]. On the other hand, their application as structural materials is limited due to their relatively low impact resistance^[1]. Another group of important polymers are polyurethane (PUs) foams, especially as core material in sandwich constructions^[2-4]. However, sandwich composites suffer sensitivity to impact loading damage, and thus are limited in their function^[2-4].

To oppose these disadvantages, nanocomposites have been introduced because of their potential to exhibit impressive enhancements of material properties compared to traditionally filled polymers composites^[5]. Polymer nanocomposites make use of properties unique to the nanoscale form of materials^[6]. It follows that mechanical^[2-4;7], thermal^[8;9], barrier^[10;11], and fire retardant^[12;13] properties are often different from the properties of the same materials in bulk scale. Hence, a wide range of composites materials have been developed, especially to produce light weight structures with enhanced mechanical properties e.g. thermoplastic such as

polyamides reinforced with aluminate silicate clays, to achieve high strength-to-weight ratio and high impact resistance parts.

Typical use of nanocomposites for transport vehicles can be seen in Figure 1.1. In the automotive sector silicate clays are widely used, mainly due to their low cost and availability. The global consumption of nanocomposites is estimated to exceed 214,081 metric tons and 1.38 billion USD, by 2014^[14]. Of which the consumption of clay-based polymer nanocomposites will increase to 181,094 metric tons and 692.3 million USD by 2014^[14]. For example, one of the leading automotive manufacturers is using 300000 kg of silicate clays composites annually for various automotive exterior part/panel applications at present^[14;15]. Further, a recent market report released by Frost and Sullivan, reported that carbon nanotubes (CNTs) will penetrate about 3.6% within automotive composites^[16]. However, CNTs are still very expensive to manufacture, and hence their integration in large scales for structural components is commercially limited.

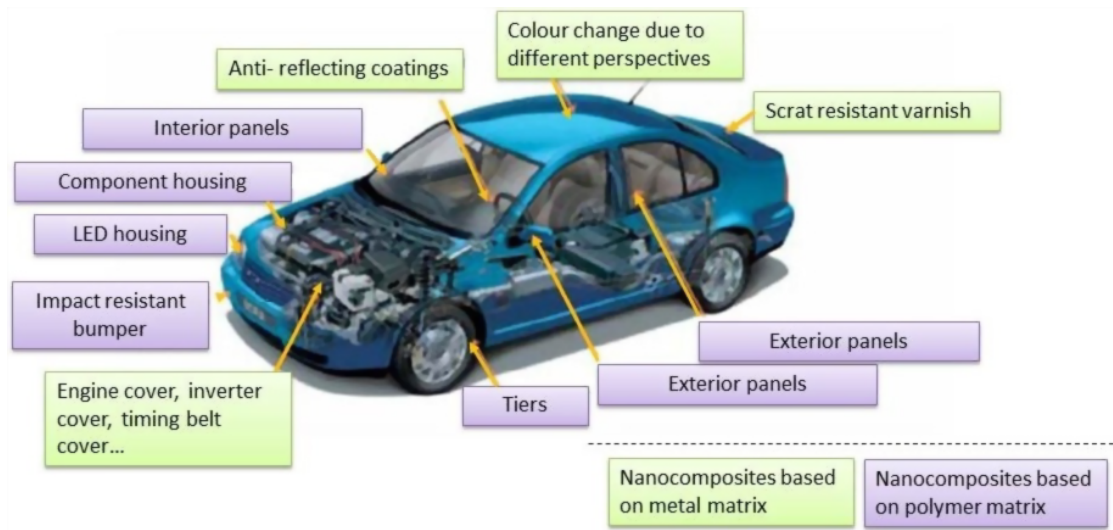


Figure 1.1: Application of nanocomposites in the automotive industry

Whilst, silicate clays are widely used in the automotive industry, they remain naturally occurring materials, which limits the shape, composition and size in which they are available. This hinders the possibility of tailoring nanomaterials

according to product needs. Clay fillers with different aspect ratios but same composition are not commercially available^[17]. Nanoparticle produced through sol-gel chemistry can offers the possibility to synthesis particles with a variety of forms and sizes. Moreover, this process allows the surface functionalisation of the particles and hence result in superhydrophobic or hydrophilic behaviour. One of the most synthesised forms of particles possess quasi-spherical shapes, which can be produced in a variety of sizes by changing the reactant ratios. Epoxy/nano-SiO₂ nanocomposite^[18;19], polypropylene/nano-SiO₂ nanocomposites^[20], polyurethane/nano-SiO₂ composites^[21], thermoplastic olefin blend (TPO)/nano-SiO₂ composites^[22], and polyamide6/nano-SiO₂ composites^[17] have exhibit improved properties when compared to the neat polymer and conventional micro-composite counterparts. For example, Zheng et al.^[18] studied the morphological and mechanical properties of spherical SiO₂ nanoparticles in a epoxy polymer matrix. A major improvement of mechanical properties was reported, with an increase in tensile strength, tensile modulus and impact strength, up to 114%, 12.6% and 56%, respectively, in comparison with the pure resin.

1.2 Motivation

While polymer nanocomposites have proven to be successful for vehicle applications, their behaviour during their life cycle is still not fully understood^[23;24]. It is clear that once nanocomposites are used for applications, they will undergo mechanical stress situations as well as ageing. Further, it is obvious that at some point these nanocomposites need to be disposed or recycled. However, at present little is known about how nanocomposite will perform over their whole life cycle, especially in the usage and end of life phase. Under the influence of normal and elevated environmental factors such as ultraviolet light, moisture, temperature and

mechanical actions, nanoparticles can be potentially released from nanocomposites and thus may have negative effects on the human health and the environment. Driven by the fact that some engineered nanoparticles (ENP) in pristine form, have shown negative effects on the human health and the environment^[23], the interest to determinate the alteration and transformation processes of nanocomposites during their life cycle has recently grown. Therefore, exploring sources and pathways of release helps to identify relevant situations where humans or the environment may encounter released nanoparticles. Further, this information is extremely important for the exposure and risk assessment of nanocomposites.

Within the scope of this thesis PP, PA6 and PU nanocomposites will be synthesised and investigated. To simulate continuous and spontaneous particle release from nanocomposite, specimen will be subjected to mechanical drilling and low velocity impact. The released particles will be measured methodical and characterised accordingly. With the results obtained, the effect of different parameters such as filler size, filler material and matrix material will be evaluated.

Different research groups have designed new methods to measure nanofillers released from nanocomposite^[25–29] materials or coatings^[30–34] under a variety of influences. The main aim of these studies was to investigate if the nanoparticles released from a nanocomposite or nanocoating are of the same nature as the pristine nanofillers. These studies however missed a crucial point. The quantity and properties of particle released from a nanocomposite or coating is not only influenced by the pristine fillers, but by more complex interaction between particle/matrix and furthermore the arising properties of the nanocomposite. To understand the full release mechanism and hence the alteration and transformation processes of nanocomposites it is crucial to look at all effects that might influence the quantity and the properties of the particles released. This thesis therefore focuses on identifying the potential effects such as matrix material or filler properties that might influence the particles released as shown in Figure 1.2.

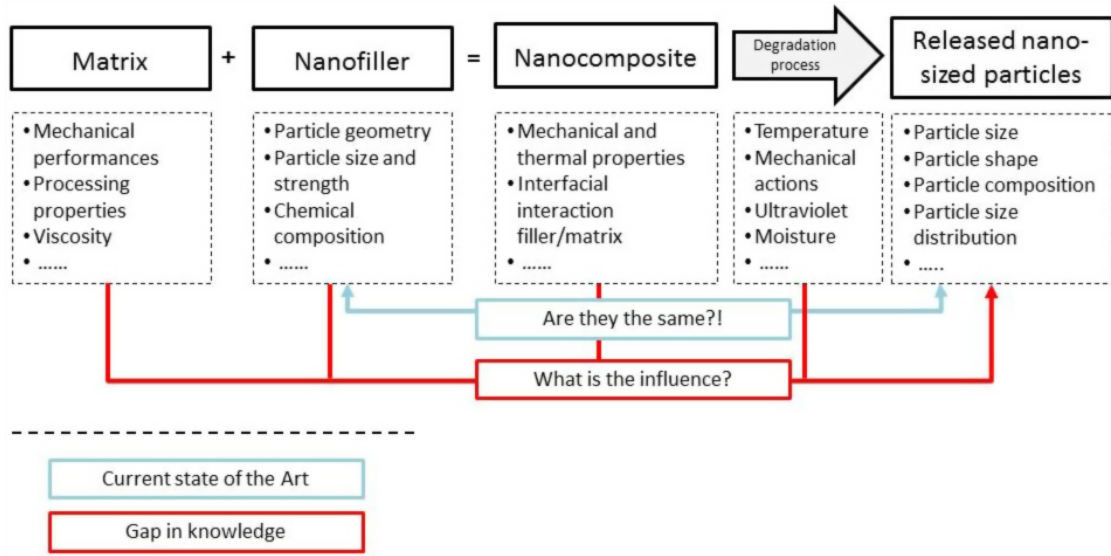


Figure 1.2: Current state of the art and gap in knowledge

Here it should be noted that according to the recommendations of the European Commission^[35] a nanomaterial is a material whose particle size distribution includes over 1% of nanoparticles (1-100nm) in an unbound state, either as an aggregate or as an agglomerate, as demonstrated in Figure 1.3. In the context of this thesis any particles released from solid material, with an geometric mean size less than 1000 nm, will be classed as a nano-sized particle.

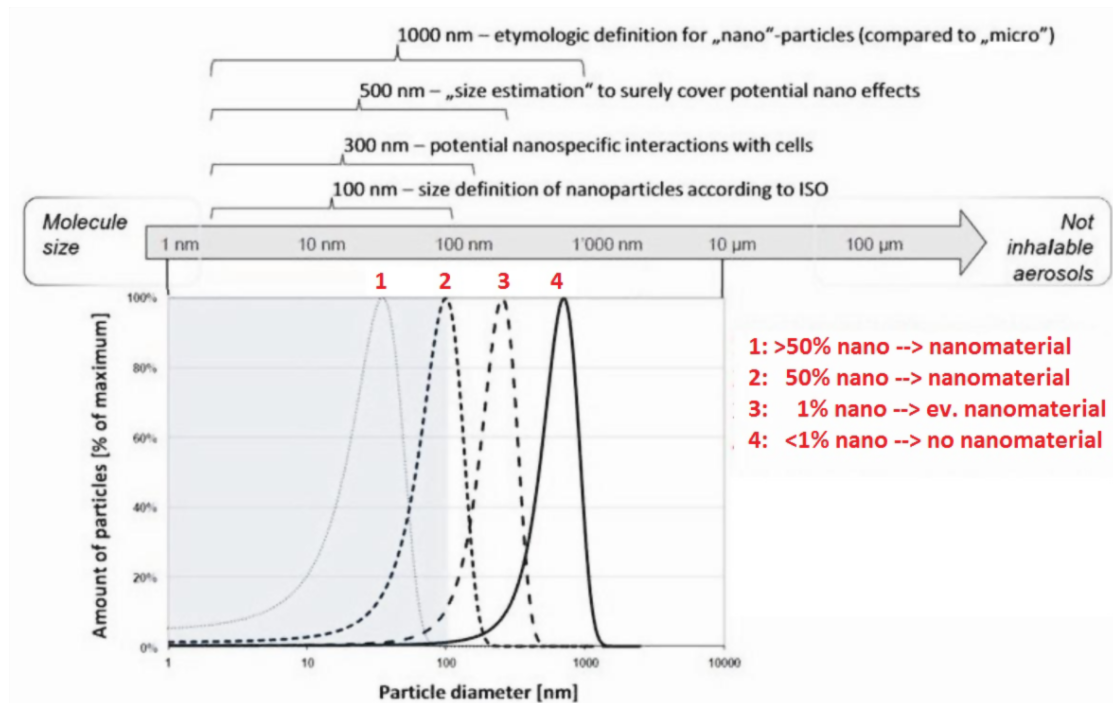


Figure 1.3: Definition of nanomaterials according to the recommendation of the European Commission

Source: Official Journal of the European Union, 2011/696/EU, OJ L 275/38:38-40, 2011.

1.3 Aims and Objectives

This thesis aims to identify the effect of filler size, filler and matrix material on the nano-sized particle released during mechanical drilling and low velocity impact of the solid composite material. The following key objectives are set to reach this aim:

- Fabrication of nanocomposites of polymers (PP, PA6 and PU) in combination with nano and micro fillers (silicate clays, nanosilica, microsilica, foam-glass crystal material and conventional glass fibres)
- Identify morphology, mechanical and thermal properties of the manufactured nanocomposites
- Design new methods to measure nano-sized particle release and establishing

a sampling protocol for systematic characterisation of the emitted nano-sized particles

- Utilise the developed methods to simulate release scenarios during which nano-sized particles are measured and sampled
- Carry out an extensive nano-sized particles characterisation to study particle size distribution, particle shape and morphology
- Identify influence such as matrix material, filler type, and filler size, on the particle emission

1.4 Thesis approach

In order to meet the above objectives, the following thesis approach will be chosen (Figure 1.4). First a literature review will be conducted on which basis an adequate sampling protocol will be developed and selection of appropriate nanofiller and polymer matrices. Once the nanocomposites are manufactured, some specimens will be used to determine morphological as well as mechanical and/or thermal properties, while the other specimens will undergo mechanical degradation processes, i.e. drilling and low velocity impact tests. Two types of particles will be measured, sampled and characterised, (i) airborne particles and (ii) deposited particles. Once all data is collected, particle emission rate will be calculated and the influence of matrix material, filler type, and filler size, on the particle emission will be identified. It has to be noted that the sampling protocol will be updated continuously in case the chosen measurement, sampling and characterisation techniques are not sufficient or are inadequate for the nano-sized particles investigated.

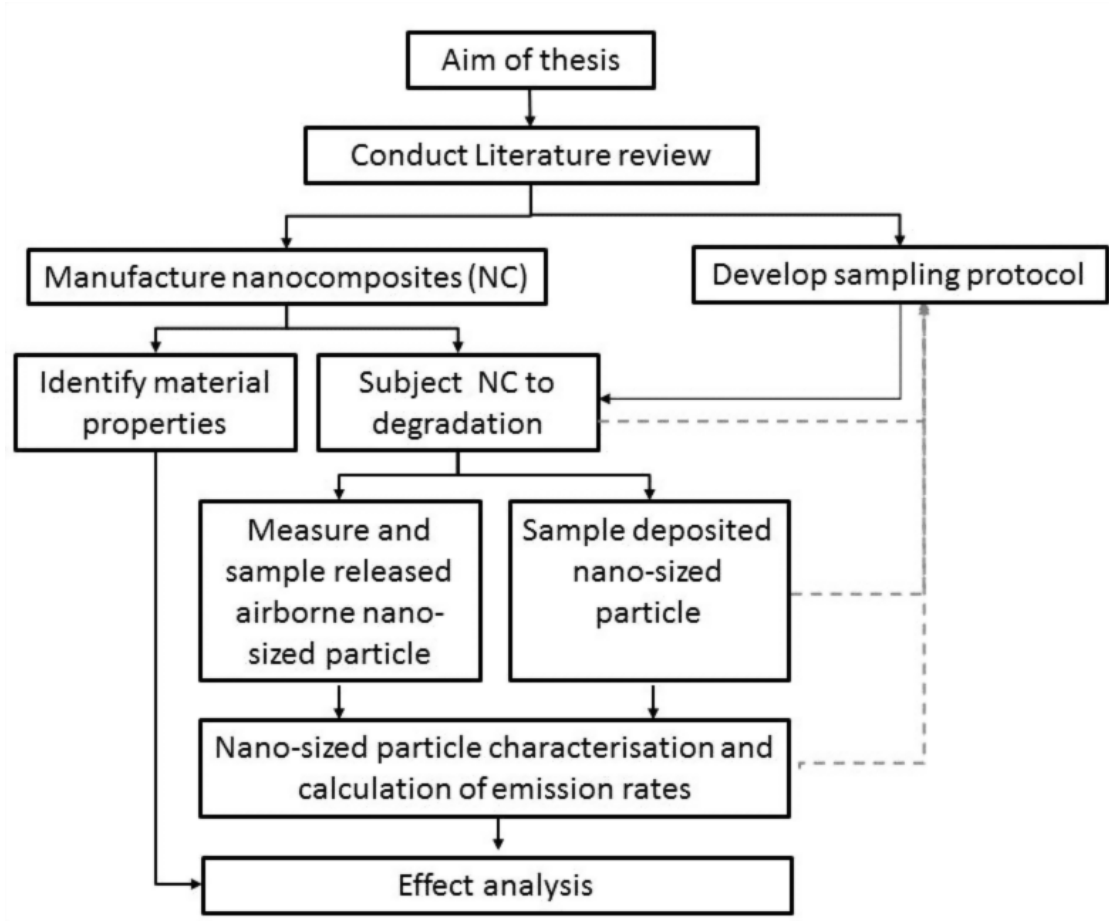


Figure 1.4: Work flow chart for thesis approach

1.5 Thesis Structure

Chapter 1 is structured to give the reader relevant background information in objectives, approaches, motivation and the thesis structure. Typical materials (silica based polymer nanocomposites) relevant to the study are presented to emphasise the importance of the current work for the automotive sector.

Chapter 2 is a comprehensive literature review undertaken to present the current state of the art and current gap in knowledge. Polymer nanocomposites are briefly introduced, followed by an insight into the impact behaviour of nanocomposites. Further, release scenarios of engineered nano-sized particles from nanocomposites are introduced and discussed. This chapter ends with a brief consideration of the

current possibilities and methods for the measurement of airborne nano-sized particles.

In Chapter 3, the experimental investigation is carried out to assess the nano-sized particles emitted during drilling of synthesised and manufactured silica based PA6 and PP nanocomposites specimen. This chapter focuses on the thermal behaviour of the nanocomposites and its correlation in terms of particle emission. Chapter 4 studies the nano-sized particles emitted during low velocity impacts of synthesised and manufactured silica based PP- and PA6-glass fibre-nanocomposites cones. This chapter emphasises on the mechanical and failure behaviour of the nanocomposites, in relation to their particle emission. In Chapter 5, sandwich panels are fabricated with PU/silicate clays foams cores and glass fibre reinforced PP and PA6 face sheets. These sandwiches are subjected to low energy impact tests under localised point and surface loads, in an instrumented impact test setup. Additionally, quasi static compressive behaviour of the sandwiches panels are studied, as well as the particle released from 5wt.% loaded PU foam cores under surface load.

An overall discussion of the results obtained in the previous chapters, is given in Chapter 6. It focuses on the influence of matrix material, filler type, and filler size, on the particle emission during drilling and low velocity impact of silica based PP, PA6 and PU nanocomposites. The work summary and scope for further work are outlined in Chapter 7, followed by a personal profile and appendices.

Chapter 2

Literature Review

2.1 Introduction

A comprehensive literature review on the impact behaviour of nanocomposite is conducted, aiming to familiarise the reader with the current state of the art. Further, different studies are identified and evaluated in which nanocomposites are subjected to mechanical stress situations or material ageing, to assess their life cycle behaviour. The emphasis is given on the new methods that have been designed to measure nanoparticles release from nanocomposites or coatings under different solicitations e.g. mechanical, thermal and ultraviolet. Finally, a brief discussion on the current possibilities and equipment for measuring airborne nano-sized particles is given, as it is a critical issue to assess particle release and exposure, especially for production and scale-up of nanocomposites. Hence, this review offers a extended discussion on technology, characterisation and behaviour for nanocomposites throughout their life cycle.

2.2 Polymer nanocomposites

Composites are multiphase material systems, which are composed of one or more fillers and a matrix material^[36]. In nanocomposite the filler material is defined by having at least one dimension in the nano range (less than 100 nanometers)^[37;38]. To enhance specific polymer properties, nanofillers are used. Nanofillers can be distinguished by their shape e.g. nano-fibres, nano-tubes, nano-particles or nano-plates, and claim large surface-to-volume ratios. Figure 2.1 represents the surface area to volume of different nanoparticles with respect to their aspect ratio, α , and their largest dimension (R = radius, H = height, length). Fully exfoliated and dispersed nanoplates or nanorods generate internal interfacial area comparable to that of macromolecular structures and will affect the surface area-to-volume ratio by three orders of magnitude^[39].

The hierarchical microstructures of polymer nanocomposites is directly related to the nanocomposites properties^[5;40]. Beside the interfacial bonding, the arising properties are influenced by several parameters such as properties of the matrix, properties and distribution of the filler, and by the synthetic or processing methods^[5].

2.2.1 Nanocomposites filled with nanoplates

Nanoplates are classified by having only one dimension in the nanometer range. The most widely utilized types of nanoplates are silicate clay minerals (montmorillonite) and graphite, which both exist in the form of layered materials. The main advantage of layered nano-materials is their potentially large aspect ratio and unique intercalation/exfoliation characteristics. Clay-polymer nanocomposites can be divided into four main categories, as shown in Figure 2.2. In a conventional miscible material state the enhancement of the composite properties are of little meaning. The distance between clay plates are minimal and there is no inter-

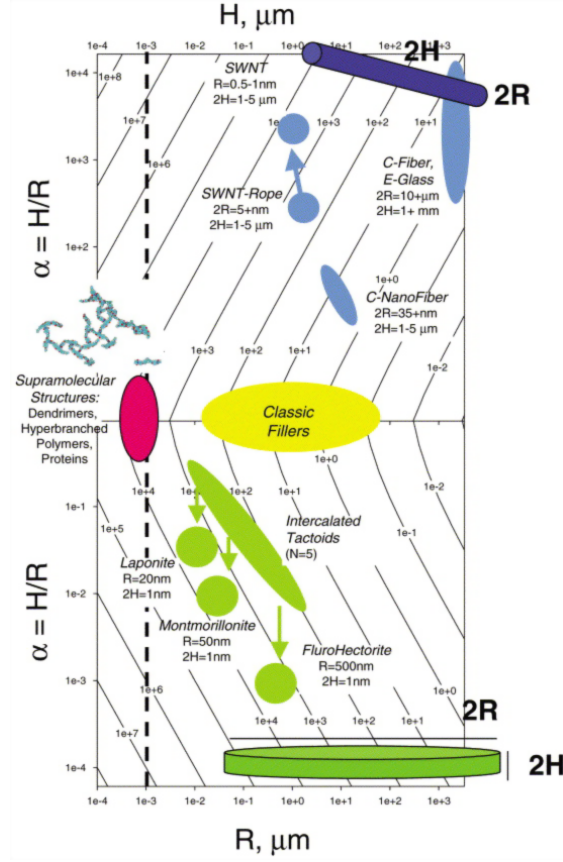


Figure 2.1: Logarithmic isolines of interfacial (surface) area / volume ($\mu m^1 = m^2/ml$) with respect to the aspect ratio, $\alpha = H/R$, and largest dimension of particle ($R =$ radius, $H =$ height, length) based on approximating particles as cylinders (area/volume = $1/H + 1/R$).

Source: R. A. Vaia and H. D. Wagner. *Framework for nanocomposites. Materials Today*, 7(11):32-37, 2004.

calation of the polymer matrix into the gallery. In case of intercalated state, the polymer matrix exists between the clay layers, leading to an enhancement of the polymer's properties. If the nanoplates are fully separated and dispersed within the matrix, then the clay is in an exfoliated state. Exfoliated composites exhibit better properties in relation to the intercalated ones, due to the higher homogeneity of the phase. Achievement of the full exfoliation is a challenging technical problem, because of the large longitudinal dimensions of the nanoplates and their strong tendency to agglomerate. The most common state of nanoplates composites is a mixed state of intercalation and exfoliation. In this case the exfoliated and intercalated layers are distributed randomly within the matrix and a significant

increase in modulus and strength can be observed when comparing with the raw matrix.

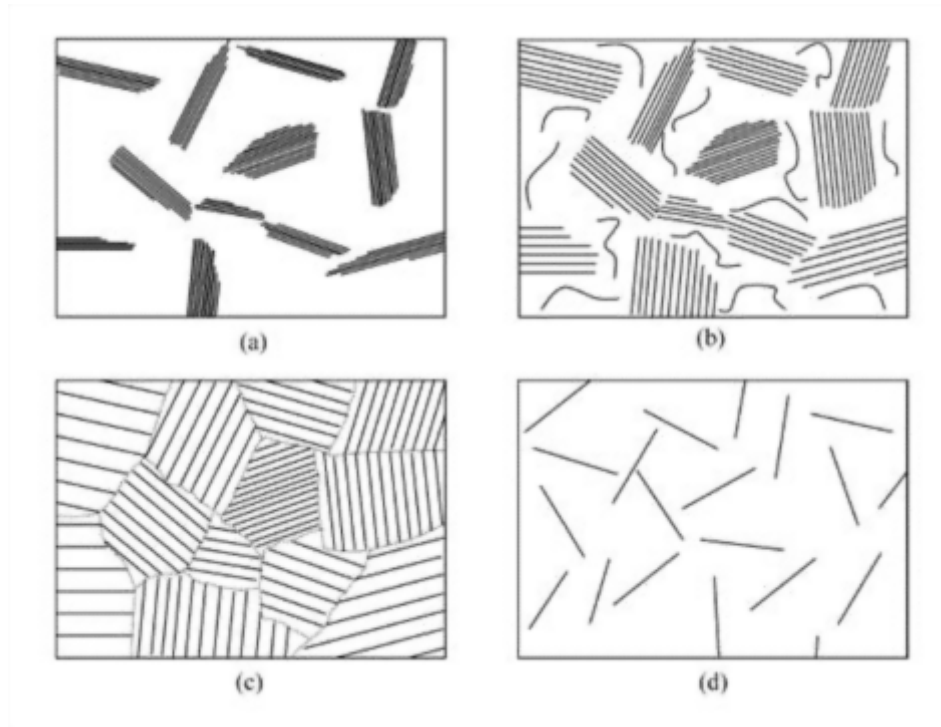


Figure 2.2: Morphology of nano-clay composites: (a) conventional miscible, (b) partially intercalated and exfoliated, (c) fully intercalated and dispersed and (d) fully exfoliated and dispersed

Source: J.-J. Luo and I. M. Daniel. Characterization and modeling of mechanical behavior of polymer/clay nanocomposites. Composites Science and Technology, 63(11):1607-1616, 2003.

To increase the interlayer distance of the nanoplates and hence facilitate the intercalation of the polymer into the layer galleries, the clays are modified with organic surfactants. The first ever polymer/organic modified montmorillonite (OMMT) nanocomposites were synthesised using in-situ polymerisation^[41]. Figure 2.3 shows the schematic principle of preparing polymer/OMMT composites by this technique^[42]. The first step consist of swelling the organic-modified layered silicate within a liquid monomer or a monomer solution so that the monomer can penetrate into the interlayers^[41]. In the second step a polymerisation reaction is initiated between the intercalated sheets by heat, radiation, diffusion of a proper initiator or by a catalyst fixed through cationic exchange inside the interlayer before the

swelling, resulting into a nanocomposite^[43].

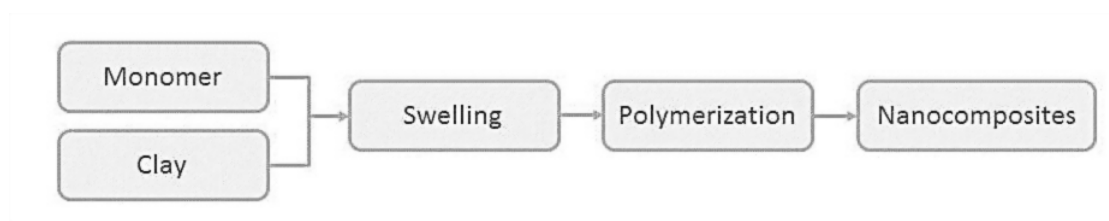


Figure 2.3: Schematic diagram showing the in situ polymerisation process

Interestingly, PA6/OMMT composites prepared by melt blending show similar properties to those prepared by the in-situ polymerisation method^[44]. Luo et al.^[45] prepared PA6/organoclay nanocomposites using direct melt compounding with a conventional twin screw extruder. The resulting morphological and mechanical properties were then compared to PA6/organoclay nanocomposites prepared through in- situ polymerisation process. The authors reported that the organoclay was well exfoliated into the PA6 matrix when compounded with the twin screw extruder. However, the use of a single screw extruder was far less effective, in terms of OMMT exfoliation. The method of in-situ polymerisation has been used for the manufactured of polyamide nanocomposite in various studies^[46–49].

Direct intercalation or exfoliation in silicate galleries of OMMT is very difficult, in hydrophobic polymers as they do not have any polar groups in its chain^[50]. In general, this results in a significant adhesion problems between the hydrophilic filler and the matrix, creating poor bonds between matrix and filler^[50]. However, only little difficulties should be encountered with polar polymers if the montmorillonite surface is modified with certain organic surfactants e.g. the alkylammonium cation^[51]. The modification of the clay with organic surfactants expand the interlayer distance. However, when dealing with nonpolar polymers, employing O-MMT will facilitate nanocomposites development only to a limited extent^[52]. This means that for achieving an exfoliated (or at least intercalated) nanocomposites the addition of extra compatibilisers is required^[53]. This was first reported by

Usuki et al.^[54] in 1997, while using a new approach to prepare PP nanocomposites using a functional oligomer (PP–OH) with polar telechelic OH groups as compatibiliser. With this technique the interaction between filler and polymer is enhanced by strong hydrogen bonding between OH or COOH groups and the oxygen groups of the silicate^[55].

Today, studies^[56–60] have shown that the possibility to prepare exfoliation and dispersed PP/OMMT nanocomposites, depends not only on the organic modifier of the OMMT, but further on the initial interlayer spacing, the concentration of functional groups in the compatibiliser and its overall concentration in the composite, the viscosity (or molecular weight) of polypropylene, and the processing conditions.

Recently, Boumbimba et al.^[61] prepared PP/OMMT nanocomposites by melt compounding. In this process high temperature and high shear forces are used to disperse nanofillers in the polymer matrix^[62]. This process is the most promising for the production of nanocomposites at an industrial scale, due to the ease of processing high quantity of granulates with twin screw extruder. In general extrusion melt compounding allows nanocomposites to be formulated using ordinary compounding devices: extruders or special mixers, without the necessity of using advanced polymer technology^[44]. Further, this method is very common for processing polymers that are not suitable for adsorption or in-situ polymerisation^[43]. To obtain the best particle distribution it is crucial to understand the major process variables, such as balance of *dispersive* and *distributive* mixing and further, in turn, length of the different zones, design of blocks, design of screw, specifically length and position of mixing zone, screw length, melt temperature, residence time of melt, and shear^[57;61]. A clear distinction between *dispersive* and *distributive* mixing mechanisms, as well as the identification of the important process characteristics enhancing the realisation of these mechanisms, are essential for a fundamental understanding of the mixing process and its optimisa-

tion possibility^[42]. Dispersive mixing involves the reduction of the cohesive minor components, such as clusters of solid nanoparticles, while distributive mixing involves spreading the minor component throughout the matrix in order to obtain a good distribution^[63]. These two mechanisms may occur simultaneously or stepwise^[42]. Dispersive mixing conditions are determined by the the balance between the cohesive force holding nanoparticle agglomerates together and the disruptive hydrodynamic forces^[63]. Additionally, the amount of stresses applied plays a decisive role in determining the particle size distribution^[64].

For the PP/OMMT nanocomposites prepared through melt compounding by Boumbimba et al.^[61] the result showed that the yield stress was significantly affected by the extent of exfoliation. The experimental results further indicated that the yield stress was sensitive to the strain rate, temperature, and organoclay concentration.

2.2.2 Nanocomposites filled with nanoparticles

To enhance the physical and mechanical properties of thermoplastic resins, silica (SiO_2) nanoparticles can be introduced. Several studies reported significant improvements in properties such as: tensile strength, strain to failure, Young's modulus and impact strength; after introducing nanoparticles into the virgin material^[48;65;66]. Jun Ma et al.^[65] showed that the addition of 20wt% silica nanoparticles lead to an increase in: Young's modulus by 40%, toughness from 0.73 to 1.68 MPa/m² and a slight increase in the tensile strength. The manufacturing process of the nanocomposite has a significant effect on the achievable property enhancements. It dominates the dispersion of particles within the matrix material. The existence of agglomeration regions, which can act as stress concentrators, may lead to an significant drop in composite performances^[67]. Zheng et al.^[18] compared the mechanical properties of nanocomposites with different quality of dispersion. The authors reported that the material with uniformly distributed particles exhibits significant property improvements, while poorly distributed ma-

terial indicates only slight increase in the mechanical properties. Three different approaches have been studied by the authors in order to determine the most suitable manufacturing technique. The first technique involved utilising an ultrasonic energy to mix the unpretreated SiO_2 particles in the. In the second attempt particles were pre-treated using a coupling agent and afterwards treated exposed to the ultrasonic waves. In the last approach the pre-treated particles were also dispersed using the ultrasonic waves but with assistance of high-speed homogenizer with a rotational velocity of 24,000 rpm. After studying the morphology, using transmission electron microscope (TEM), it was found that particles dispersion obtained using the second and the third approach resulted in a good particle dispersion. Dispersion achieved using the first approach was relatively poor with visible particles agglomerations. By using the second and the third method, an increase in mechanical properties up to 30% and 110% could be measured respectively. In a different study, Vladimirov et al.^[20] studied polypropylene/nanosilica nanocomposites. These nanocomposites were prepared via melt mixing using a twin-screw extruder. A compatibiliser (maleic anhydride grafted polypropylene (PP-g-MA)) was used to improve the degree of dispersion in the matrix. The results showed that with increasing silica content the formation of silica agglomerates in the matrix increased. However, due to the utilisation of the compatibiliser the agglomeration degree of the nanoparticles could be controlled and a significant property enhancement could be demonstrated.

2.2.3 Impact behaviour of nanocomposites

The major reason for adding fillers into virgin polymers is to enhance the composites strength and stiffness properties. The most important parameter which affects these properties is the load transfer between the composite phases, realised via shear stress induced in the interface region. In the case high-modulus filler are added into low-modulus matrix, the stress in the composite is transferred into

the stiffer phase, causing more load being carried by the filler phase. Hence, the efficiency of the stress transfer across the composite phases depends on the quality of the interfacial region, which includes interfacial strength and stiffness^[5]. The major influences on the impact behaviour of nanocomposites is summarised in the following.

2.2.3.1 Effects of particle stiffness

Viana^[68] has shown that the particle stiffness influences the properties of the polymer matrix. While soft/elastic fillers improve the impact toughness, at the same time those filler reduce the modulus of elasticity of the polymer blend. However, increasing the amount of hard/rigid fillers improves both the impact toughness and the modulus of elasticity. For instance, the addition of OMMT (less than 5 wt. %) into a Polyurethane foam matrix, significantly improved the failure strength and energy absorption of the foam, with over a 50% increase in the impact load carrying capacity when compared to the unenforced matrix^[69]. Another example is the addition of rigid CaCO_3 (diameter=600 nm, 0.2 vol.%) in high density polyethylene (HDPE), which improved the impact strength by more than 200 %^[70]. Such exorbitant improvements are not typically observed for composites reinforced with conventional micro particles. Subramaniyan et al.^[71] reported that core shell rubber (CSR) nano particles having a soft rubber core and a glassy shell improved the fracture toughness of an epoxy vinyl ester resin significantly more than OMMT clay, having the same weight fraction. However, hybrid blends of CSR and OMMT were found to yield the best balance of toughness, modulus and strength. The same investigators highlighted that when the OMMT were used to enhance the polymer matrix in a conventional glass fiber reinforced composite, the interlaminar fracture toughness of the composite was less than that of the unenforced composite. As a possible reason for this result the arrangement of the OMMT along the fibre axis was suggested. Two factors dominate the capacity

if rigid particles for energy dissipation at high loading rates^[72]. The ability of the dispersed particles to detach from the matrix and to initiate the matrix local shear yielding in the vicinity of the voids and the size of the voids. Therefore, the optimal minimal rigid particle size for polymer toughening should assure two main requirements: (i) be smaller than the critical size for polymer fracture and (ii) have a debonding stress which is small compared to the polymer matrix yield stress.

2.2.3.2 Effects of particle geometry

Typical fillers for the reinforcement of polymer matrices are particles e.g. Silica or aluminum oxide particles, tubes e.g. nanofibres or nanotubes and plates e.g. nanoplatelets. Significant enhancement of impact strength of polymeric nanocomposites was achieved by adding amino-functionalised MWCNTs or small amounts of SWCNTs^[73]. Furthermore, the impact toughness of PMMA (polymethyl- methacrylate) has been improved considerably by the addition of CNTs and the toughness and modulus of MWCNTs reinforced PP exhibited a maximum at 1 wt.% CNTs^[73]. Additionally, the impact toughness and stiffness of CNT-reinforced polymer matrix have been found to be functions of the Young's modulus of the nanotubes^[74]. The impact toughness of polymers containing inorganic nanofillers such as MMT (Montmorillonite) OMMT, based polymer composites was found to decrease

2.2.3.3 Effects of particle size

To investigate different toughening or energy absorption effectiveness for fillers with micro- and nano scale size, d, Wacharawichanant et al.^[75] measured tensile and impact properties of POM/ZnO (71 nm) and compared them with those of composites having micron- size ZnO (0.25 μm). It was shown that the nanocomposite has a higher mechanical properties e.g. tensile strength, Young's modulus and impact strength than the microcomposite. Fu et al.^[76] investigated the me-

chanical behaviour of polypropylene (PP)/CaCO₃ nanocomposites. The particle size varied from 10 nm, 80 nm, 1.3 to 58 μ m. The study has shown that the composite strength increases with decreasing particle size due to higher total surface area for a given particle loading. This indicated that the strength increases with increasing surface area of the filled particles through a more efficient stress transfer mechanism. Furthermore, the Izod toughness was also found to increase with decreasing particle size.

2.2.3.4 Effects of stochastic variation of particle size and strength

Due to Individual stochastic variation in the strength, different Carbon nanotubes may have direct effect on the fracture mechanisms as in micro-based fibre composites. Xiao et al.^[77] measured the relation between individual CNT and CNT bundle strengths and a method for determining the tensile strength distribution of individual CNTs or CNT sub bundles from experimental measurements on CNT bundles was proposed. The Weibull shape and scale parameters of the tensile strength distribution of CNTs were found to have wide variability of strength. Tomar et al.^[78] highlighted, that a microstructure less prone to fracture shows higher variations in fracture response when compared to the one which offers least resistance to crack propagation. Additionally, for a particular micro-structural morphology, the levels of variations in the crack surface area generated and the variations in the energy release rate are of the same order as the levels of variations in constituent properties.

2.2.3.5 Effects of type of polymer matrix and fillers

The energy absorbent of nanocomposites depends on the polymer clay affinity. For example, leads the reinforcement of polyacrylate (PA), polyimide (PI) and polypropylene (PP), with silica to striking variation in impact toughness behaviour under identical processing conditions. The maximum stress intensity factor of PA

based enhanced significantly as compared with to PI and PP based composites. Additionally the steady state fracture toughness of PA composite is approximately 45% and 25% higher than pure polyacrylate and both PP-based and PI-based hybrid specimens^[79].

2.2.3.6 Effects of interfacial adhesion

Hybrid organic–inorganic composites usually exhibit enhanced mechanical properties compared to those of their separate components. The dispersion of the inorganic components into the inorganic matrices affects the mechanical performance of the materials. So that homogeneous dispersed filler components are desirable. The employment of inorganic bulk fillers that can be exfoliated into well organized nano size fillers in the polymer matrices is one method to get well dispersed inorganic reinforced organic matrix nanocomponent. For example, Park et al.^[80] confirmed that silanetreated MMT could be successfully intercalated and dispersed in the epoxy matrix. The experimental results show that silane coupling agent (SCA) treatments cause an increase in both the specific component (due to the epoxide ring and amine group) and the dispersive component (due to the increase of the specific molecular volume). It was considered that the presence of SCAs leads to an increase of the interfacial adhesion between the MMTs and epoxy resin, which results from the improvement of the polar functional groups or of the specific component of the surface free energy of the MMTs. This enhances the mechanical interfacial strength between the MMTs and the epoxy matrix. Hamming et al.^[81] studied the quality of dispersion and the quality of the interfacial interaction between TiO₂ nanoparticles and host polymer on properties such as glass transition temperature (T_g), elastic modulus and loss modulus. T_g is an attractive target property because of its high sensitivity to chain mobility and its use as a benchmark in other studies. The results showed that as the degree of dispersion improved (finer scale agglomerations) the T_g was depressed for samples

of unmodified TiO_2 nanoparticles in PMMA and increased for samples of modified TiO_2 nanoparticles in PMMA. These results indicate that the quality of dispersion shifts T_g . However, the direction of shifts depends on the interfacial interaction of the nanoparticles with the matrix. This study indicated that the bulk properties of nanocomposites are highly sensitive to the quality of the interfacial interaction and quality of dispersion of the nanoparticles.

2.2.3.7 Distribution status of fillers

A number of experiments have shown that fracture toughness improved with addition of clay nanoplatelets to epoxy when the clay nano-platelets were not fully exfoliated, and intercalated clay nanoplatelets were present^[82]. Xidas et al.^[82] showed that quaternary alkylammonium ion-modified organoclays (C18 alkylammonium ion and hydrogenated tallow ammonium ions) provided highly intercalated structures, which led to significant increase of tensile strength and strain at break.

2.3 Identification of release scenarios of nano-sized particles from nanocomposites

Polymer nanocomposites have proven to offer a big range of benefits, however their behaviour during their whole life cycle is not well understood^[23;24]. It is clear that once nanocomposites are used for applications, they will undergo mechanical stress situations as well as ageing^[83]. Further it is obvious that at some point these nanocomposites need to be disposed or recycled. However, at present little is known about how nanocomposite will perform over their whole life cycle, especially in the usage and end of life phase^[84]. Depending on a number of factors, including the type of matrix material and specific release scenario, nano-sized particles can be released in a unbound or bound state^[85]. The further exposure of these

nano-sized particles and their influence on the human health and the environment is not well understood^[85]. Currently, there is a lack of information in the open literature on nano-sized particles release from nanocomposites and consequently their impact on the environmental and human health is unclear.

There are many ways nano-sized particles can be released from a nanocomposite during their full life cycle^[84]. Excellent review studies have focused on researching the potential environmental and health risks of nano scale particles and nanomaterials^[23;84;86–89]. The majority of these studies published in the field of nanotoxicology and related risk assessment, are focusing on pristine engineered nanoparticles (ENP) e.g. SiO₂, SWCNT, OMMT etc. However, if nano-sized particles are generated and released into the environment, changes of physicochemical properties are very likely e.g. geometrical changes or surface modification^[24;83], as shown in Figure 2.4.

Therefore, only a minimum of information is available on the environmental transformation, behaviour, and fate of the ENP once integrated into a composite matrix. Changes in physicochemical properties are currently not considered in nanotoxicological investigations, even though they are crucial for risk assessment. It is of highest importance to understand various factors that control mechanical, photolysis, and incineration degradation, rather than focusing only on a particular case study. At present only one generic release scenario for carbon nanotubes (CNT) in diverse composites matrices has been published^[83]. The authors^[83] have evaluated how different environmental conditions affect the alteration of the nanocomposite, as well as the transformation of the CNT once released from the composite. The conclusion of Nowack et al.^[83] was that it is not possible to assess the risks associated with the use of engineered nanomaterial by investigating only the pristine form of the engineered nanomaterial.

Currently there is no clear definition of exposure/release scenario found in the literature^[83]. Therefore, for the purpose of this review a release scenario will

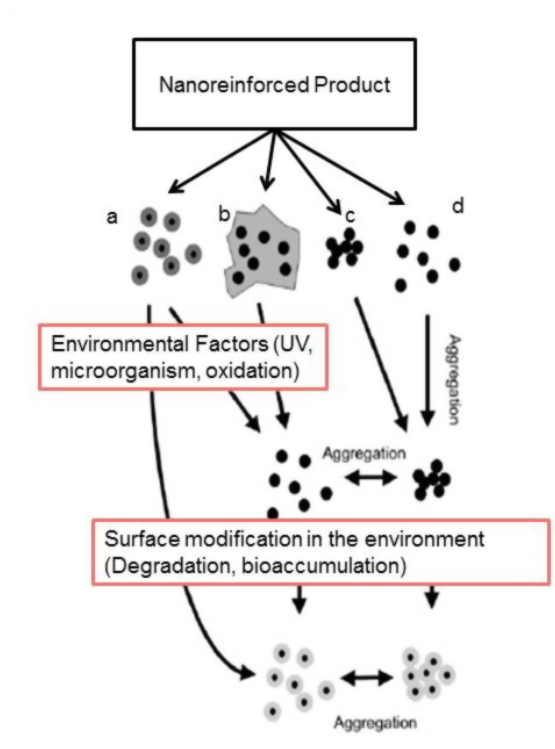


Figure 2.4: Release of NP from products and (intended or unintended) applications: (a) release of functionalized NP, (b) release of NP embedded in a matrix, (c) release of aggregates of NP and (d) release of free NP. Environmental factors (e.g. light, microorganisms) result in formation of free NP that can undergo aggregation reactions. Moreover, surface modifications (e.g. coating with natural compounds) can affect the aggregation behavior of the NP.

Source: B. Nowack and T. D. Bucheli. Occurrence, behavior and effects of nanoparticles in the environment. Environmental Pollution, 150(1):5-22, 2007.

be defined as the operational and/or environmental conditions of any treatment or stress that nanocomposite are subjected to during all life-cycle phases that results into the emission of nano-sized particles into indoor environments and/or environmental compartments. Further, the set of parameters to describe the type, form and magnitude of release need to be recorded. The emission of nano-sized particles from nanocomposites might occur throughout the whole materials life cycle, depending on the circumstances of manufacture (production and processing), the intended use of the material in specific environments, and its disposition at the end of life^[84]. Following information is essential to identify and characterise release scenario^[90]:

- Description of operational conditions and sampling conditions e.g. open/closed

systems, continuous or batch, duration and frequency, temperature and pressure, material use rates or mass flows, description of the treatment, etc.

- Description of degradation processes involved e.g. mechanical, photolysis, and incineration processes
- Description of type and route of release e.g. continuous or intermittent, atmospheric or aquatic routes and target compartment
- Description of particle size and distribution
- Description of particle form and shape

To date, only a few studies in the published literature have focused on the potential releases of nanoparticles due to individual processes from nanomaterials. However an increasing research has been conducted in the field of nanotoxicology. As an example, Figure 2.5 shows the increase of peer reviewed papers between December 2010 and August 2011. A significant increase in nanotoxicological studies on pristine nanoparticles could be found. However, only a minor increase in the number of peer reviewed journal papers related to nanoparticle release were noticed according to the data collected and investigated within the NEPHH project^[91].

Studies related to nano-sized particle release can roughly be classified by (i) nanomaterial used for coating and (ii) nanomaterials used for composites. Coatings could be understood being a thin layer of composite material, as the ENP are embedded in a matrix material. However, for the purpose of release studies, composites and coating cannot be compared and have to be analysed separately. Table 2.1 summarises studies found in the open literature presenting and discussing different release scenarios of nano-sized particle from coatings and composite materials.

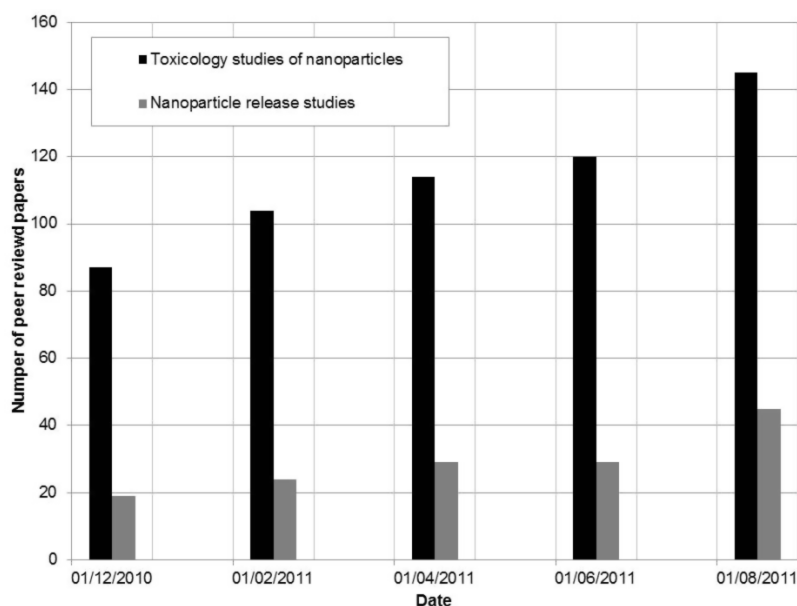


Figure 2.5: Number of peer reviewed journal papers related to nanotoxicology and nanoparticle release in the time period of December 2010 to August 2011

2.3.1 Nano-sized particles released from surface coating

Koponen et al.^[30] investigated the exposure risk of sanding dust released from paints produced with and without engineered nanoparticles. The objectives of this study was to generate nanoparticles from different materials and sources and to compare their size distribution spectra. For the nanoparticle characterisation an aerosol particle sizer (APS, Model 3321, TSI Inc.) and a fast scanning mobility sizer (FMPS, Model 3091, TSI Inc.) were used. The APS measured the size distributions of particles from 0.542 to 19.81 μm and the FMPS measures the particle size distribution from 5.6 nm to 542 nm. The sampling of nanoparticles occurs via electrostatic precipitation, with a commercial electrostatic precipitator (ESP) for subsequent physicochemical and toxicological analysis. The results showed that some coatings showed higher others lower release rates when ENPs were added to the coating. According to the results of this study, the sander was a main source of particles smaller than 50 nm. The results showed that the total emission number size distributions were five modal, as shown in Figure 2.6. The first two modes

Table 2.1: Nanoparticle release scenarios found in open literature between 2009-2012

Investigated Nanomaterial	Activities	Used equipment	Reference
Coatings			
TiO ₂ , Carbon Black	Sanding	APS, FMPS	[30]
ZnO	Abrasion	CPC, SMPS	[31]
OMMT	Abrasion	CPC, SMPS	[32]
Fe ₂ O ₃ and ZnO	Sanding	FMPS	[33]
TiO ₂	Abrasion	ELPI	[34]
Composites			
Polymer/CNT	Dry/wet drilling	FMPS, APS	[25]
Polymer/CNT	Dry/wet abrasive	FMPS,CPC	[26]
POM/CNT, PA/SiO ₂ & cement/CNT	Sanding & weathering	SMPS	[27]
Epoxy/CNT	Abrasion	SMPS	[28]
Polymer/CNT	Burning	ELPI	[92]
Epoxy/CNT	Sanding	CPC	[93]
PP/OMMT	Shredding	DustTrak and FMPS	[29]
PA/OMMT & PA/SiO ₂	Drilling	SMPS+C	[94]

CPC - Condensation Particle Counter; SMPS - Scanning Mobility Particle Sizer; FMPS - Fast scanning Mobility Particle Sizer; ELPI - Electrical Low Pressure Impactor; APS - Aerodynamic Particle Sizer; TEOM - Tapered Element Oscillating Microbalance

had peaks below 20 nm and these were identified as sander emissions. Mode 3 was found at about 200 nm, which contained particles from the sander and paints. Mode 4 and 5 were at 1 and 2 μm and they contained mostly particles released from the paints.

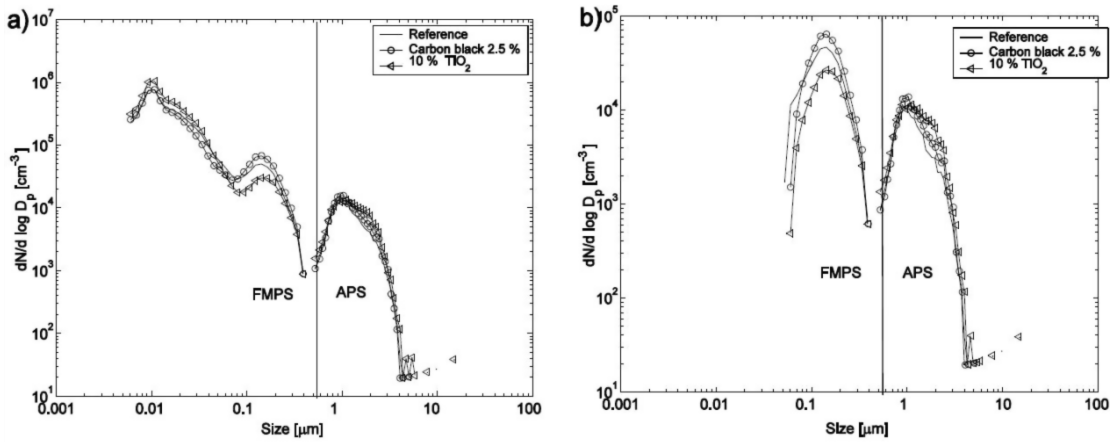


Figure 2.6: Particle number concentration spectra measured during sanding: (a) with sanding machine emissions and (b) corrected for sander emissions.

Source: I. K Koponen, K. A. Jensen, and T. Schneider. Sanding dust from nanoparticle containing paints: Physical characterisation. Journal of Physics: Conference Series, 151(1):012048, 2009.

Vorbau et al.^[31] developed a new method for the quantification of the nanoparticle release into air from surface coatings. The method is based on a combination of a defined abrasion process with highly sensitive methods to quantify airborne particle concentration. The quantification of the release rate of particles smaller than 100nm was conducted via SMPS (Model 3934, TSI Incorporated, USA) and CPC (Model 3022, TSI Incorporated, USA). The two instruments were employed in the test rig; the SMPS for the determination of the number size distribution and the CPC for measuring the particle concentration. For the abrasion test three different coatings were chosen with and without ZnO nanoparticles. The study showed that the developed test rig can be applied to simulate and quantify the nanoparticle release from surface coatings by a rather slow abrasion process. The study further highlighted the need for further development especially in the field of measurement techniques. The relatively long duration of the current aerosol measurement restricted the intensity of abrasion. Higher abrasion intensity would have meant that the coating would be worn off before the measurement finishes. Golanski et al.^[34] used two methods for characterising the nanoparticles released

through abrasion of paints. Particle concentration was measured using an Electrical Low Pressure Impactor (ELPI, Dekatis). Further, generated particles were sampled on grids and studied using TEM. The results showed that abrasion was found to produce submicrometric and micrometric airborne particles, however no nanoparticles. Further, characterisations by SEM confirmed that no free or agglomerated nanoparticles were emitted and hence nanoparticles remained embedded in the paint matrix. While TEM showed nanoparticles only embedded in the matrix.

In general very low amounts of nano-sized particle were released and/or could be detected in the reviewed studies investigating nanocoatings.

2.3.2 Nano-sized particles released from nanocomposites

Bello et al.^[26] investigated airborne exposures to nanoscale particles and fibres generated during dry and wet abrasive machining of advanced composite systems (3 phase systems) containing carbon nanotubes (CNTs), micron-diameter continuous fibres (carbon or alumina) and thermoset polymer matrices. Particle exposures were measured with a suite of complementary instruments, including two real-time particle sizers (FMPS Model 3091 and APS 3321 TSI Inc., St. Paul, MN, USA) and a condensation particle counter (TSI CPC 3007). No significant difference between composites with and without CNTs could be found in terms of overall particle release levels, peaks in the size distribution of the particles, and surface area of released particles. Additional SEM and TEM images of collected and filtrated aerosol particles showed typical background particles but no individual or bundles of CNTs.

Wohlleben et al.^[27] tried to identify the potential particle exposure from thermoplastic and cementitious nanocomposites, through different processes. Size-selective sampling was conducted using an universal nanoparticle analyzer (UNPA). The morphology, the size distribution and surface chemistry of the wear powders

were analysed. For the weathering experiments, the matrices were subjected to UV radiation according to ISO 3892-2:2006. Under this condition, the results showed that the polymer degraded to expose free CNTs up to $10\mu\text{ g cm}^{-2}\text{ year}^{-1}$, however a necessarily release could not be proven. Further, no nano-sized particles could be measured from the cement-CNT matrix during abrasion and ageing.

Sachse et al.^[94] studied real-time characterisation of the size distribution and number concentration of nano-sized particles (5.6-512 nm) emitted from polyamide 6 nanocomposites during mechanical drilling. Further, the respective emission rates were determined based on the particle population and the time. The measurements showed that the particle emission rates ranged from $1.16\text{E}+07\text{ (min}^{-1}\text{)}$ to $1.03\text{E}+09\text{ (min}^{-1}\text{)}$ and that the peak diameters varied from 29.6 to 75.1 nm. The authors^[94] showed that nano-sized airborne particles were emitted from all investigated materials, even the non reinforced polymer.

Schlagenhauf et al.^[28] used a rotary Taber abraser and silica/alumina abrasive wheels to investigate the release of particles from epoxy/MWCNT composite. A SMPS with a long DMA column (Model 3080, TSI) and a CPC (Model 3775, TSI) were used to monitor the release of airborne nanoparticles. All samples showed four different modes of particle size distribution, with the smallest size mode of between 300 nm and 400 nm, and the other three modes contain particle size between $0.6\text{ }\mu\text{m}$ and $2.5\text{ }\mu\text{m}$. The results showed that the addition of MWCNTs to the epoxy results in a shift of 70 nm to 90 nm to the smallest size mode and increases the size of the abraded particles. However, as shown in Figure 2.7, TEM micrographs revealed that free-standing individual CNTs and agglomerates were emitted during abrasion.

Similar to the studies conducted on nano-coatings, low quantities of nano-sized particles were measured. Therefore, the question about the release-ability of nano-sized particles and the compatibility of the measurement methods needs to be raised.

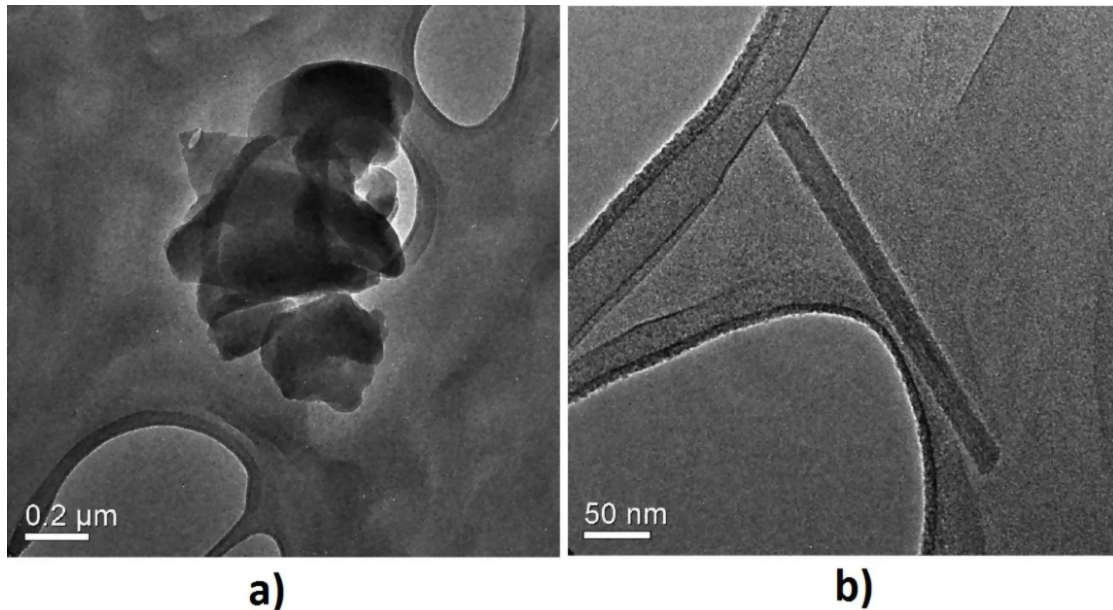


Figure 2.7: TEM images of abraded particles. (a) Agglomerated particles from the pure epoxy sample; (b) free-standing individual CNTs

Source: L. Schlagenhauf, B. T. T. Chu, J. Buha, F. Nueesch, and J. Wang.

Release of carbon nanotubes from an epoxy-based nanocomposite during an abrasion process. Environmental Science Technology, 46(13):7366-7372, 2012.

2.4 Measurement of airborne nano-sized particles

Airborne particles embrace a very wide range of sizes, mainly of solid material or droplets floating in the atmosphere^[95]. The smallest being only a few nanometres in diameter whilst the largest range up to 100 μm in diameter^[96]. Particles with a diameter smaller than 10 μm are able to remain airborne for a long period; in some cases those particles can stay in the air for several weeks, while those particles with a diameter larger than 10 μm are large enough to deposit quickly under the influence of gravity^[96].

To date it is evident that nano-sized airborne particles can be released from bulk nano-composite materials and nano-coatings during a variety of mechanical processes such as abrading^[27;28], sanding^[27;93], sawing^[26], drilling^[26;94;97], scratching^[34] and shredding^[29]. To measure the release and characterise these nano-sized particles, different sampling strategies and measurement devices can be utilised.

Measurement and sampling devices for airborne nano-sized particles presently used in release studies are summarised in Table 2.2. Additional, information about the different air monitoring devices can be found in Appendix A.

Table 2.2: Summary table of widely used air monitoring instruments

Instrument	Measurement parameter	Size range [μm]	Response time [s]	Sample flow rate (l/min)
CPC	Number concentration	0.003-0.025	4	0.3-3
SMPS	Size distribution, number concentration	0.0025-1	30-600	0.2-4
FMPS	Size distribution, number concentration	0.0056-0.56	1	10
ELPI	Size distribution, number concentration	0.03 -10	< 5	10 or 30
TEOM	Mass concentration	2.5-10	0.5	0.5-5

CPC - Condensation Particle Counter; SMPS - Scanning Mobility Particle

Sizer; FMPS - Fast scanning Mobility Particle Sizer; ELPI - Electrical Low Pressure Impactor; APS - Aerodynamic Particle Sizer; TEOM - Tapered Element Oscillating Microbalance

2.4.1 Scanning Mobility Particle Sizer (SMPS)

The SMPS measures the particle number size distribution and is composed by a Differential Mobility Analyser (DMA) and a Condensation Particle Counter (CPC)^[98]. Figure 2.8 shows the schematic working principal of a DMA and CPC. The CPC measures the particle numerical concentration in the air through laser optical detection^[99]. The requirements for using optical detection are particles with diameter bigger than 100 nm, therefore nanoparticles must be artificial enlarged^[100]. The measured nanoparticles are used as alcohol or water vapour condensation nuclei^[99], which enables the detection of nanoparticles with diameters

of 3nm^[100]. The optical detection is based on light scattering^[99]. The droplet enters the laser illuminated optical volume and generates scattered light by passing the laser beam, which is collected at 90° scattering angle with a mirror onto a photodiode^[101]. At present the main applications for CPC are applied for mobile aerosol studies such as; work place monitoring^[102–104], roadside monitoring^[105–107], environmental and climatic studies^[108], fundamental aerosol research^[109–111], filter testing^[112] and nanotechnology process monitoring^[27;28;31].

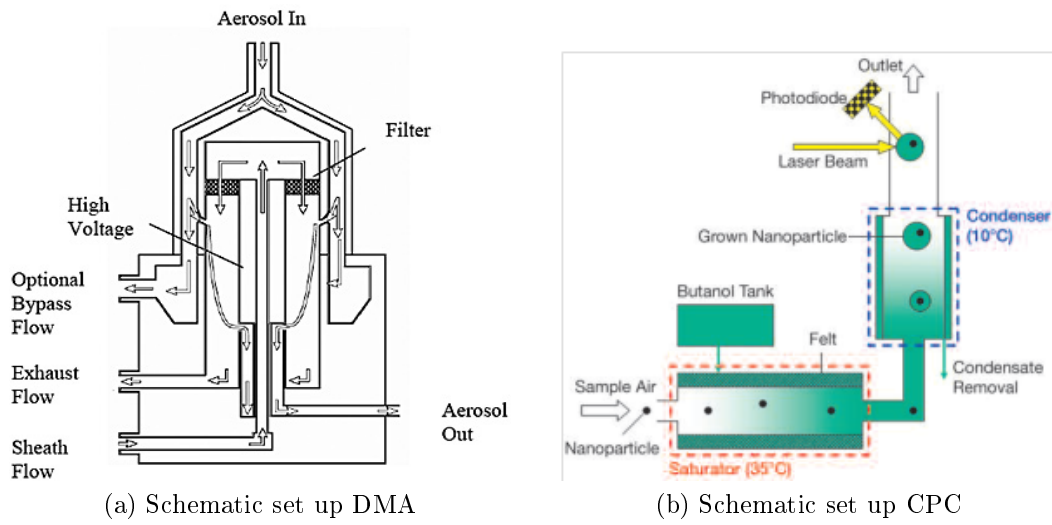


Figure 2.8: Schematic set up of a DMA and CPC

The DMA and the CPC are coupled in series and work as follows; in the first step the DMA selects a particle size interval of the sampled aerosol and then the CPC counts the particles exiting the classifier^[99]. The selection within the DMA is performed by applying an electric field between two concentric electrodes^[99]. The electrical charged particles move along a trajectory, which allows them to reach the outlet. Before the particles can pass into the DMA they have to be neutralised using radioactive sources (Kr85, Am241) to reach a state of charge equilibrium^[113]. Electric field scanning then allows different particle size to be selected for building up the particle size distribution^[100]. With this instrument a particle size range from a few nanometres to a micron can be measured. The SMPS

limited to static measurement e.g. environmental studies, due to its considerable size and weight^[114–117]. In some European countries, the presence of an internal radioactive source further restricts its use to laboratory applications^[23;118].

2.4.2 Fast Mobility Particle Sizer (FMPS)

The FMPS spectrometer measures sub-micrometre aerosol particles and can be considered as an *inside-out DMA* arrangement^[98]. Figure 2.9 shows the schematic working principle of a FMPS. It draws aerosol samples into the inlet, where the particles are positively charged using a corona charger^[98]. The charged particles are then introduced to the measurement region near the centre of a high voltage electrode column and transported down the column via high efficiency particulate air^[100]. A positive voltage is applied to the electrode and creates an electric field and according to their electrical mobility the particles are repelled outwards. Charged particles hit the respective electrometers and transfer their charge^[100]. Particles with high electrical mobility hit an electrometer near the top, while particles with a lower electrical mobility hit an electrometer lower the stack. The FMPS technique dramatically increases the speed of the particle-size and concentration measurements, in comparison to a SMPS^[113;116]. For measuring airborne particles it is common to combine FMPS with an additional CPC, as studied in published literature^[26;30;116;117;119].

2.4.3 Electrical Low Pressure Impactor (ELPI)

ELPI is a low-pressure cascade impactor, which measures the particle number concentration and particle number size distribution in real time^[120]. The working principle is shown in Figure 2.10. The corona charger at the instrument inlet, neutralises the particle charge and hence makes the deposition of particles at each collection stage (corresponding to their aerodynamic diameter) possible^[98]. The

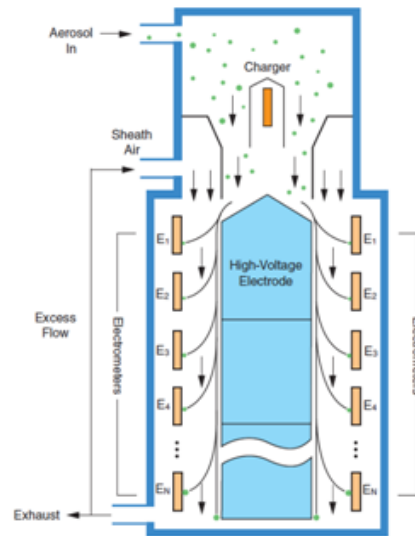


Figure 2.9: Schematic set up of a FMPS

current detected at each collection stage is then used to determinate the particle number concentration. The particle density is an essential parameter for the usage of the ELPI^[98]. As the particles are collected on each collection stage, chemical analysis can be performed on the particles, which offers an attractive option for the last four stages, which cut-off diameters are in the nanometric range^[23;121]. The particle density affects the impact location of each particle^[120]. However, the ELPI is limited to static, fixed station sampling due to its size and weight.

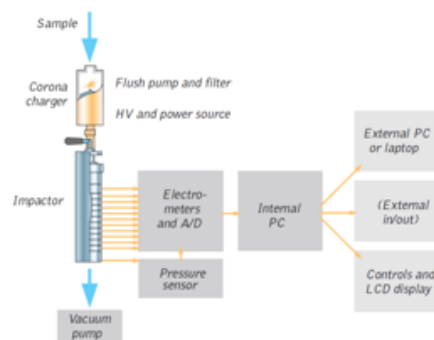


Figure 2.10: Schematic set up of a ELPI

2.4.4 Tapered Element Oscillating Microbalance (TEOM)

This instrument allows the automatic measurement of aerosol mass concentration^[98]. At present this is the only instrument measuring the mass of airborne particles in a single operation. The usual procedure to collect particles is to collect the aerosol on a filter and in a second step measure the deposited mass^[98]. A schematic drawing of the TEOM is displayed in Figure 2.11.

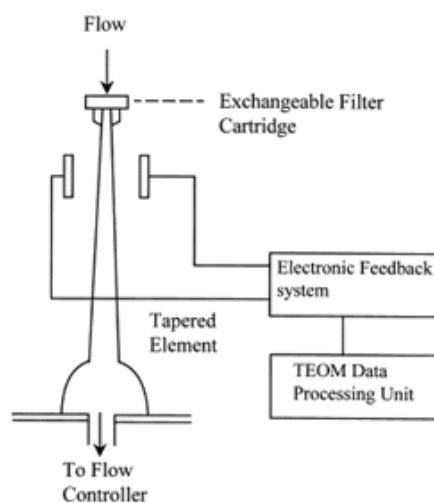


Figure 2.11: Schematic set up of a TEOM

Aerosol mass concentration ranging from $\mu\text{g}/\text{m}^3$ to g/m^3 can be measured by the TEOM, and particles can be collected on a glass tube-mounted filter. When airborne particles are collected the variation in oscillation frequency is observed. This variation of frequency is directly proportional to the mass of the particle^[122]. The TEOM is mainly used for environmental air quality monitoring stations, as it makes the sampling of aerosols with aerodynamic cut-off diameters of 10, 2.5 or $1\ \mu\text{m}$ possible^[122]. However, values given by these aerodynamic cut-off diameters, are rather different to aerosol fractions collected in industrial hygiene, especially in relation to the respirable fraction given for a four μm cut-off diameter^[98].

2.4.5 Comparison of devices for measuring airborne nano-sized particles

Presently, there is a number of devices and instruments to measure the properties of airborne nano-sized particles on the market. However, those instruments are limited to provide one parameter at a time and are mostly static because of their dimensions and their weight. Table 2.3 shows the advantage and disadvantage of the different instruments.

Table 2.3: Comparison between different measurement devices for nano-sized particles

Instrument	Advantage	Disadvantage
CPC ^[114;115;123]	+ Portable CPC available (small dimensions) + Some models compatible for use with SMPS	- Only number concentration measured - For some models external vacuum source needed
SMPS ^[114-117]	+ Highest-resolution (up to 64 channels/decade)	- Retarded response time
FMPS ^[114-117]	+ Use unipolar charger (eliminate the need for a radioactive neutralizer) + Real-time particle size distribution and total concentration	- Only for monitoring particle size up to 0.56 μm - Particle concentration vary by size
ELPI ^[115;124]	+ Possibility for chemical characterisation of size classified samples + Real-time particle size distribution and total concentration	- High acquisition cost - High sample flow rate & heavy (35 kg)
TEOM ^[125]	+ Real-time mass concentration averages + Only instrument that measures mass concentration	- Weight - Unstable behaviour when operating with particle free air

2.4.5.1 FMPS vs. SMPS

A comparison of a FMPS (Model 3091, TSI Inc., St. Paul, MN, USA) and a C-SMPS (Model 3785, nano-DMA, TSI Inc.) incorporating an CPC (Model 3786, TSI Inc.) was studied by Jeong et al.^[116]. The number concentration was substantially lower measured by SMPS than by FMPS ($\text{FMPS}/\text{SMPS} = 1.56$). The SMPS number concentration was on average $\approx 15\%$ higher than the FMPS data ($\text{FMPS}/\text{C-SMPS} = 0.87$). Furthermore, a good correlation ($r^2 = 0.91$) was found between C-SMPS and FMPS for the total particle number concentrations in the size range of 6 nm to 100 nm, measured at a road-side urban site. The particle size distribution measured by the C-SMPS was different from the size distribution measured by the FMPS. An empirical correction factor was obtained by comparing the FMPS data to size-segregated CPC number concentrations for atmospheric particles. The appliance of the correction factor to the FMPS data greatly improved the agreement of the C-SMPS and C-FMPS size distributions, as shown in Figure 2.12.

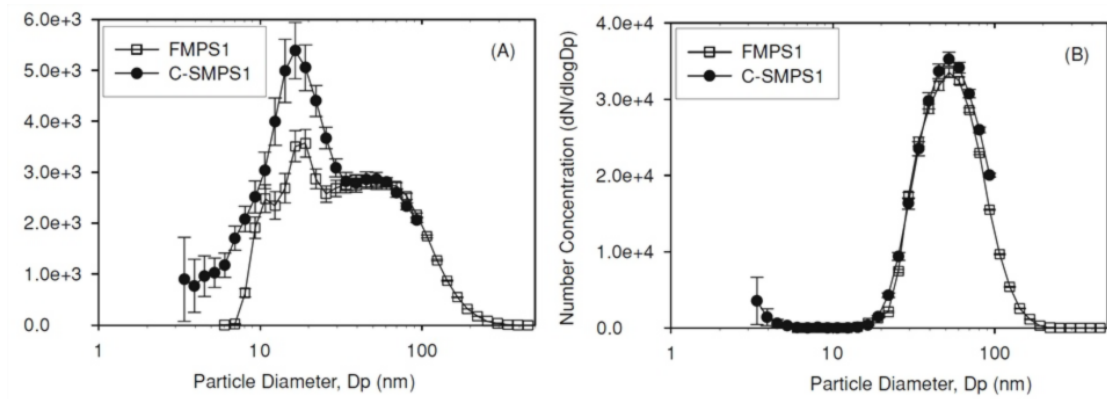


Figure 2.12: Average size distributions of indoor particles (A) salt particles (B) measured by the diffusion loss corrected SMPS (SMPS1) and FMPS (FMPS1).

Source: C.-H. Jeong and G. J. Evans. Inter-comparison of a fast mobility particle sizer and a scanning mobility particle sizer incorporating an ultrafine water-based condensation particle counter. Aerosol Science and Technology, 43(4):364-373, 2009.

Jeong et al.^[116] conclusion were that:

- Total number concentrations of particles measured by the three instruments were significantly correlated
- Size distributions measured by the FMPS and C-SMPS were different
- There is a need of empirical correction procedure to take into account the discrepancy between the FMPS and SMPS

Similar results were obtained by Asbach et al.^[117] while comparing four mobility particle sizers with different time resolution for stationary exposure measurements. Three SMPSs (TSI/3936, TSI/3936, Grimm/SMPS+C) and one FMPS (TSI/3091) were challenged with either NaCl or diesel soot particles. The results of this investigation showed that the sizing of all tested instrument was similar with only the FMPS size distributions consistently shifted toward smaller particle sizes.

2.4.5.2 SMPS vs. ELPI

Maricq et al.^[124] studied the perspective of characterising the particulate matter in motor vehicle exhaust by comparing SMPS (TSI model 3934L) with an ELPI (Dekati, Tampere, Finland) measurements. Although the ELPI and SMPS measure different physical properties, the aerodynamic diameter and mobility diameter, and the steady state particle size distributions were in close agreement. With one exception for the 37 nm impactor stage of the ELPI which overestimated particle number by up to a factor of two relative to the SMPS. The disagreements had little effect on the volume, or mass, weighted distribution. These, were generally in good agreement, although discrepancies appeared at large particle size due to multiple charging effects in the SMPS and to electrometer offsets and the small particle loss correction for the ELPI. Figure 2.13 shows a transient number

weighted distribution of gasoline vehicle particulate matter emissions recorded by ELPI and SMPS.

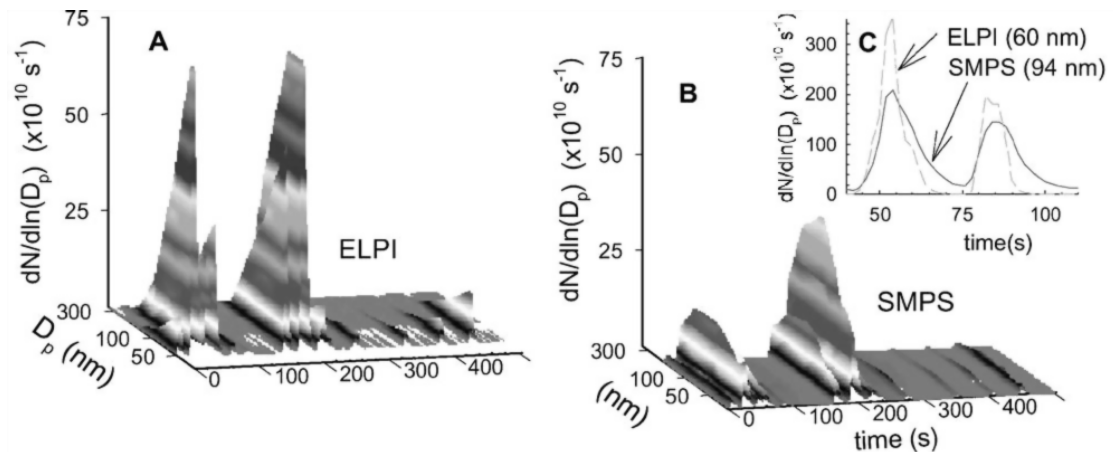


Figure 2.13: Comparison of ELPI (A) and SMPS (B) distributions of gasoline vehicle PM emissions versus particle diameter and time. C: Transient response of ELPI versus SMPS.

Source: M. M. Maricq, D. H. Podsiadlik, and R. E. Chase. Size distributions of motor vehicle exhaust pm: A comparison between elpi and smps measurements. Aerosol Science and Technology, 33(3):239-260, 2000.

2.4.6 Collection of airborne particles

For full nano-sized particle characterisation it is crucial to be capable to collect a fraction of the particles for further investigations e.g. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) or for toxicological studies^[113]. A common method for collecting airborne particles is the utilisation of electrostatic precipitators (ESPs)^[95]. The basic operation of an ESP particle sampler entails the steering of the subject aerosol through a flow channel^[95]. Within the channel an intense electric field is created. As aerosol particles enter the electric field and become charged by ions generated during corona discharge at the anode needle^[95]. The charged particles subsequently drift at a velocity determined by their electrical mobility, in the strong electric field toward a grounding/collection plate onto which a sampling substrate e.g. TEM grid, is mounted^[126]. The effective particle collection surface area of the ESP is significantly smaller compared to

a filter so that sampling artifacts, such as vapour adsorption and particle evaporation, can be reduced. However, due to the usage of high-voltage electrical fields and corona discharges the ESP generates ozone and oxidant ions, such as O^{2+} , O^+ , N^{+2} , N^+ , NO and H_3O^+ ^[95]. These by-products have the potential to react with both particles and vapours that enter the plasma region. Degradation of particle bound compounds by these reactions may limit or even preclude the use of ESPs as a sampler for aerosol particles^[127].

The main challenge for sampling airborne particles for characterisation studies lies in obtaining good and quantifiable recovery of all size fractions of particles. Table 2.4 shows the main features of the sampling instruments presently available on the market.

Table 2.4: Sampling instruments for nano-sized particles

Instrument	Model/ Manufac- turer	Size range [nm]	Sample flow rate [l/min]	Sampling substrate	Additional instru- ments
ESP	5.561/Grimm Aerosols	0.8 -1100	0.3 to 5	SEM/TEM Ni-grids	DMA
NAS	3089/TSI	2 -100	0.2 to 2.5	SEM/TEM Ni-grids	DMA
LPI	DLPI/Dekati	30 - 10 μm	10 or 30	Collection plates	N/A
BAS	Different Filter sizes/SKC	<100 μm	4	Filter	N/A

ESP - Electrostatic Precipitator; NAS - Nanometer Aerosol Sampler; LPI - Low Pressure Impactor; BAS - Button Aerosol Sampler

2.4.7 Deficiencies of devices for measuring airborne nano-sized particles

2.4.7.1 Particle losses

Particle losses have been observed during several studies^[116;121;128;129]. As smaller particles have larger diffusion coefficients, the larger particles, diffusion losses are more significant for particles smaller than 10 nm. Wang et al.^[129] discovered that diffusion losses can be caused by low air flow through bends even in the same length of sampling tubing. Jeong et al.^[116] compared a FMPS with a SMPS incorporating a CPC. The study showed an increasing particle loss due to differences in penetration efficiency arising from diffusion losses during transport through the sampling system of the SMPS. Diffusion and space charge losses could also be detected by Tzankiozis et al.^[128] in the ELPI based investigations. Marjamaeki et al.^[121] evaluated the performance of EPLI and criticised the high particle loss for particles larger than 2 μm , which vary from the specification given by the manufacturer. The reason for this discrepancy was the loss of highly charged coarse particles. The perpendicular design of the aerosol flow and electrical field directions are the reasons for higher particle losses.

2.4.7.2 Background noises

Another major problem with the measurement and sampling of aerosols is the avoidance of *background noise* of natural origin and from human activities. This *background noise* must be taken into consideration while measuring aerosols and if possible eliminated, especially when measuring the numerical particle concentration. For example, Koponen et al.^[30;119] used a sander to generate nanoparticles from paints and noted that the sander was the main source of particles smaller than 50 nm.

2.4.7.3 Low volume flows

As shown by Wang et al.^[129] low air flow, in the measurement devices can induce particle losses. Additionally the low flow volume limits the most instruments for particle sampling, because of the long sampling times. Furthermore, the possibility to obtain good and quantifiable recovery of all size fractions of particles is still inaccessible. Studies addressing concentration enriched systems^[130–132] have shown a good approach to simplify particle sampling for toxicological studies. However, the development of those systems is still at infancy and further research must arise.

2.4.7.4 Contamination of sampled particles

Sampling of particles seems a major problem, not only due to the low flow rates, long sampling time and the inability to recover quantifiable particles of all size fractions. Sampling of particles via filters has several potential sources of contamination. Filtration is susceptible to both physical and chemical contamination occurring during sampling, including evaporation of semi-volatile compounds, adsorption of gases on the filter material, and possible reactions between collected particles and gaseous compounds, because of the large effective surface area of the filter matrix^[133]. The alternative for collecting airborne particles the electrostatic precipitators (ESPs) has some contamination issues as well. The usage of high-voltage electrical fields and corona discharges generates ozone and oxidant ions, such as O^{2+} , O^+ , N^{+2} , N^+ , NO and H_3O^+ ^[95]. These by-products have the potential to react with both particles and vapours that enter the plasma region. Degradation of particle bound compounds by these reactions may limit or even preclude the use of ESPs as a sampler for aerosol particles^[127].

2.5 Conclusion

Polymer nanocomposites, although known for many years, are still engaging communities worldwide, and the scientific literature is being enriched at an increasing rate. Today, nanocomposites can be prepared by melt blending of the polymer and the fillers, in large scale. However, other preparation routes such as in-situ intercalative polymerisation are very attractive, especially when this method is directly combined with polymer extrusion.

In case of polymer for lightweight structures, silica based particles gain importance, due to their good mechanical properties and high thermal stability. However, in most cases, they first need to be surface- modified in order to become miscible with the chosen polymeric matrices. Additionally, factors such as type of polymer, the preparation technique and the processing conditions are affecting the formation of nanocomposites. In general, once a nanocomposite is successfully fabricated significant improvements in mechanical, chemical and physical properties are reported.

While polymer nanocomposites bear significant benefits, only little information is available on the material behaviour once subjected to mechanical, photolysis, and incineration processes. Hence, in recent years the investigation of release scenarios of nano-sized particles from nanocomposites and nanocoatings, gained academic and industrial research interest. However, release studies so far have looked at only a very small set of possible material systems and release scenarios. The characterisation of the released particles was only executed to a limited extent. The information obtained from these studies such as knowledge about particle size, composition, and surface characteristics is therefore extremely scarce. Further this literature study revealed the prevailing lack of insights under which conditions and in which life cycle phases nano-sized particles may be released from nanocomposites.

Different devices were used to measure and characterise the nano-sized particle release. The quantity and properties of released nano-sized particles depended on factors such as; type and quantity of nanomaterials, work practices and working environment. However, the lack of standard set ups and sampling protocols makes the evaluation of the results reviewed in this study very challenging. Nano-sized particles come in numerous different sizes, shapes and compositions. Therefore, it is crucial for the measurement instrument to be suitable for all nano-sized particles and their wide concentration range. However, current instruments are limited to provide one parameter at a time and are mostly static because of their dimensions and their weight. Furthermore, additional instruments, e.g. filters or electrostatic precipitator are needed to sample the particles. Additionally, microscopy methods, especially SEM, TEM, and AFM have strengths and weaknesses with regard to possible media, availability, practicality, and potential for quantification.

At this time, the knowledge base and instrumentation for measuring the properties of nano-sized particle released from polymer-based composites is limited, and opportunities abound for scientific and technological advances in this important area.

Form this literature review the following key findings can be summarised:

- During the past decade, polymer nanocomposites have emerged as a novel and rapidly developing class of materials and attracted considerable investment in research and development worldwide. Importantly, the possibility of tailoring properties as needed makes polymer nanocomposites very attracted.
- Currently there is a lack of information in the literature on nano-sized particle emission from these materials. It is crucial for the assessment of the potential environmental and health risks of nano-sized particles to understanding the exposure mechanism. Therefore, attention must be paid to particles that are released from nanomaterials during different processes.

- At present there are no systematic characterisation standards and sampling protocols, and hence those need to be developed and published. Devices for measurement and characterisation of nano-sized particle still lacks in the capability of reproducing similar results.
- The exposure studies so far have looked at only a very small set of possible material systems and release scenarios. The characterisation of the release particle was only executed to a limited extent and any kind of correlation between material properties and particle release was missed.
- A risk, related to nano-sized particles may only arise if both a hazard potential and exposure exist both and can be identified. If nanomaterials can not be tracked, it will be almost impossible to determine how benign or harmful their presence is.

Chapter 3

Physical characteristics of nano-sized particles emitted during drilling of polypropylene and polyamide 6 nanocomposites

3.1 Introduction

Intense structural applications in various fields, such as aerospace, automotive, marine, infrastructure, military, etc., have driven the commercial importance of polymer composites^[36]. While traditional composites, consist of macro fillers and polymer matrix, in recent years composites based on nanofillers have received increasing research interests. Due to the increased filler/matrix interface area, nanofillers are believed to have positive influence on the composites properties^[5]. Therefore, a large quantity of nanofillers, such as nanotubes, nanofibres, layered nanostructures or nanoparticles, are presently available due to the establishment of well-developed manufacturing technologies. Among various nanocomposites, much attention has been paid to polymer/silica nanocomposites, because of the

enhanced mechanical properties^[1;3-5], high thermal stability^[8;9] and high flame retardants^[12;13]. Therefore, nanocomposites have proven huge potential for both mechanical and thermal application^[39;134].

At the same time, this new industry is only capable of succeed if it takes part to a responsible development for humans and the environment. Due to the absence of reliable data on the toxicological impact of nano-sized particles emitted by nanocomposites, the only way to guarantee risk free exploitation is to verify that nanocomposites do not release their nanofillers during their life cycle. Emphasis, in particular, needs to be given to composites intended for direct contact with consumer, especially in usage and end of life phase.

Up to date, only little attention has been paid to the end user contact with nanocomposites. Despite the worst case scenario of a nanocomposite being the encounter with a do it yourself worker^[84]. During mechanical processes such as drilling, sawing, and sanding shear forces may detach free nanofillers or polymer/nanofiller hybrids as nano-sized particles. As in general, the do it yourself worker's personal protection consist of an low-cost filter mask, which might be inadequate for protection against particle in nanosize and hence risk of inhalation of the particles is considerable. If not inhaled, nano-sized particle once released from nanocomposites will deposit eventually and might cause a threat to soil and ground water systems^[96].

While profound studied have been carried out on the dust emitted from milling, grinding, turning, boring, and drilling of different metals and metal alloys^[135-137], the field of machining of polymers and polymer composites seem untouched at present.

In the current work, silica based polyamide 6 and polypropylene nanocomposites were manufactured and their thermal properties were investigated. Further, particles emitted by the nanocomposites by mechanical drilling were investigated in a controlled environment. The particle number concentration and the size distribu-

tion of airborne particles were measured continuously using a particle sizer. The airborne particles emission rates were calculated and the deposited particles were sampled and characterised.

3.2 Experiments

3.2.1 Preparation of nanofillers

Surface modified montmorillonites (DELLITE[®] 43B and 72T, Laviosa) were used as a filler for the integration into the polymeric matrices. DELLITE[®] 43B and 72T are OMMTs deriving from a naturally occurring montmorillonite especially purified and modified with a quaternary ammonium salt (dimethyl benzylhydrogenated tallow ammonium, in the case of DELLITE[®] 43B and dimethyl dihydrogenated tallow ammonium, in the case of DELLITE[®] 72T).

In addition, fumed nanosilica particles (AEROSIL[®] R 974 and 200, Degussa, Evonik Industries) were investigated as nanofillers. AEROSIL[®] R 974 was a hydrophobic fumed silica aftertreated with DDS (dimethyldichlorosilane) based on a hydrophilic fumed silica, while AEROSIL[®] 200 was a hydrophilic fumed silica. At present, these types of modified montmorillonite (OMMT), and nanosilica (nano-SiO₂) are produced in large scale from major global producers, with intention of nanocomposite fabrication. Hence, some nanocomposites currently on the market might already have these types of nanofillers integrated and therefore a suitable choice for this study.

Further, foam-glass crystal material (FGC) which was a nano-structured foam glass material was synthesised, by the Department of Silicate Technology and Nanotechnology at Tomsk Polytechnic University, Russia. Figure 3.1 illustrated the process of FGC production. After the selection and mixing of the raw materials (broken glass), quenched cullets were synthesised by thermal treatment of the mixture at

1400-1500°C. After a cooling period, the cullets were ground to a fine powder. This powder was then mixed at 800 - 900°C with a gas foaming agent, for the production of the final foam-glass crystal material. FGC are high performance, long lasting, durable and environmentally friendly insulation for building. As fillers in cementitious materials or polymer they offer huge potentials in the construction industry and rapidly gaining importance.

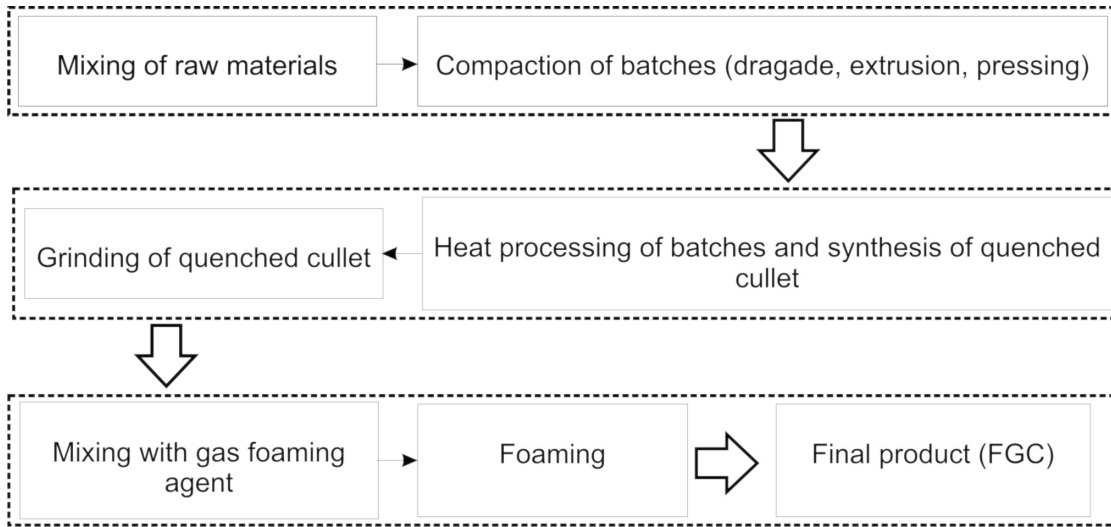


Figure 3.1: The principal procedure for foam-glass-crystal materials

To understand the difference in release scenarios between nano and micro filled composites, conventional glass fibres (TGFS 202P and TGFS473H, Taiwan Glass Fibres Corporation) were used for micro composite fabrication.

3.2.2 Preparation of polymer nanocomposites

The most common engineering thermoplastic polymers used, especially in the automotive industry, are polypropylene (PP) and polyamide (PA) because of their good mechanical performances, processing properties and low cost. Therefore, for the intention of this study both PP and PA6 were chosen as matrix materials.

The initial selection among different types of polyamides and polypropylenes was made on the basis of their melt flow index value and mechanical properties. Based

on those criteria polypropylene (Moplen HP500J, Basell Polyolefins) with a melt volume flow rate of 4.3 g/10 min (230°C/2.16 kg), tensile modulus of 1500 MPa, tensile stress at yield of 34 MPa and Charpy notched impact strength of 4 kJ/m² (at 23°C) and polyamide 6 (Tarnamid T-30, Azoty Tarnow, Poland) with a melt volume flow rate of 25.0 g/10 min (275°C/5.0 kg), tensile modulus of 1100 MPa, tensile stress at yield of 28 MPa and Charpy notched impact strength of 5 kJ/m² (at 23°C) were chosen as appropriate polymeric matrices.

Compounding of nanofiller and matrix material was conducted in a twin-screw extruder (ZMK/ 116/ 10, ZAMAK- Cable Machinery Plant, Poland). The matrix material and 5 wt.% of the nanofiller were premixed and batched by the main feeder to the first barrel zone. Extruder screw diameter was 24 mm, had a length/diameter ratio of 32 and consisted of 6 barrel zones. A conventional screw configuration was used for material compounding, equipped with two high-shearing zones in the second and fifth zone. The obtained granulate was then used for nanocomposite panel manufacturing by compression moulding. The mould temperature was kept at 250°C over the compression time of 5 min. Due to the high dimensions of the panels, cooling of the polymer melt was completed in the mould in order to avoid warping. Correspondingly, neat PP and PA6 panels were manufactured as reference material.

Additionally, a single-screw extruder (ZMK/ 116/ 10, ZAMAK- Cable Machinery Plant, Poland) with length/diameter ratio of 25 and a screw diameter of 25 mm was used to manufacture the polymer/glass fibres composites. The single-screw extruder provided an effective homogenisation of classic fillers, without geometry changes of the filler material during mixing.

3.2.3 Characterisation

A JEOL-200CX transmission electron microscope was used to investigate the morphology of nanofillers. Particles for TEM investigation were first suspended in ultra

pure water and sonicating for 2 hours. A drop of this suspension was then placed on a carbon-coated copper TEM grid (200-300 mesh) and left to dry in air.

Crystalline structure of the manufactured nanocomposites was studied with help of powder X-ray diffraction (XRD). XRD studies were performed between 3° and 60° scattering angle, using a Philips X-Pert diffractometer, with graphite monochromator placed in the front of detector ($\lambda_{Cu} = 1.5418 \text{ \AA}$).

With help of a small angle X-ray diffraction (SAXD) morphological analyses were performed on a powder diffractometer Philips PW 1830 equipped with a Kratky's camera (MBraun Austria), at a voltage of 40 kV and a plate current of 30 mA. The exposition time varied between 600 and 900 s.

For the differential scanning calorimetry (DSC) measurements a Netzsch DSC 200, operating in dynamic mode (heating/cooling rate = 10 K/min), was employed. Samples of 5 mg were placed in sealed aluminium pans. Prior to use the calorimeter was calibrated with indium and mercury standards and liquid nitrogen was used as cooling medium. Two heating scans were conducted, as the first heating scan was necessary to remove the thermal history of the materials, which was introduced to the material during manufacturing. In order to estimate the percentage of crystallinity χ , the following equation was used^[138–140]

$$\chi = \frac{\Delta H_f}{(1 - \Phi_p) \cdot \Delta H_f^0} \cdot 100 \quad (3.1)$$

where Φ_p is the weight fraction of filler in the composite, ΔH_f is the heat of fusion of the analysed sample (J/g), and ΔH_f^0 is a reference value which represents the heat of fusion for a 100% crystalline polymer. Wunderlich^[141] has created tables of best estimate values for the heats of fusion for a wide variety of linear polymers with values reported in joules per mole of repeat unit. However for use in thermal analysis, these enthalpy values need to be normalised to the mass. For PP the

heat of fusion ΔH_f^0 was 207 J/g, and for PA6 it was 226.1 J/g^[142].

A Netzsch thermogravimetric analyzer TG 209 was used to investigate the thermal stability of the obtained nanocomposites. The samples were heated in an open α -Al₂O₃ pan, from 30 to 650°C at a heating rate of 10K/min under air atmosphere.

3.2.4 Measurement of airborne particles concentration and size distribution

To characterise the physical properties of particles generated during drilling, composite panels were fixed in a chamber, with dimensions 69 cm (width) x 33 cm (depth) x 56 cm (height) as illustrated in Figure 3.2. The particle emissions were measured using a condensation particle counter "CPC" 5.403 with classifier "Vienna"-DMA 5.5-U (SMPS, Grimm Aerosol, Germany). SMPS measured sub-micrometer particles generated during drilling process over a particle size range of 5.6-1083 nm and a particle size resolution of 32 channels in total. An angle drill (Makita BDA351Z 18V LXT Angle Drill) with a maximum speed of 1800 min⁻¹, adapted with a conventional drill bit of 10 mm diameter was used for drilling. Prior to the measurements, the chamber was purged with laboratory air for 20 min. Each sampling cycle comprised a 60 min background air monitoring in the chamber, 14 min of active drilling, and a 60 min post-drilling period. The experiment was repeated 3 times for each material composition. A total of about 2000 to 3000 data sets were collected for each particular sequence. During the measurements the accumulative particle size distribution of released nanoparticles could be followed on the monitors, as shown by the screen shot in Figure 3.3. By this on-line measurement the actual (green line) and the series of previous scans (yellow line) could be reviewed, which gave good indication on the release scenario during drilling.

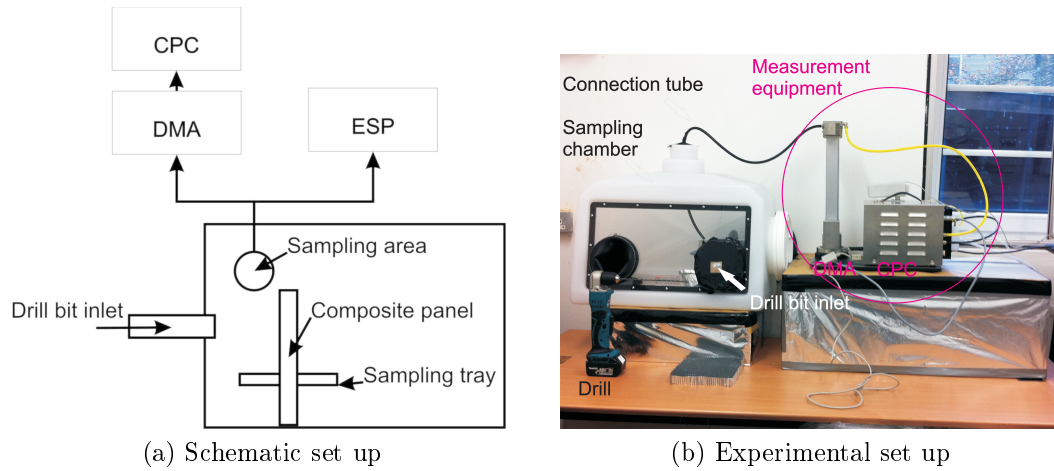


Figure 3.2: Apparatus and setup for the experimental measurement of airborne particles concentration and size distribution via SMPS in a closed environment

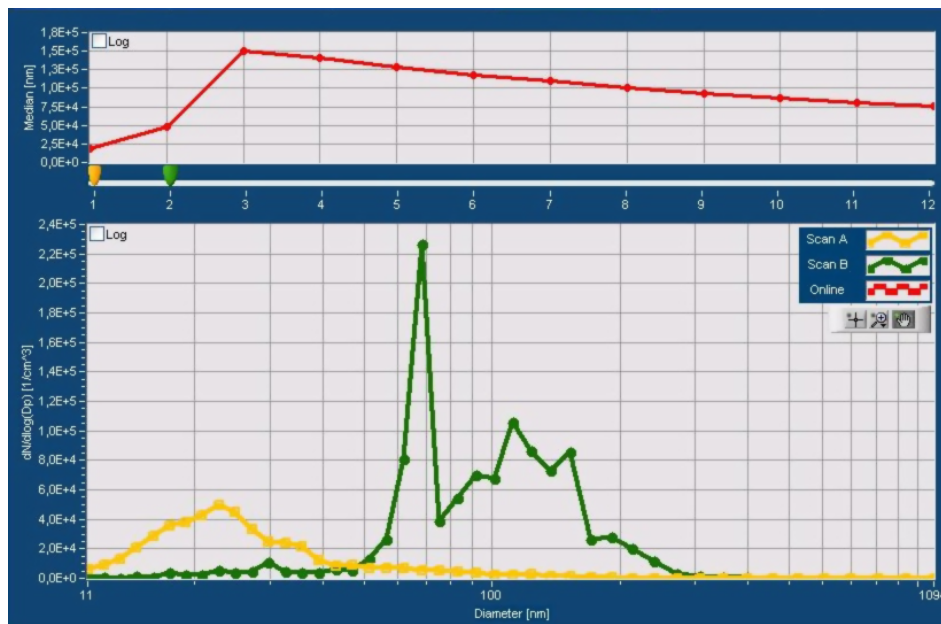


Figure 3.3: SMPS on-line measurement of the particle size distribution (difference in the natural logarithm of the particle concentration vs. mean particle size) during drilling; the green line represents the actual measurement and the yellow line represent the previous measurements

3.2.4.1 Determination of emission rates

The emission rates of particles of different sizes were determined from the number concentration and size distribution data based on a single compartment population balance model. Liu et al.^[143] used a mass balance model to estimate emission rates of particles based on mass concentrations. As reported by See et al.^[144], the mass balance model calculation can also be used to estimate the particle emission

rate based on particle population. Basic assumptions for this model were made as followed: (i) background concentration is zero, (ii) particle concentrations are homogeneous within the chamber, and (iii) emission rate and decay rate of the particles remain constant throughout the entire period of generation.

The respective removal rates k_x (min^{-1}) of a particle with the size x were evaluated using the following equation:

$$k_x = \frac{\ln(C_x/C_{max;x})}{t_{max}-t}; \quad \text{for } t_{max} \leq t \quad (3.2)$$

where C_x (cm^{-3}) represents the number concentration of particles of a size x at the time t (min), while $C_{max;x}$ (cm^{-3}) represents the maximum concentration of particles of a size x at the time t_{max} (min). The background concentration of particles, averaged over the 60 min pre-drilling interval, was subtracted from the concentration C_x (cm^{-3}) and $C_{max;x}$ (cm^{-3}).

After calculating the removal rates k_x , the emission rate of particles of size x , P_x (min^{-1}) in the chamber volume $V=1.265 \times 10^5 \text{ cm}^3$, was calculated from:

$$P_x = \frac{VC_x k_x}{1 - e^{k_x t}}; \quad \text{for } 0 \leq t \leq t_{max} \quad (3.3)$$

The sequential alteration of the total number concentration of particles for a typical sampling cycle consists of a 60 min background measurement ($t \leq t_{max}$), a 14 min drilling period ($0 \leq t \leq t_{max}$), and a 120 min post-drilling period ($t \geq t_{max}$).

3.2.5 Sampling and characterisation of deposited particles

Figure 3.4 represents the outline of the generation, sampling and characterisation process followed for the deposited particles.

Deposited particles were collected on the sampling tray inside the drilling chamber. Deposited particles (30mg) were sampled in a dry state and analysed by suspending them in solution (20 ml). This solution was first filtered using general

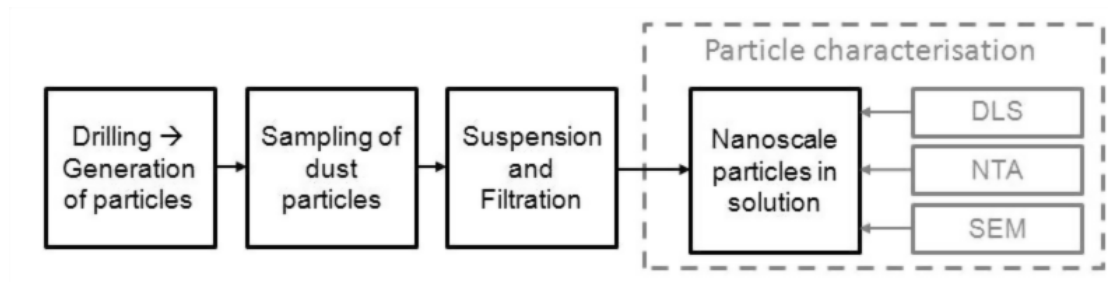


Figure 3.4: Outline of generation, sampling and characterisation processes for deposited particles

porpoise filter paper (Whatman, Standard Grades 11 μm) and in a second step, ultrafiltrated (Vivacell 250 ultrafiltration system, Sartorius StedimBiotech GmbH, Germany) for size fractionation. Filters with a molecular weight cutoff of 5000 were used under 3.5 bar pressure.

Particle size distribution was measured by dynamic light scattering (Zetasizer nano zs, Malvern Instruments Ltd.). Dynamic light scattering (DLS) is widely used to determined particle sizes from the fluctuations in scattered light intensity due to the Brownian movement of the particles^[145;146]. With a sterile syringe 1.5ml of the solution was extracted and inserted in the appropriate vials for DLS.

Samples were also analysed via nano scale particles tracking analysis (NTA) provided by Nanosight (Model LM20, NanoSight Ltd.). This technique is a combination of laser light scattering microscopy with a charge-coupled device camera, which enables the visualization and recording of nano scale particles in solution. In addition the image processing software (NTA) identify and tracks individual nano scale particles moving under Brownian motion and relates the movement to a particle size according to the Stokes-Einstein relation. The solution was introduced to the nanosight equipment using a disposable syringe.

Additionally, the particles morphology was investigated by using a FEI XL30 field emission scanning electron microscope (SEM). The operating voltage was in the range of 10-20 kV to minimise charging of the sample. Specimens were prepared by sonicating the solution for 15min at 35kHz, then a drop of the solution was

dropped on a silicon chip specimen substrates (SPI substrate) and left to dry.

3.3 Results and Discussion

3.3.1 Nanofillers

Surface modified clays (OMMT) were necessary to make the intercalation of the polymers into the interlayers possible. Due to the ion-exchange reactions of the cationic surfactant with the alkylammonium cations, the surface energy of the inorganic MMT was lowered and the interlayer spacing of the layered MMT increased. The increase in interlayer distance can be seen in the WAXD diffractogram, which is illustrated in Figure 3.5. The diffraction peak was observed at $2\theta = 6.5^\circ$ ($d_{001} = 1.35$ nm) for the unmodified MMT. The peak for the OMMT shifted to the left, hence the diffraction peak was observed at $2\theta = 5.32^\circ$ ($d_{001} = 1.63$ nm). Shifting of the diffraction indicated an increase in interlayer spacing from 1.35nm to 1.63nm (according to Braggs' law).

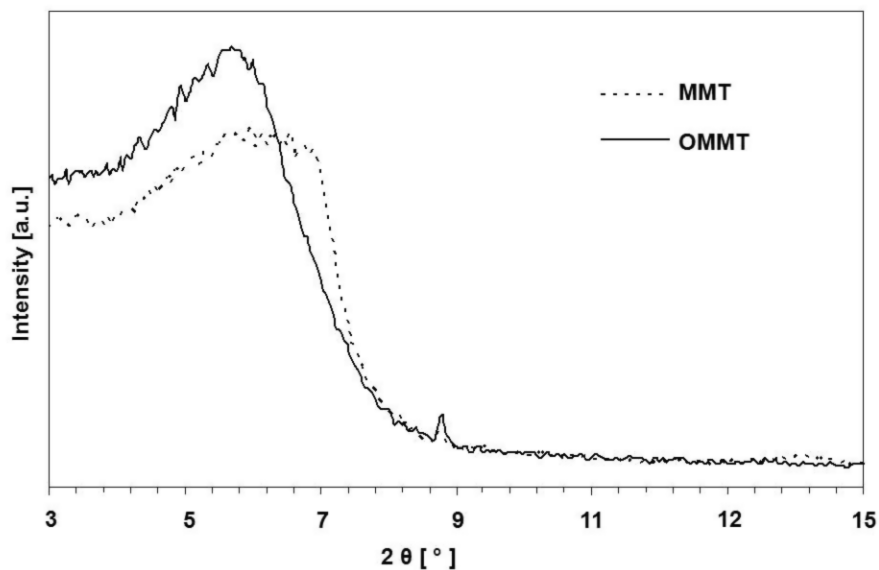
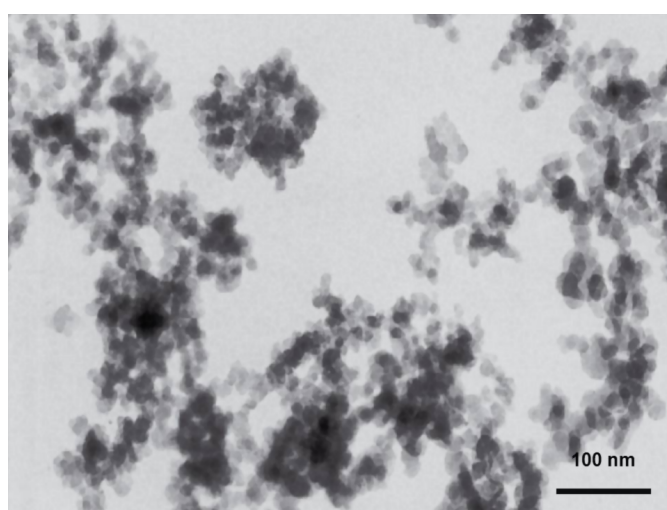


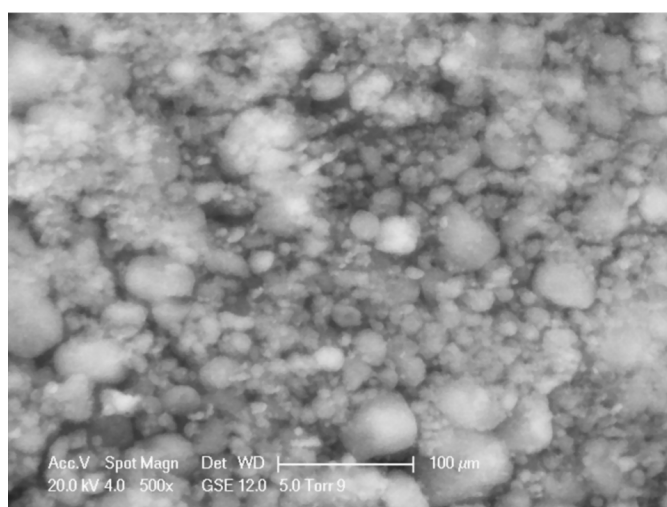
Figure 3.5: WAXD diffractogram of unmodified and OMMT

Primary particles of the nano-SiO₂ were virtually spherical and free from pores.

Aggregate bodies were formed which accumulate reversibly into agglomerates, as shown in Figure 3.6a. Spherical particles of 7-12 nm in diameter could be detected which were bonded in branched agglomerates. From the SEM micrographs (Figure 3.6b) it can be seen that the agglomerates of nano-SiO₂ had sizes up to 50 μ m. However, for polymeric compositions, fumed silica is especially recommended for practical use because the branches of nanometric diameter are already evenly distributed materials. Thus, the complex process of dispersing may even be replaced by a simple mixing process.



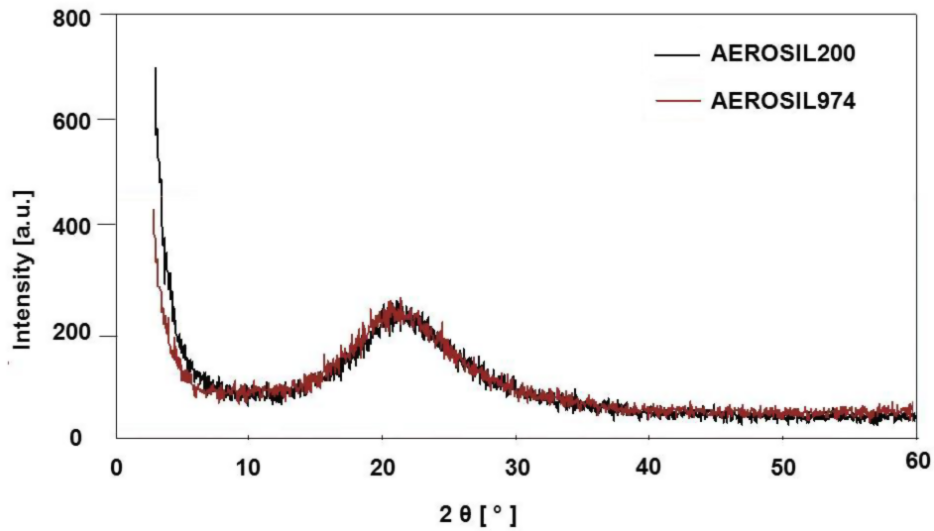
(a) TEM



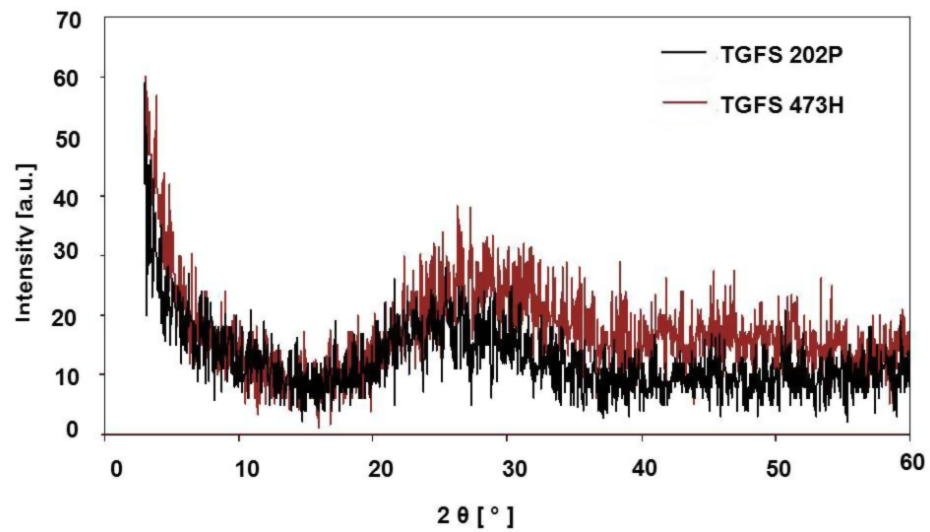
(b) SEM

Figure 3.6: TEM and SEM micrographs of AEROSIL 200

Figure 3.7a shows the WAXD diffractograms of the fumed silica. The diffraction pattern for the hydrophilic AEROSIL 200 and hydrophobic and AEROSIL 974 are similar and did not showed any presence of crystal silicon dioxide phase. Both glass fibres for polyamide (TGFS 473H) and polypropylene (TGFS 202P) were amorphous since their WAXD diffractograms presented only wide amorphous phase without diffraction peaks from a crystalline phase, as shown in Figure 3.7b.



(a) Nano-SiO₂

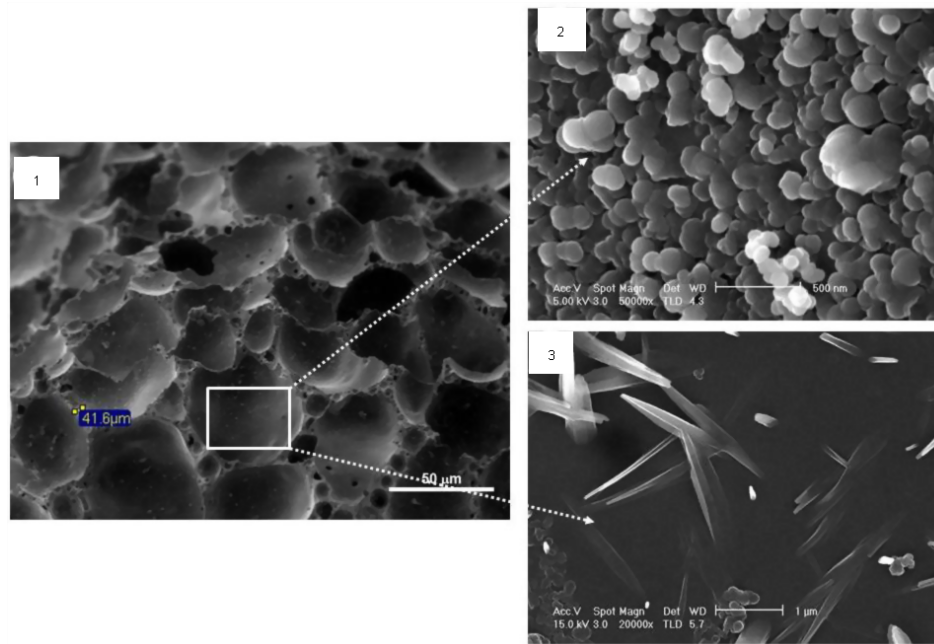


(b) Glass fibres

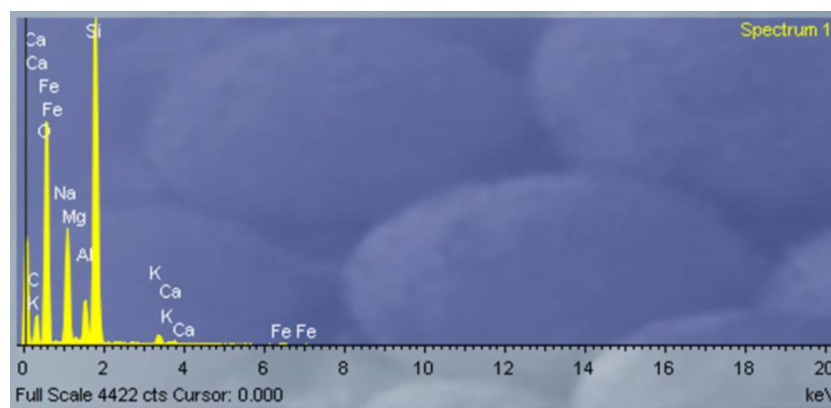
Figure 3.7: WAXD diffractograms of nano-SiO₂ and glass fibres

Foam glass crystal material displayed a complex porous morphology with macro-

cells up to 50 μm in diameter. FGC morphology can be seen in Figure 3.8a and its EDX spectrum is shown in Figure 3.8b. The EDX spectrum consisted of 46.54 wt.% oxygen, 19.74 wt.% carbon, 17.39 wt.% silicon, 11.55 wt.% sodium, 2.84 wt.% aluminium and traces of calcium, iron enlargement of the pore walls (Figure 3.8a B and C) showed the existence of two heterogeneous nano structure in the material, caused by the presence of interpore partitions formed by the structural units. Nano-scaled plates with diameter between 80-500 nm could be found (Figure 3.8a B), as well as fibrous structures (Figure 3.8a C). As reported by^[147], the major difference between this structural units and the amorphous phase is the increase of SiO_2 content. Therefore, it can be concluded that the spatial heterogeneity of the glass phase is caused by the dissolution of the residual quartz of the glass granulate during the primary treatment of the material during foaming.



(a) SEM



(b) EDX

Figure 3.8: SEM micrographs (1) surface area (2)(3)pore walls at higher magnifications and EDX spectrum of FGC

3.3.2 Structure and morphology analysis of nanocomposites

3.3.2.1 PP composites

Figure 3.9 shows the nanocomposites panels manufactured in laboratory scale. As neither additives nor stabilizers were used and the PP manufacturing was found very sensitive to temperature changes during production, some panels indicate signs of degradation (yellow and brown marks on the surface of the panels).

Figure 3.10 shows the WAXD diffractogram of the manufactured PP nanocom-

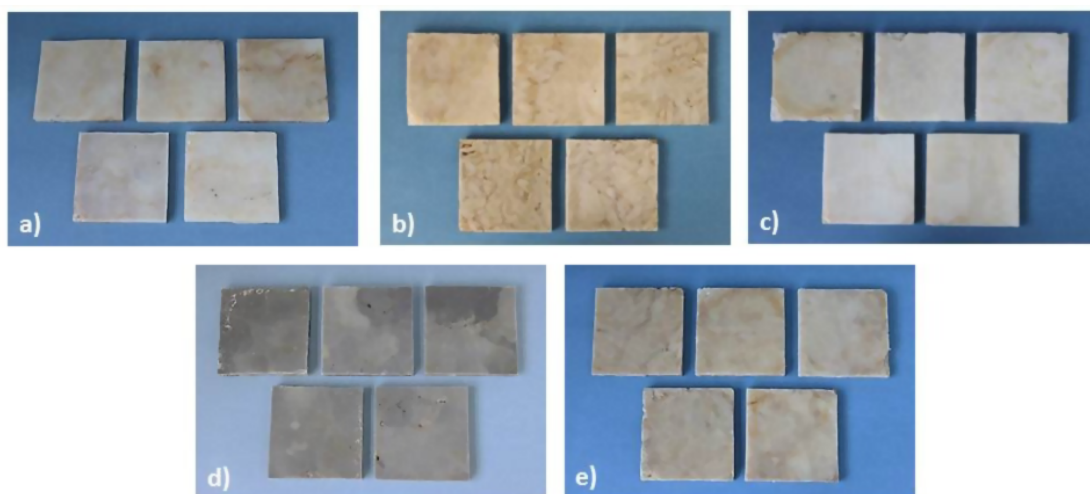


Figure 3.9: Manufactured nanocomposite based on PP matrix a) neat panel, b) OMMT c) Nano-SiO₂ d) foam-glass-crystal, and e) glass fibres

posite systems. The diffractogram for the neat PP matrix had a peak at $2\theta = 15.95^\circ$, which is associated with the 300 plane of β -phase crystals. However, the WAXD peak was weaker for the OMMT composites, indicating some changes in crystal structure of the material (Figure 3.10a). The group of diffraction peaks at 14.05° , 16.8° , 18.5° and 21.2° corresponds to the primary diffraction of the α -phase crystals. Similar polymorphic behaviour was observed for the PP/nano-SiO₂ nanocomposite (Figure 3.10b) and the PP/FGC (Figure 3.10c) composite. However, this could not be observed for the PP/GF (Figure 3.10d) composite. It is likely that due to the filler size, the particles had a more intimate contact to the matrix and therefore a stronger influence on the crystallisation process.

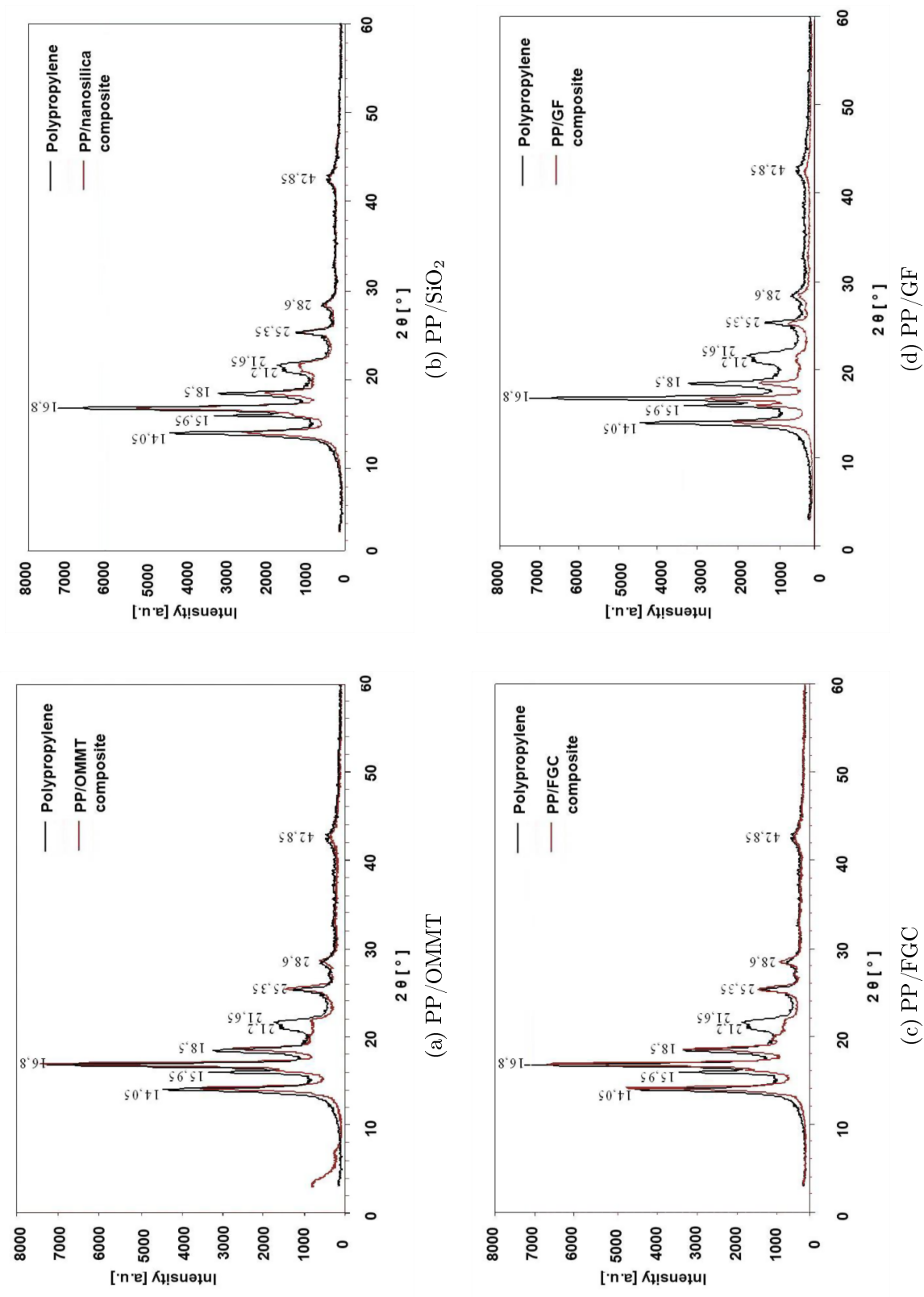


Figure 3.10: WAXD diffractograms of manufactured PP nanocomposites

Additionally, SAXD for a diffraction angle of $1-8^\circ$, was employed to assess the structure of the OMMT in the polymer (Figure 3.11). The peaks observed for the PP/OMMT nanocomposite was moved towards lower values of 2θ indicating a process of polymer intercalation inside the clay galleries. The regular structure of clay layers were however maintained and intercalative structure was postulated in the PP/OMMT nanocomposites.

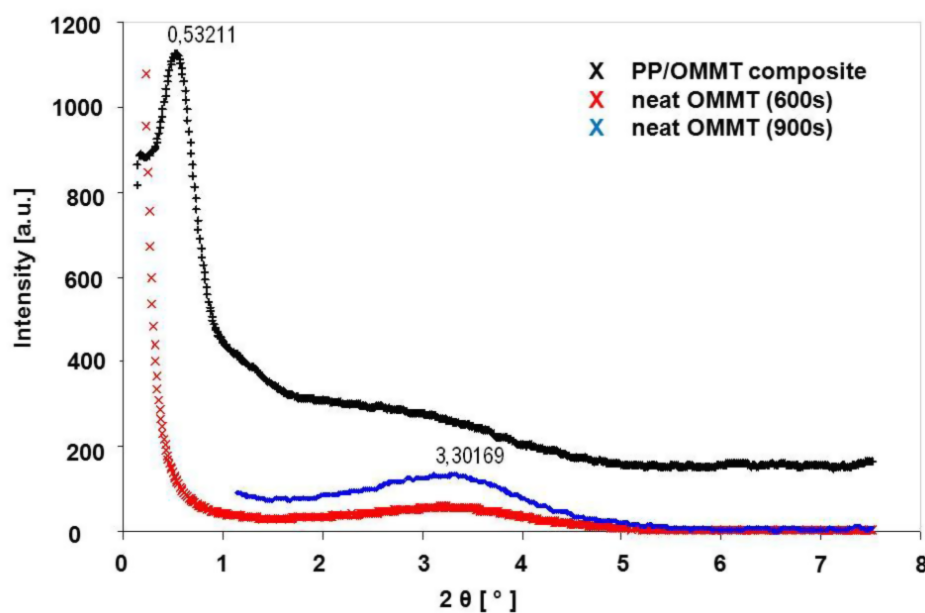


Figure 3.11: SAXD comparison between PP/OMMT composite and neat OMMT

3.3.2.2 PA6 composites

Similar to the manufactured PP composite panels the PA6 panels were manufactured without the utilisation of stabilisers or additives and hence for some panels indication of matrix degeneration could be seen (Figure 3.12).

The WAXD diffractograms of the PA6 nanocomposites are shown in Figure 3.13. Neat PA6, reflected a strong diffraction peak with a maximum at $2\theta = 21.5^\circ$ and small peak at $2\theta = 379^\circ$. The location of the first peak corresponded to the γ -phase. Such crystal morphology could origin from the processing condition, where the polymer was subjected to high shearing and cooling rates which favoured

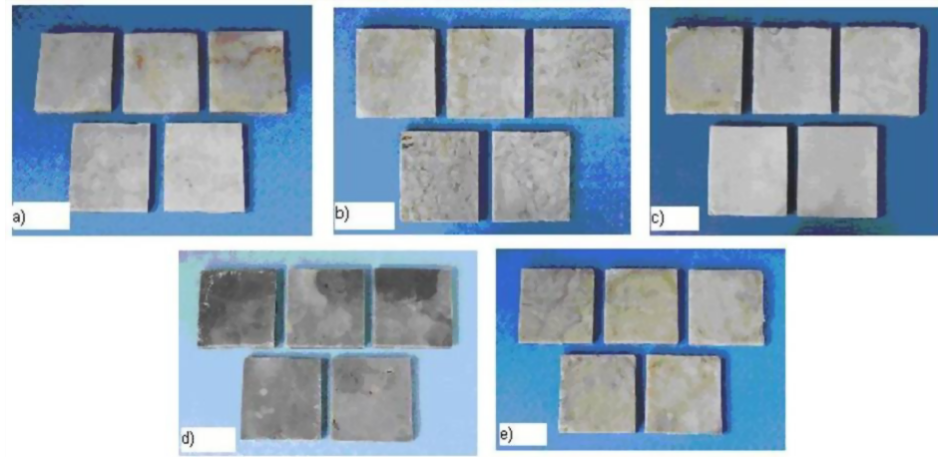


Figure 3.12: Manufactured nanocomposite based on PA6 matrix a) neat panel, b) OMMT c) nano-SiO₂ d) foam-glass-crystal, and e) glass fibres

the formation of γ -crystals. The same diffraction peaks were observed for the nanocomposites (Figure 3.13 a-d), therefore it can be assumed that no changes in the crystallographic structure of PA6 were induced. Positioning differences of the samples in the measurement equipment caused smaller shifts of 2θ between the measurement but do not need any further notice.

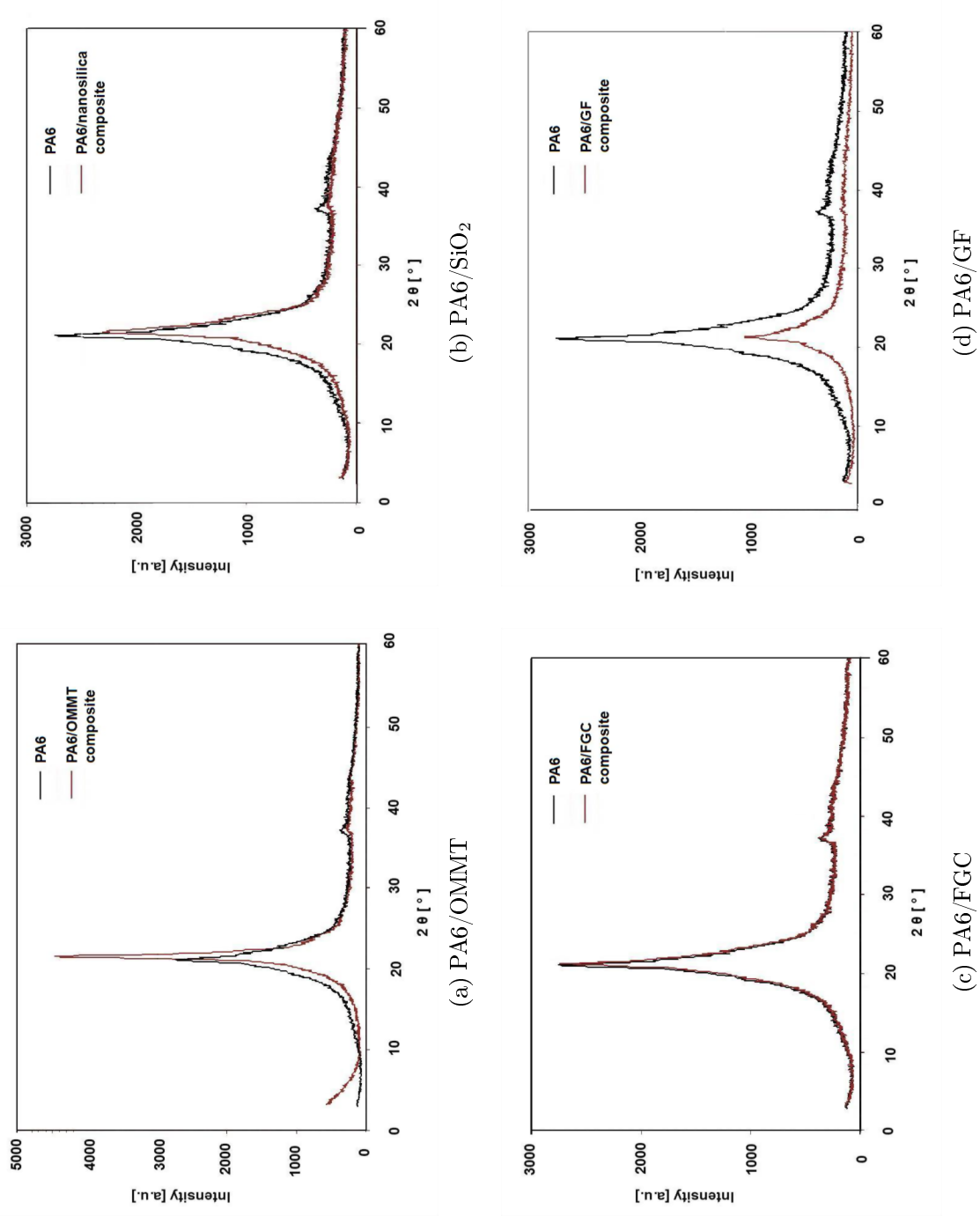


Figure 3.13: WAXD diffractograms of manufactured PA6 nanocomposites

No diffraction peaks were observed in the diffraction angle range of 3-10° on WAXD diffractogram suggesting a high degree of exfoliation of the OMMT layers in the polymer matrix. The formation of a nanostructure was also confirmed by SAXD, as shown in Figure 3.14. Peaks characteristic for the pristine OMMT disappeared completely indicating the destruction of parallel arrangement of the OMMT layers in the matrix. Peaks occurring at about 1° may reflect regular secondary structures of the OMMT layers.

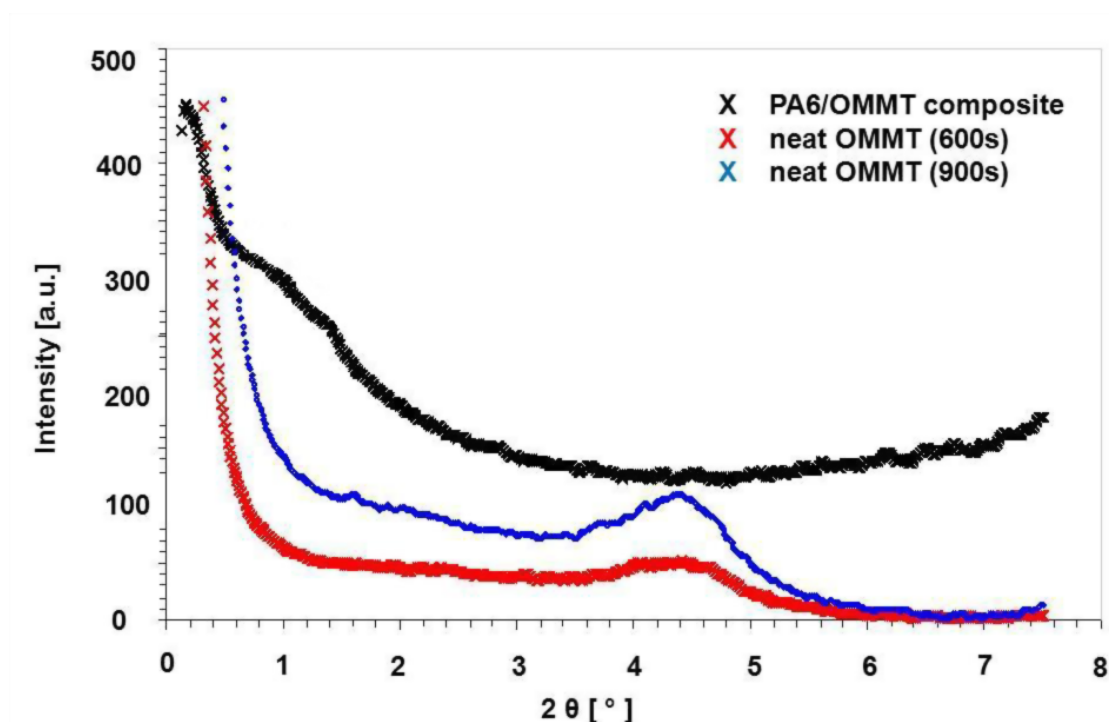


Figure 3.14: SAXD comparison between PA6/OMMT composite and neat OMMT

3.3.3 Thermal properties of manufactured nanocomposites

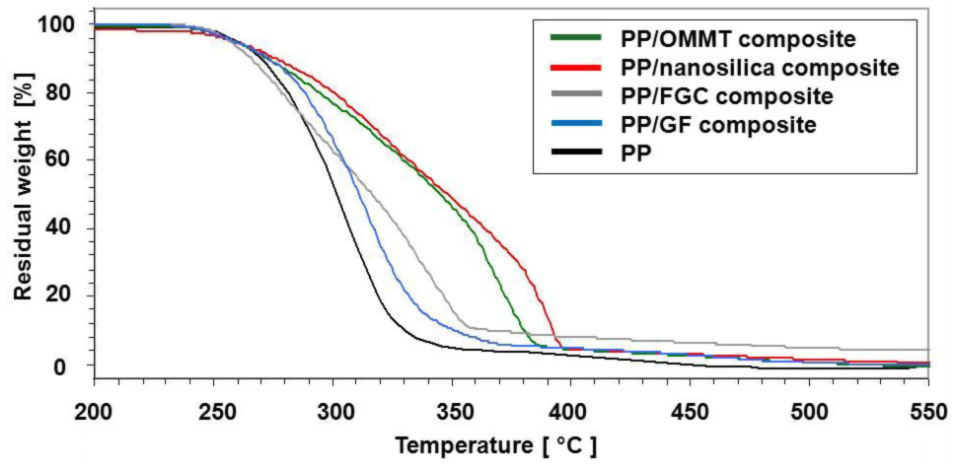
3.3.3.1 PP nanocomposites

The thermogravimetric analysis (TGA) profile of the PP nanocomposites are shown in Figure 3.15a. In a comparison of the thermal decomposition temperature of the PP/OMMT and PP/nano-SiO₂ nanocomposites with that of the pure

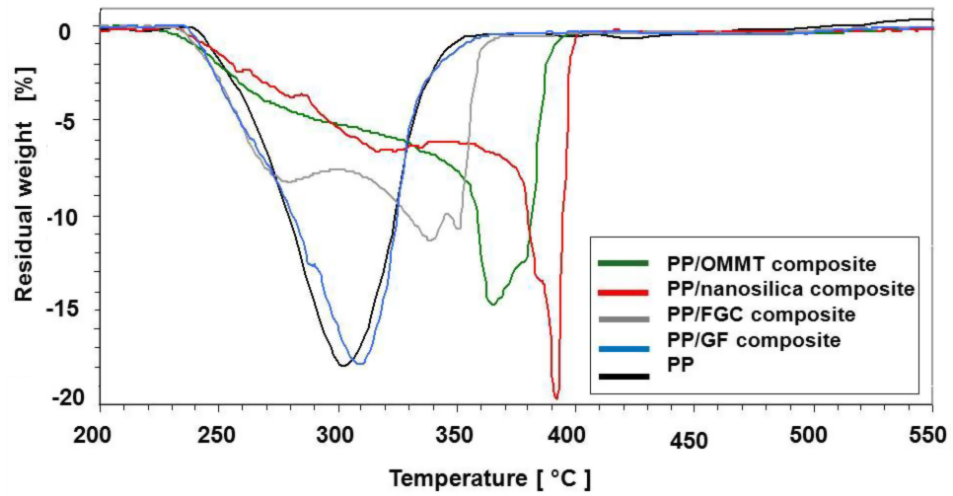
PP, the thermal stability of the nanocomposites is much higher than that of the pure PP. The integration of FGC and glass fibres slightly increased the thermal stability of the composites, when compared to the neat matrix. As shown in Figure 3.15a, the effect of nano-SiO₂ on the thermal stability of the nanocomposite is more pronounced.

The derivative thermogravimetry curves (DTG) are shown in Figure 3.15b. The DTG shows the dependency of derivation weight loss on temperature of the PP composites. The DTG curves show multi-step decomposition of the composite materials as compared with neat PP and reduction of mass loss rate in the first and second stage of degradation. The exception was PP/nano-SiO₂ nanocomposite which showed higher maximum rate of mass loss than neat PP, however clearly moved towards higher temperatures. Overall the PP/nano-SiO₂ had the highest thermal stability of all PP composites. Increase in thermal stability, could be caused by the physical entanglements of the PP macromolecular chains of PP/nano-SiO₂ composites, which restrict the thermal motion of the PP chains. Gilman^[148] suggested that the high thermal stability of filled polymers is caused by the hindered thermal motion of polymer molecular chains. It is well known that a small amount of OMMT integrated into a polymer matrix will improve the thermal stability of the composite. The improved thermal stability for polymer/OMMT nanocomposites is mainly caused by the formation of char. The formation of char hinders the out-diffusion of the volatile decomposition products, as a direct result of the decrease in permeability. This is usually observed in exfoliated nanocomposites^[13;51;148–150]. However, the mechanism of the improvement of thermal stability in polymer nanocomposites is not fully understood yet^[8;9].

Figure 3.16 presents the DSC cooling scan thermograms of PP and the PP composites. Neat PP showed an exothermic crystallisation peak at 110.5 °C while the crystallisation temperature was moved towards higher temperatures for all composites. The biggest shift was observed for the PP/OMMT and PP/nano-



(a) TGA profile

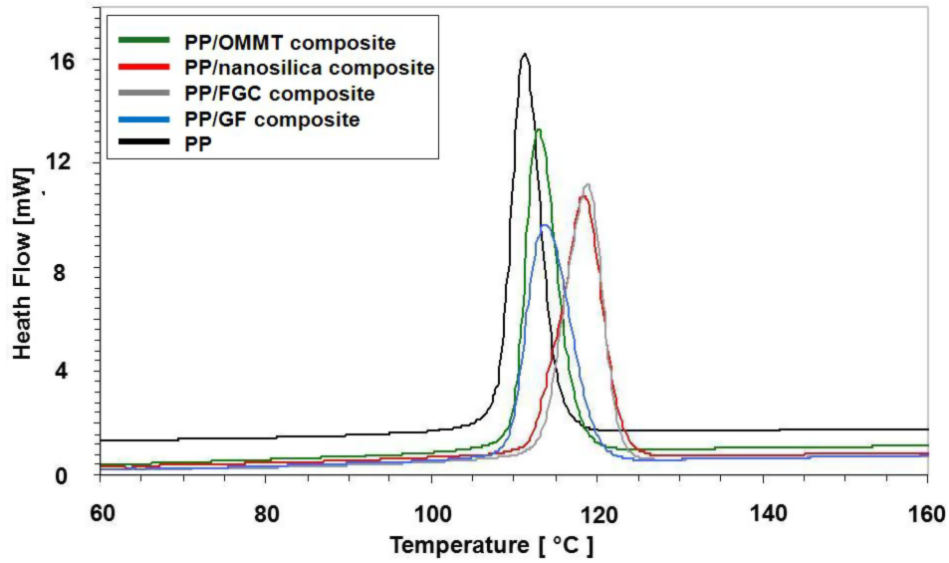


(b) DTG profile

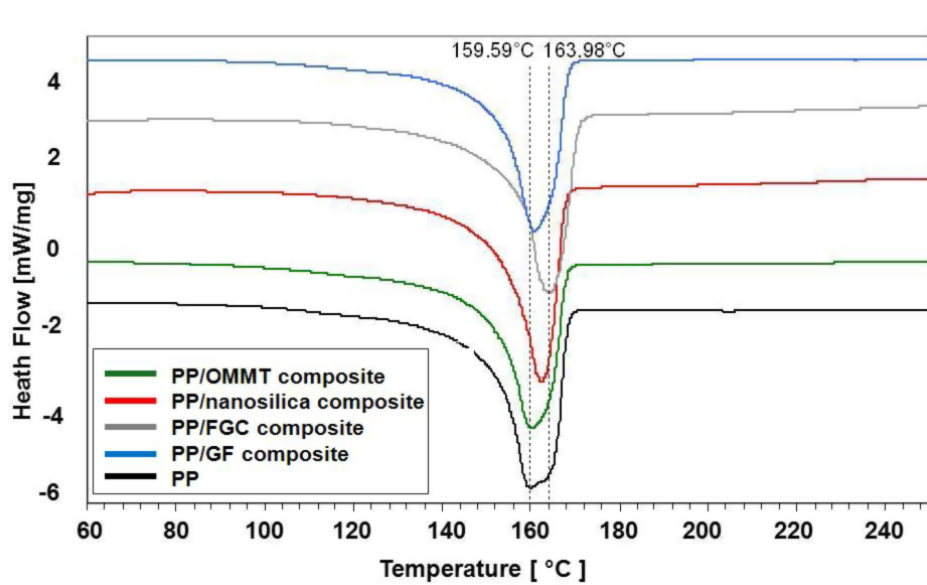
Figure 3.15: TGA and DTG thermograms of PP and PP nanocomposites

SiO₂ nanocomposites, with a crystallisation temperature of 119°C and 118.5°C. The clear increase of crystallisation temperature of the polymer matrix, due to the OMMT fillers can be explained by the assumption that the silicate layers act as efficient nucleating agents for the crystallisation of the polymer^[55]. The same assumption can be made for the nano-SiO₂, suggesting a nucleating effect in the matrix, which enhances the crystallisation rate and promotes the formation of intercrystalline links^[22;151].

Figure 3.16b shows the second DSC heating scan thermogram of the neat PP, which evidenced that the polymer melted in two overlapping processes. The first shoulder was observed at about 159.6°C and the second at 164°C. However, the PP composites just melted in one step.



(a) Cooling profile



(b) Second heating profile

Figure 3.16: Cooling and heating scan during DSC analysis of PP and PP composites

The melting temperature T_m , the heat of fusion ΔH_f , the crystallisation temperature T_c and enthalpy of crystallisation ΔH_c obtained from the DSC studies

Table 3.1: DSC results for PP composites

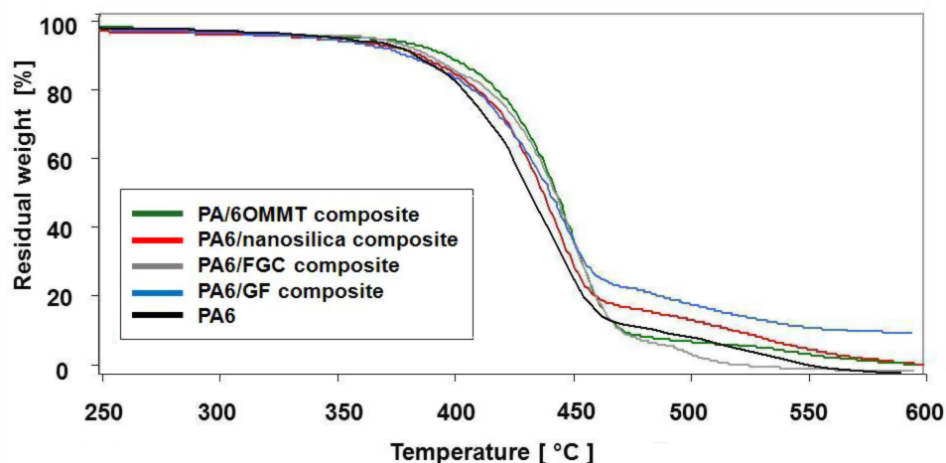
Filler	T_m	ΔH_f	χ	T_c	ΔH_c
	[°C]	[J/g]	%	[°C]	[J/g]
No filler	159.59	-102.51	49.5	111.95	96.17
OMMT	160.14	-101.84	49.2	113.51	90.74
Nano-SiO ₂	162.29	-93.01	44.9	118.92	90.90
FGC	163.98	-94.78	45.8	119.27	89.54
GF	160.65	-89.36	43.2	114.20	86.44

are summarized in Table 3.1. The DSC result showed that the fillers changed the thermal properties of PP. While an increase of melting temperature and crystallisation temperature was recorded, the degree of crystallinity decreased. It was evident that the fillers reduced the size of PP spherulites of the nanocomposite considerably, confirming that the fillers act as nucleating sites for PP crystallisation. The nucleating agent enhances the crystallisation rate and promotes the formation of intercrystalline links.

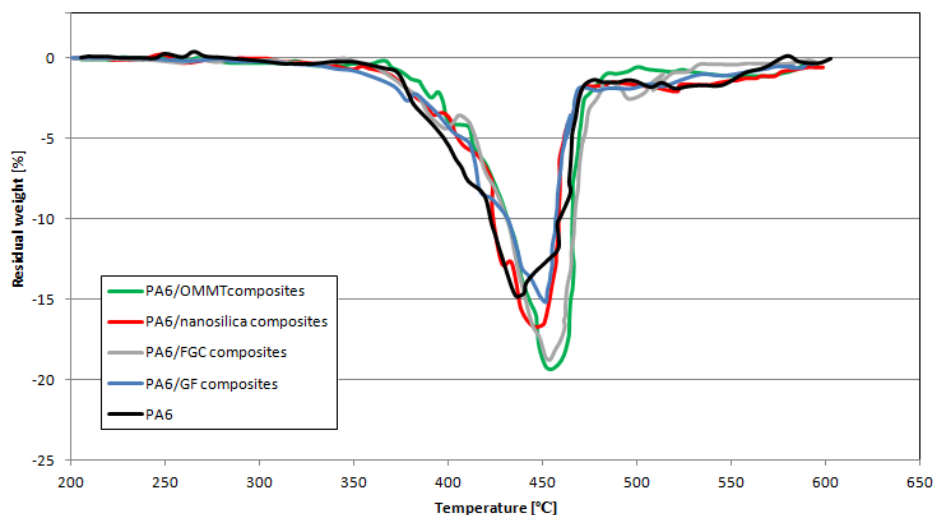
3.3.3.2 PA6 nanocomposites

Figure 3.17a shows the TGA profiles of the thermo-oxidative degradation of neat PA6 and PA6 composites containing 5 wt.% of fillers. The profiles of the nanocomposites resembled that one of neat PA6, but shifted towards higher temperature. However, the difference in thermo-oxidative degradation of the nano- and micro-composites was small, in contrast to the PP based composites discussed earlier. Therefore, it can be assumed that the effect of the nanofillers on the thermal stability of the PA6 nanocomposite is less pronounced. Figure 3.17b shows the dependency of derivation weight loss on temperature of PA6 and PA6 composites. The degradation of nanocomposites ran in three main steps; the first step of mass loss was measured around 380°C, the second at around 450°C, and the third between 500-525°C. However, the neat PA6 degraded in just two steps; the main step and one

high-temperature step of mass loss.



(a) TGA profile



(b) DTG profile

Figure 3.17: TGA and DTG thermograms of PA6 and PA6 nanocomposites

Figure 3.18a presents the DSC cooling thermograms of PA6 and PA6 nanocomposites. Neat PA6 showed an exothermic crystallisation peak at 185°C while the crystallisation temperature was moved towards higher temperatures for the PA6/FGC composite, reflecting strong heterogeneous nucleation of polymer crystallisation. Interestingly, the opposite effect was detected for PA6/OMMT nanocomposite material, as the crystallisation peak was found at 181°C. This may reflect some restriction of polymer crystallisation occurring during the presence of dis-

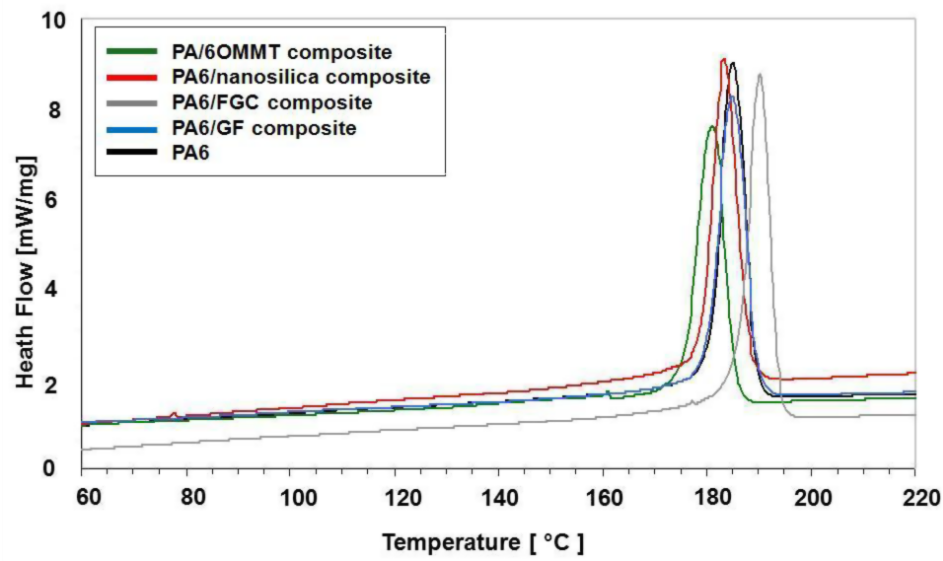
persed OMMT layers. It is likely that strong interfacial interactions interfere the thermal processes. Zhang et al.^[152] studied PA6/OMMT composites and reported that the crystallisation peak was largely narrowed, which showed a strong heterophase nucleation effect of the clay.

Additionally, the crystallisation peak for the PA6/nano-SiO₂ composite moved towards lower temperatures. No effect on the crystallisation could be found for the PA6/glass-fibre composite. The second DSC heating thermograms evidenced that the polymer melted in two overlapping processes (Figure 3.18b). The first shoulder was observed at about 215°C and the second at 220.7°C. The high-temperature peak corresponds to the α -phase and the low-temperature peak corresponds to the γ -phase of the polymer^[153]. In the PA6/OMMT nanocomposite, the melting peak corresponded to the γ -phase and is strongly enhanced and therefore increased fraction of γ -phase crystals in crystal phase of PA6 matrix is evidenced. Similar moderate changes due to polymorphic behaviour of PA6 were observed in PA6/FGC.

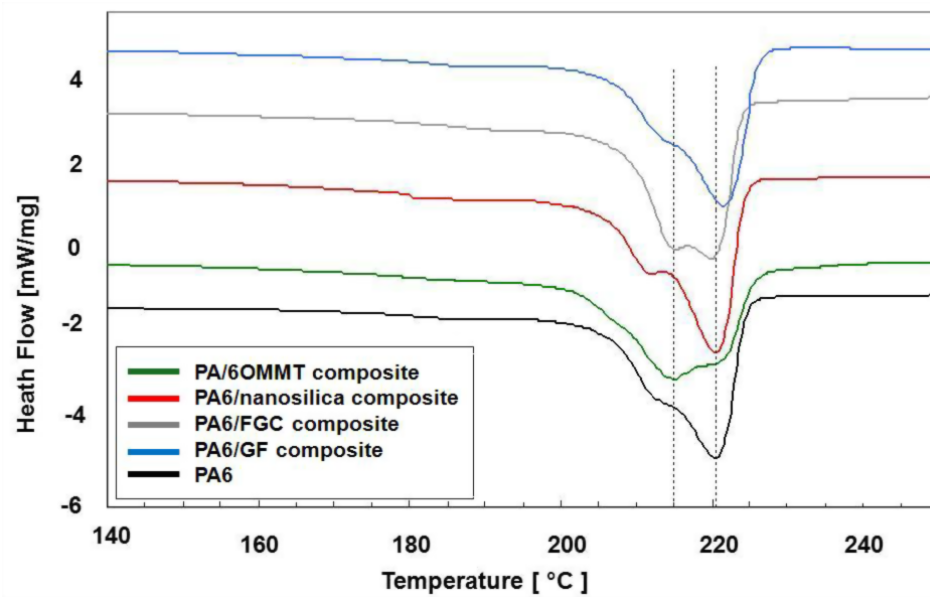
The melting temperature T_m , the heat of fusion ΔH_f , the crystallisation temperature T_c and enthalpy of crystallisation ΔH_c obtained from the DSC studies are summarized in Table 3.2. In order to estimate the percentage of crystallinity χ , equation 3.1 was used.

Table 3.2: DSC results for PA6 composites

Filler	T_m [°C]	ΔH_f [J/g]	χ %	T_c [°C]	ΔH_c [J/g]
No Filler	220.13	-83.46	36.91	186	73.17
OMMT	214.83	-84.20	37.24	181	65.11
Nano-SiO ₂	220.11	-77.44	34.25	184	69.90
FGC	219.82	-95.25	42.13	191	67.82
GF	221.28	-74.07	32.76	186	68.03



(a) Cooling profile



(b) Second heating profile

Figure 3.18: Cooling and second heating scan during DSC analysis of PA6 and PA6 nanocomposites

3.3.4 Airborne Particle

3.3.4.1 Sequential alteration of number concentration and size distribution

Due to the nature of the SMPS+C in each measurement cycle, different particle size are selected to build the particle size distribution. Figure 3.19, shows the

raw data obtained from each measurement cycle. It can be seen that the number concentration depends on the measurement time as well as the particle size.



Figure 3.19: SMPS on-line measurement of the particle size distribution (difference in the natural logarithm of the particle concentration vs. mean particle size) during drilling; the green line represents the actual measurement and the yellow line represent the previous measurements

To evaluate the total particle concentration over the time, the total particle concentration during each measurement cycle was calculated by the SMPS+C and this data was then used to evaluate the sequential alteration of the total number concentration of nano-sized particles emitted.

The sequential alteration of the total number concentration of particles for a typical sampling cycle is shown in Figure 3.20. It consists of a 60 min background measurement ($t \leq t_{max}$), the 14 min drilling period ($0 \leq t \leq t_{max}$), and a 120 min post-drilling period ($t \geq t_{max}$). Figure 3.20, shows that the total number concentration of particles was essentially constant with an average of 1000 particles/cm⁻³ before the drilling process. As soon as drilling started inside the experimental chamber, the number concentration increased rapidly. The maximum number concentration, C_{max} , was reached at time t_{max} . Subsequently, the particle decay was observed with the concentration falling back to the original background level approximately

after a post drilling period of 2h. In significant research studies^[30;119;154;155] the influence of the machining engines as *background* noises on the results has been reported, as important in airborne nano-sized particle measurements. As the drilling was conducted in a controlled environment, the influence of the machining engine could be reduced to a minimum.

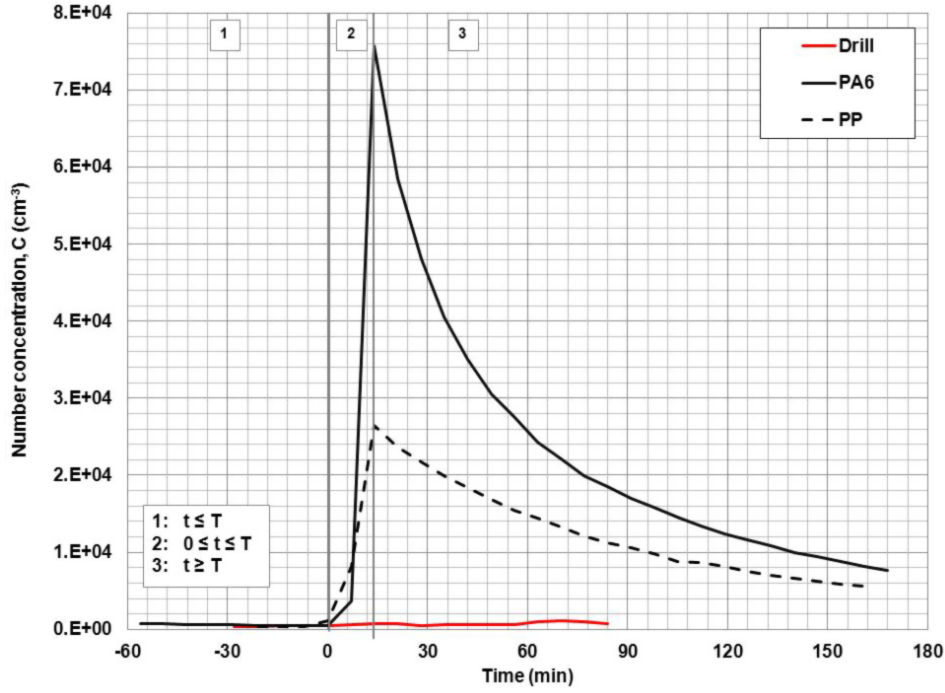


Figure 3.20: Sequential alteration of number concentration of a typical sampling cycle, consisting of a 60 min background measurement ($t \leq t_{max}$), the 14 min drilling period ($0 \leq t \leq t_{max}$), and a 120 min post-drilling period ($t \geq t_{max}$, for PA6 and PP panel (drill represents the background noises generated by the drill engine)).

The average values for C_{max} , are given in Table 3.3. In general the average concentration C_{max} , was apporx. 10 times lower for the PP based composites than for the PA6 based composites. Both neat PP and PA6 matrices generate low C_{max} , with $6.05E+02\text{cm}^{-3}$ and $67.57E+04\text{ cm}^{-3}$, in comparison to the studied nanocomposites. Surprisingly, a very low C_{max} could be measured for the PA6/OMMT nanocomposites, however the PP/OMMT nanocomposites generated the highest number concentration. This could be caused by the different integration mechanisms of the filler in the matrix. As reported in section 3.3.2,

Table 3.3: Monitoring studies for nanoparticles

Material	Max. airborne concentration [cm ⁻³]	Total airborne emission rate [min ⁻¹]
PP	6.05E+02	5.68E+06
PP/OMMT	2.64E+04	6.83E+07
PP/nano-SiO ₂	1.52E+04	2.06E+08
PP/FGC	5.58E+03	6.24E+07
PP/GF	2.61E+04	1.86E+08
PA6	7.57E+04	1.82E+07
PA6/OMMT	7.21E+02	1.16E+07
PA6/nano-SiO ₂	1.74E+05	1.03E+09
PA6/FGC	1.63E+05	3.32E+08
PA6/GF	7.62E+04	8.63E+08

the OMMT had a high degree of exfoliation in the PA6 matrix, while only a intercalated structure of the OMMT layers in the PP matrix could be detected. Integration of nano-SiO₂ caused a high particle concentration in both matrices, with 1.74E+05 cm⁻³ for PA6 and 1.52E+04 cm⁻³ for PP matrix.

Diffusion, gravitational deposition, convection, impaction, and coagulation are some of the complex processes which influence formation and removal of particles in the chamber. Removal of small particles is primarily dominated by diffusion while larger particles are mainly affected by gravitation. During diffusion, small particles collide with one another and form larger particles^[156]. This process is known as coagulation and strongly depended on particle size and concentration. While the coagulation rate of a simple monodisperse particle population can be calculated using Equation 3.4^[157],

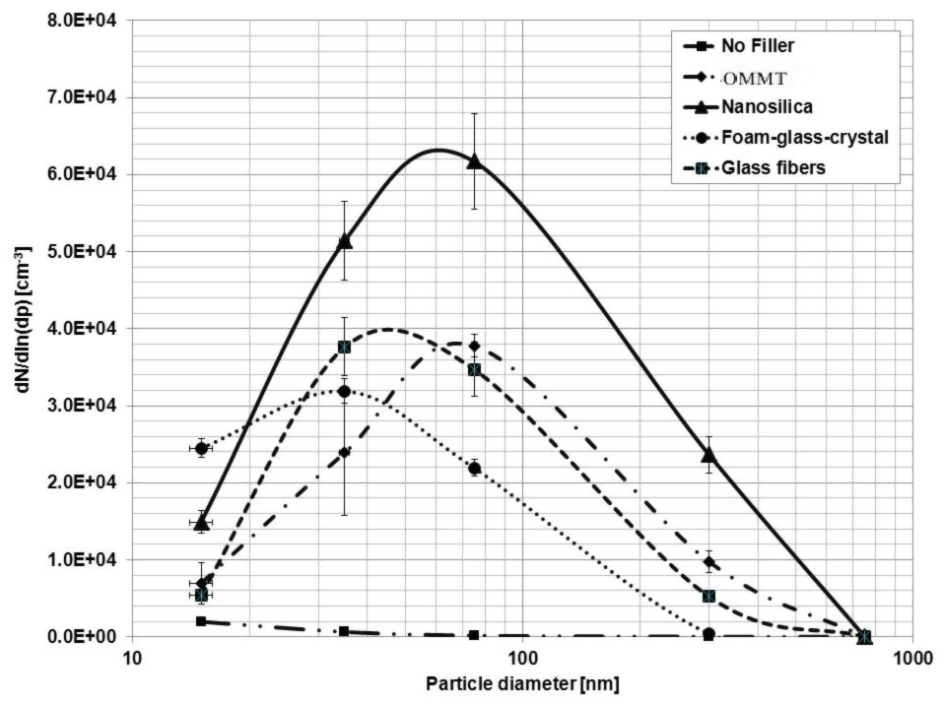
$$\frac{dN}{dt} = KN^2 \quad (3.4)$$

where N is particle number concentration and K is the coagulation coefficient. Based on this equation, the coagulation rate is directly proportional to the dif-

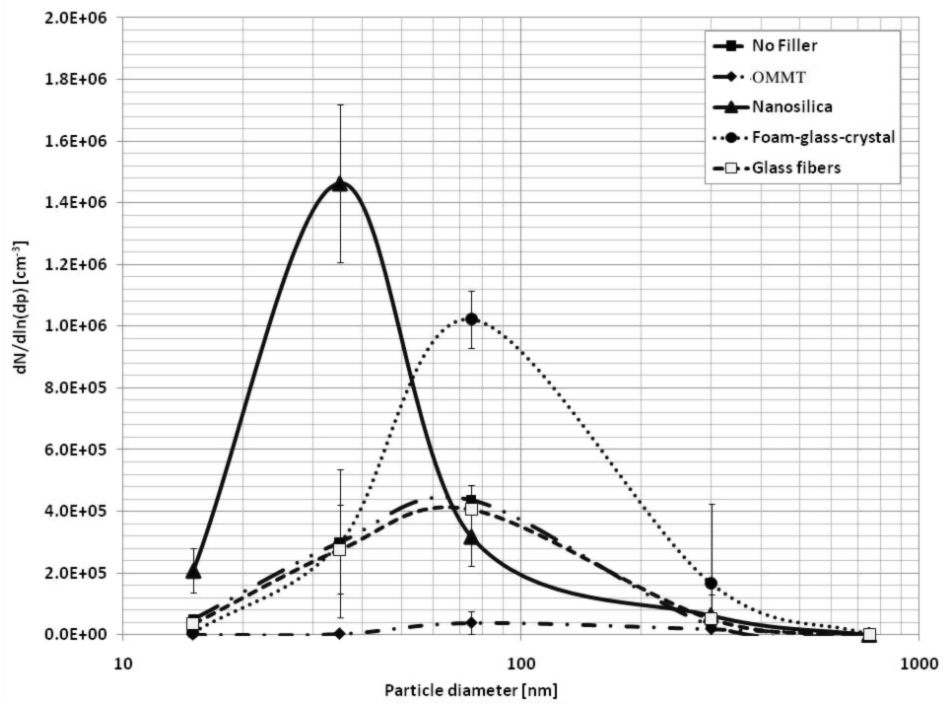
fusion coefficient and particle size and therefore, decreases with particle size. An indication of the coagulation rate can be identified by the half-life of an individual particle, which is introduced into an atmosphere embracing a defined concentration of such particles^[156]. However, according to Hinds^[157] coagulation can be neglected for laboratory experiments if the particle concentration is less than $1 \times 10^{12} \text{ m}^{-3}$. As the maximum concentration measured in this study did not exceed $1.7 \times 10^{11} \text{ m}^{-3}$, coagulation was neglected.

The particle size distributions of the generated nano-sized particles is shown in Figure 3.21.

The plots reflected particle size distributions at t_{max} , the time particle concentration reached its maximum and drilling was terminated. The plots present the normalised distribution with $\Delta N / \Delta \ln d_p$ versus the particle diameter d_p , where ΔN is the concentration of particles within a specified size interval and $\Delta \ln d_p$ is the difference in the natural logarithm of the largest and smallest particle sizes of that interval. From visual inspection of the graph, it could be noted that the distinct modal diameters were obtained depending on the filler used. For the PP based composites the peak varied from 35.5 nm for PP/FGC composite to 82.8 nm for the PP/glass-fibre composites. The peaks for the PA6 based composites varied from 29.6 nm for the PA6/nano-SiO₂ composite to 75.1 nm for neat PA6. This shift in size distribution showed that the integration of nanofillers changes the physical properties of the emitted particles. This result contradicts with the results obtained in some recent studies^[27;30;31]. For example, Wohlleben et al.^[27] noted that while comparing PP/nano-SiO₂ nanocomposites with neat PA6, that both the differences in the number concentrations and in the actual size distribution of nano-sized particles emitted during normal abrasion use were insignificant. However, these studies dealt with abrasion and sanding of surfaces and composites. The difference in mechanical processing could explain the alterations in the obtained results.



(a) PP based composites



(b) PA6 based composites

Figure 3.21: Normalised particle size distributions at time $t_{(max)}$ of PP and PA6 based composites

3.3.4.2 Particle morphology

To support the results obtained by the SMPS+C, particles were sampled via an electrostatic precipitator (ESP) and investigated using emission scanning electron microscope. The scanning electron micrographs of the particles generated during drilling of different composites are represented in Figure 3.22 and Figure 3.23. Particles generated by PP/OMMT (Figure 3.22a) showed agglomerates of small particles. However, also larger irregular shaped particles, that seem to have a layered structure. The OMMT was intercalated in the structure, however not fully exfoliated, therefore it could be possible that unbound OMMT particles were emitted during drilling of the nanocomposites. Particles released by PP/nano-SiO₂ (Figure 3.22b) and PP/FGC (Figure 3.22c) nanocomposite built spherical rings of agglomerated particles. However, from the SEM micrograph the nature of these particles could not be determined. Figure 3.22d shows particles sampled during drilling of PP/glass fibre fill composites. The particles consist of 200-500nm long fibrous shaped particles, suggesting debris from the glass fibres. Particles generated from unreinforced PP matrix (Figure 3.22e), were found in size ranges between 250-1000nm, which correspond with the reported results obtained by the SMPS+C.

Micrographs of the particles generated from PA6/FGC (Figure 3.32d), PA6/SiO₂ (Figure 3.32c) and the neat PA6 (Figure 3.32a) composites showed very similar structures of coagulated particle. Smaller particles (20-50nm) coagulated to larger particles 150nm, which were then sampled by ESP over a time frame of 2h. According to the literature^[156], the half time of particles in the size range of 10-200nm in the measured concentration would be between 16-83 min, therefore coagulates of particles is natural for a sampling period of 2h. The SEM image of the generated particles obtained from drilling of the glass fibre panels (Figure 3.32e) showed agglomeration of larger particles. Furthermore, the particles seem to be glass fi-

bres debris, as the structure is very similar to structure seen in the bulk panels. Visual investigation of the particles obtained from drilling of the OMMT composites (Figure 3.32b) were scattered over the sampling plate and no coagulation could be found. This could be explained by the low particle concentration that was measured for this composite. SEM micrographs of PP and PA6 composites showed that the shapes of the particles vary depending on the filler and matrix material.

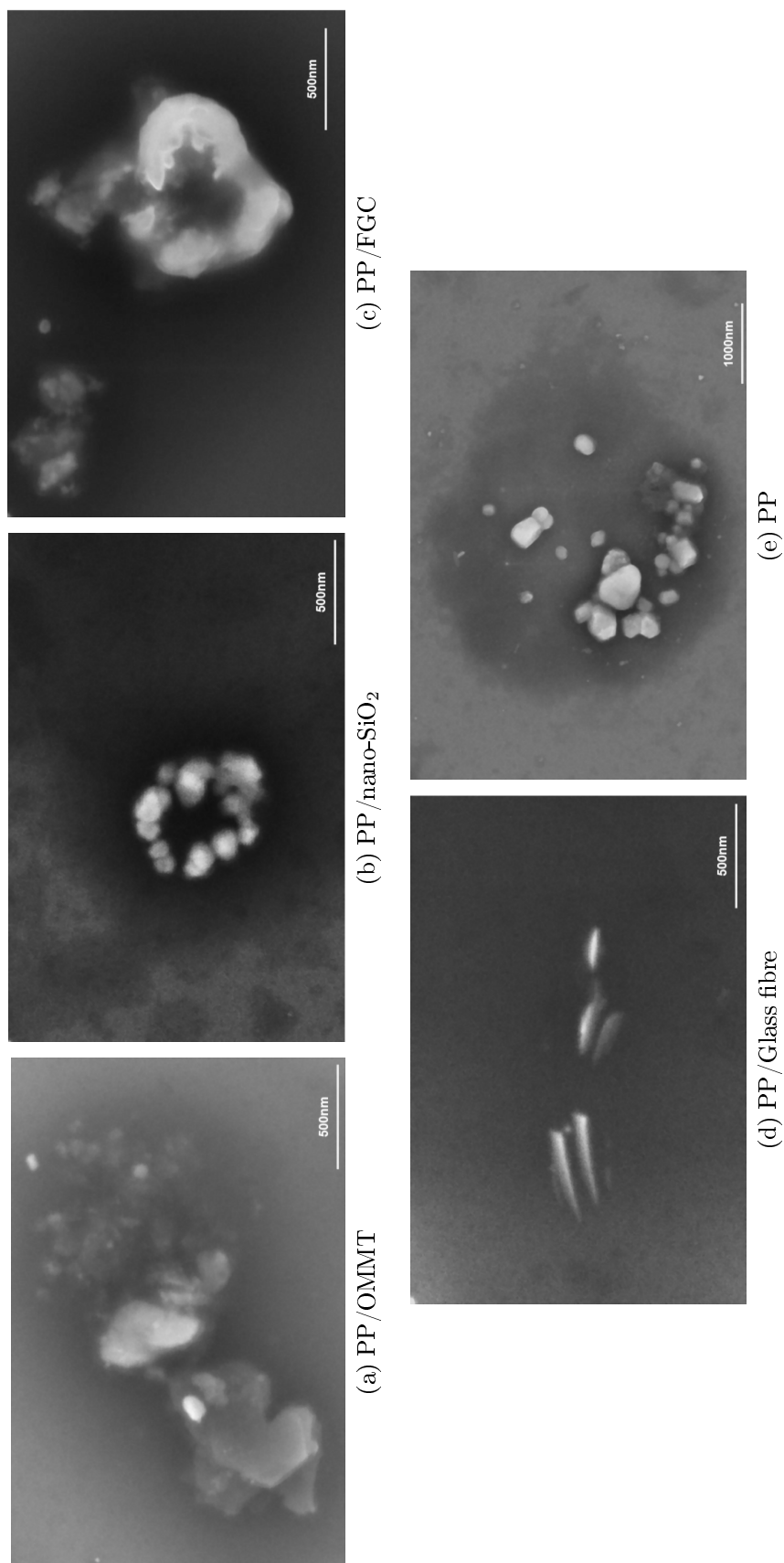
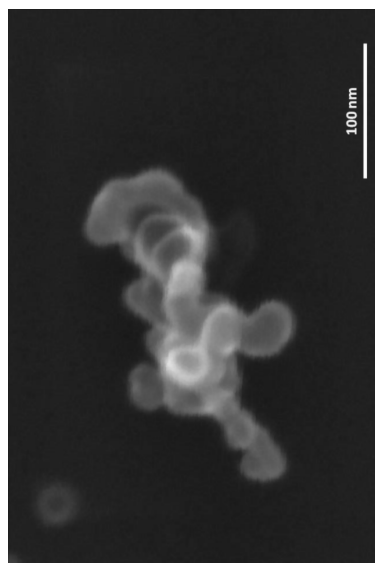


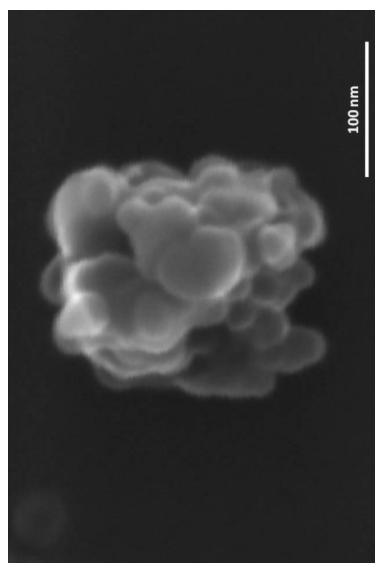
Figure 3.22: SEM micrographs of generated particles collected by ESP for each PP based composite



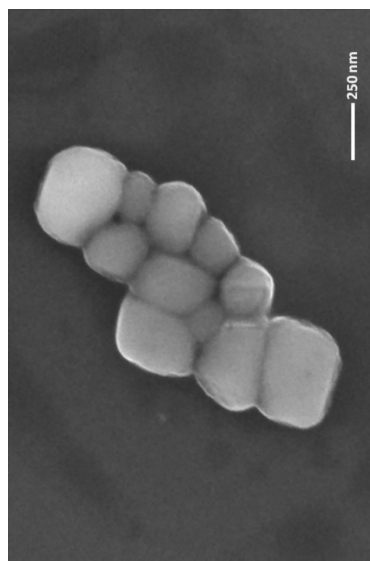
(a) PA6/OMMT



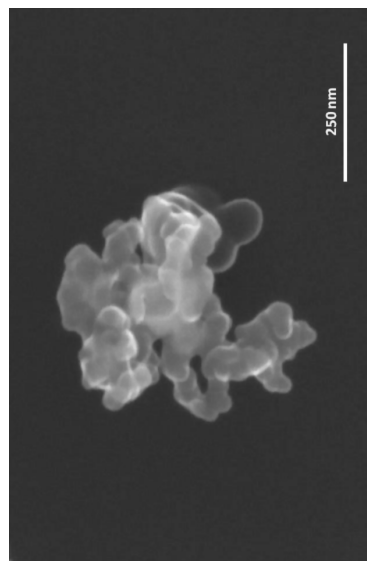
(b) PA6/nano-SiO₂



(c) PA6/FGC



(d) PA6/Glass fibre

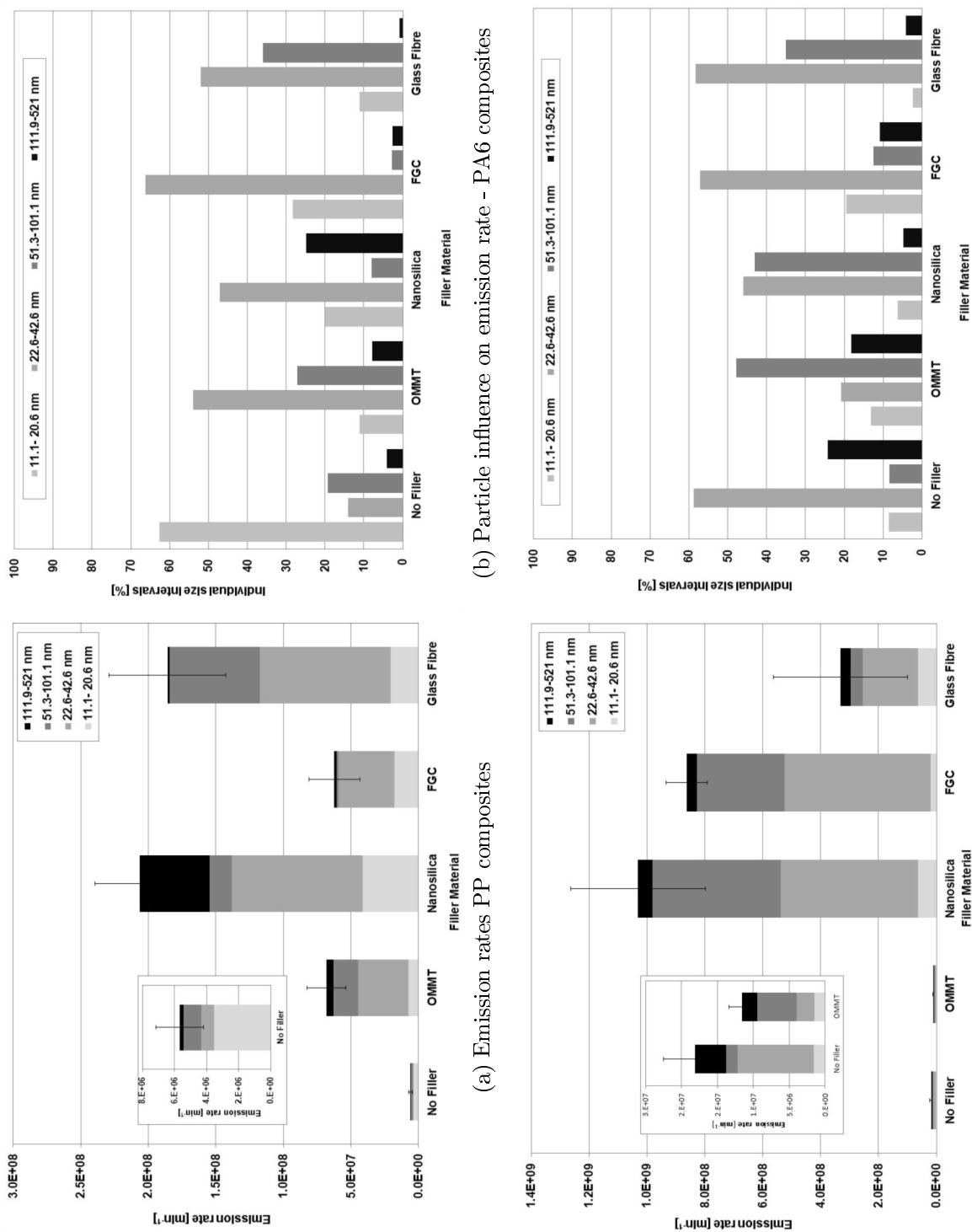


(e) PA6

Figure 3.23: SEM micrographs of generated particles collected by ESP

3.3.4.3 Emission rates of different composite materials

The particle emission rates from different composites were determined using Equation 3.3, after taking into account the removal rates of particles of different sizes from Equation 3.2. The stacked column charts of Figure 3.24 show the number of particles that were emitted per minute during drilling of the composite materials. The error bars represent the standard deviation associated with the total emission rate of particles, in the size range of 11.1-521nm, resulting from the three replicate measurements. Table 3.3 represents the total emission rates for the different composite materials. Lowest emission rates could be calculated for the neat PP matrix with $5.68\text{E}+06 \text{ min}^{-1}$, followed by the PP/FGC composite with $6.24\text{E}+07 \text{ min}^{-1}$ and PP/OMMT nanocomposite with $6.83\text{E}+07 \text{ min}^{-1}$. Highest emission was calculated for the PP/nano-SiO₂ composite material with $2.06\text{E}+08 \text{ min}^{-1}$. Emission rates for the PA6 composite behaved similar, however were 10 order of magnitude higher than from PP composites, while the lowest emission rates could be calculated for the OMMT filled composites with $1.16\text{E}+07\text{min}^{-1}$, followed by the neat PA6 panel with $1.82\text{E}+07\text{min}^{-1}$. Again for the nano-SiO₂ filled composite the highest emission rate could be calculated. However, while comparing the percentage of the individual size intervals on the total emission, it could be seen that for all materials (beside PA6/OMMT and neat PP) the majority of particles, 45-66%, were in the size range of 22.6-42.6 nm (Figure 3.24). Further the neat PA6 emitted the largest quantity of particles larger than 100nm. The emission rate increased by 56 times for the nano-SiO₂ filler and between 20-45 times for the glass fibre and foam-glass crystal fillers. Interestingly, integration of OMMT into the PA6 matrix reduced particle emission during drilling by 1.5 times, compared to the neat PA6. It is likely that the presence of exfoliated OMMT retains the formation of high quantities of airborne particles.



(a) Emission rates PP composites

(b) Particle influence on emission rate - PA6 composites

(c) Emission rates PA6 composites

(d) Particle influence on emission rate - PA6 composites

Figure 3.24: Emission rates of particles for different PP and PA6 based composites

3.3.5 Deposited particles

3.3.5.1 Particle size distribution

Deposited particles, in the following denoted as *dust particles* were collected from the sampling tray inside the drilling chamber in dry state. Figure 3.25 shows the particles sampled from drilling of the nanocomposites.



Figure 3.25: Set of dry particles sampled from drilling of nanocomposites

A defined mass of collected dust particles (30mg) were sampled in dry state and analysed by suspension in solution (20 ml). Larger particles would influence the results obtained by DLS and Nanosight, hence the solution was filtrated in 2 steps. This filtered solution was then introduced to the Nanosight and DLS using a disposable syringe. Numeric values for geometric mean sizes, with standard deviation, obtained via NTA and DLS are listed in Table 3.4. It has to be noted that no reproducible results could be obtained for the PP/FGC and PA6/FGC composites by using DLS nor nanosight.

The results obtain from the different equipment showed a high rate of discrepancy for some samples e.g. PA/GNF. Additionally, some high values for the

Table 3.4: Sample denotation

Material	Geom. mean size by NTA [nm]	Geom. mean size by DLS [nm]
PP	186 ± 86	110 ± 12.09
PP/OMMT	196 ± 58	144.85 ± 32.17
PP/nano-SiO ₂	190 ± 77	183.45 ± 15.6
PP/FGC		
PP/GF	187 ± 67	172.8 ± 88.9
PA6	260 ± 82	198.2 ± 1.7
PA6/OMMT	367 ± 485	102.7 ± 11.4
PA6/nano-SiO ₂	154 ± 40	114.9 ± 79.4
PA6/FGC		
PA6/GF	485 ± 369	116.9 ± 26.5

standard deviations were obtained e.g. PA/OMMT, especially for the NTA results. Smaller errors for the DLS results are consequences of the larger amount of statistical data collection with this technique compared with NTA^[158]. The result obtained during this study represented 3 different scenarios:

1. Good comparable results between DLS and NTA
2. Geometric mean size obtained by the two equipments are not in the same size range, even when error taken into account, however good comparability of size distribution graphs
3. Geometric mean size obtained by the two equipments are in the same size range while error taken into account, however no comparability of size distribution graphs.

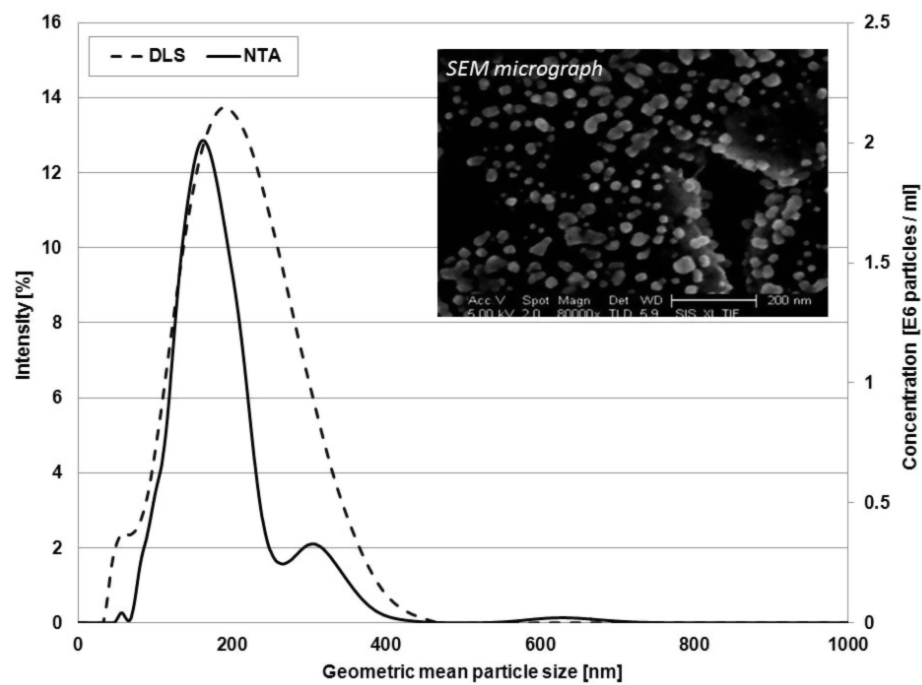
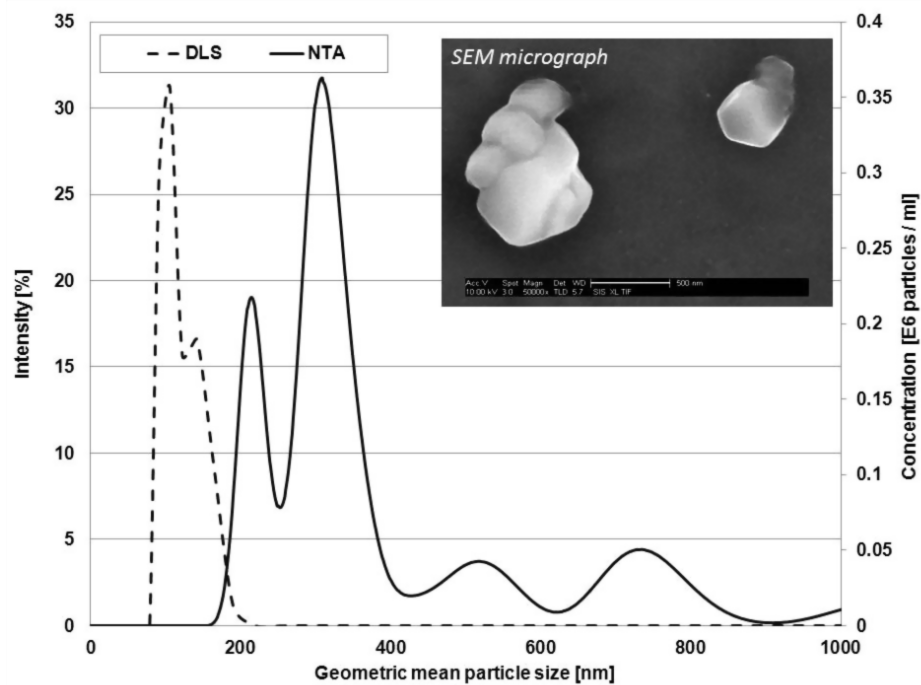
The most comparable results were obtained for the nano-sized particles generated from nano-SiO₂ reinforced samples. NTA and DLS generated similar result,

with reasonable standard deviations. Figure 3.26a shows the size distribution obtained with both equipment for the PP/SiO₂ nano-sized particles.

The intensity of particles for the DLS samples is slightly higher for particles of larger sizes compared with those of the NTA. This can be explained by the immense contribution of a few larger particles to the overall scattering, when utilising DLS^[159]. However, following SEM micrographs (Figure 3.26a) revealed that the majority of nano-sized particles generated could be found in the size range of 20-80 nm. The solution for SEM specimen preparation has been sonicated prior applying on the substrate. This could be a cause for the contrary results between the measurement equipment and the SEM micrographs, as particles agglomeration could be broken up by sonication, as the external force overcomes the van de Waals attractions. However, it is noteworthy that hard bonds of aggregates can not be broken by the applied forces^[160]. The results obtained by particles generated from PA6/glass-fibre composites, showed that the geometric mean sizes obtained by the two equipments are compatible while taking the error into account, however the size distribution graphs do not overlap. The graphs for size distribution showed a completely different behaviour (Figure 3.26b). While DLS detected particle in smaller size ranges, NTA showed polydispersed particles in larger size ranges. SEM micrographs showed particles with diameters between 400-600nm. Further SEM analysis also revealed the shapes of the particles, which were angular.

The major problem that both techniques face is that they are based on the Einstein-Stokes relation which is given for spherical particle. For example the image processing software of the nanosight identified and tracked individual nano scale particles moving under Brownian motion and relates the movement to a particle size according to the following formula derived from the Stokes-Einstein (Eq. 3.5)

$$(x, y)^2 = \frac{2k_B T}{3r_h \pi \eta} \quad (3.5)$$

(a) Size distribution PP/nano-SiO₂

(b) Size distribution PA6/glass-fibre

Figure 3.26: Size distribution for particles generated from PP/nano-SiO₂ and PA6/GF composites during the drilling process

where k_B is the Boltzmann constant and $(\overline{x, y})^2$ is the mean-squared speed of a particle at a temperature T , in a medium of viscosity η , with a hydrodynamic radius of r_h . The hydrodynamic diameter of a non-spherical particle is the diameter of a sphere that has the same translational diffusion speed as the particle, as shown in Figure 3.27. The hydrodynamic size changed, whenever the shape of a particle changed in a way that affects the diffusion speed. For example, small changes in the length of a rod-shaped particle directly affected the size, whereas changes in the rod's diameter, hardly affected the diffusion speed. For the nano-sized particles studied it could be shown that with increasing randomizing of the particle shape the results were less accurate, especially for particle with high aspect ratio. Ideally, the hydrodynamic radius can be estimated beforehand, as reported by Cavallaro et al.^[161]. However, when analysing unknown particles released during degradation processes this is not applicable. Further, DLS is at present not adapted for the measurement of multidisperse nano-sized particles as shown in recent studies^[162;163].

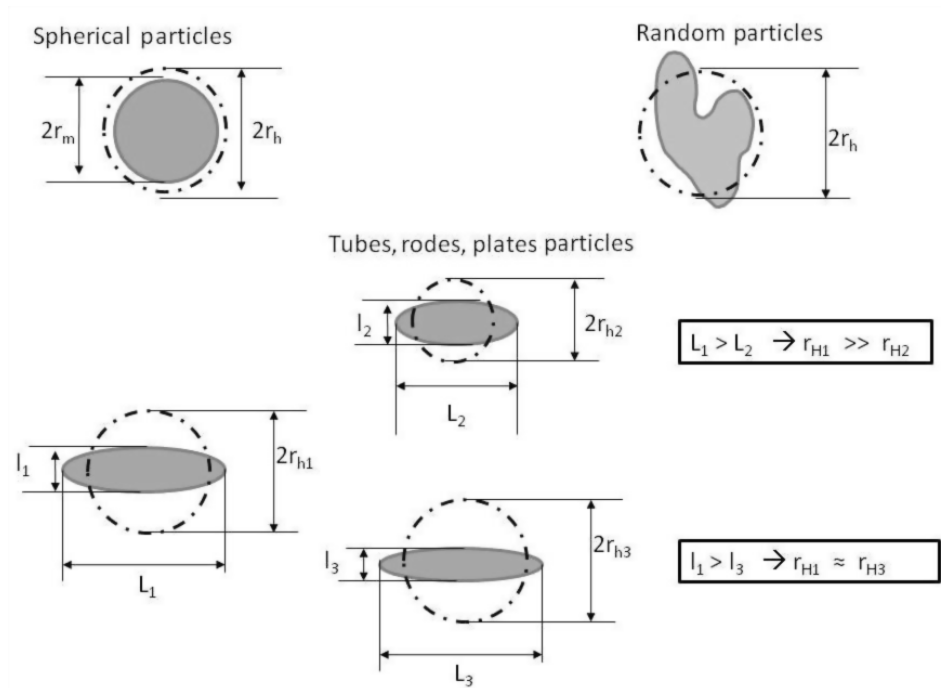


Figure 3.27: Dependency of particle shape on hydrodynamic diameter

As DLS and Nanosight are based on light scattering, the scattered lights interfere mutually, and the strength of the total light varied according to the movement of the particles. Figure 3.28 shows the light ray interaction with a spherical particle and a random particle, hitting two different locations on the particle. Some photons are reflected; others penetrate the surface and, in doing so, are refracted. The refracted ray of photons strikes the far side of the particle. At this interface, some photons penetrate and are transmitted while others are reflected internally. The reflected ray intersects with another internal interface and is partly reflected and partly penetrates. Since there is no absorption, there is no net loss of photon energy. The intensity of the scattered light is a function of the wavelength, the scattering angle, the particle size d , and the relative index of reflection n of the particle and the medium. For each size, spherical particle (of the same material and in the same medium and illuminated by the same wavelength light) produce a different detectable scattering pattern^[145;164]. However, in the case of random particles, the intensity of scattered light was not only dependent on the particle size but also on the angle the light hits the particle. This might explain the results obtained during this study for rather random shaped particles.

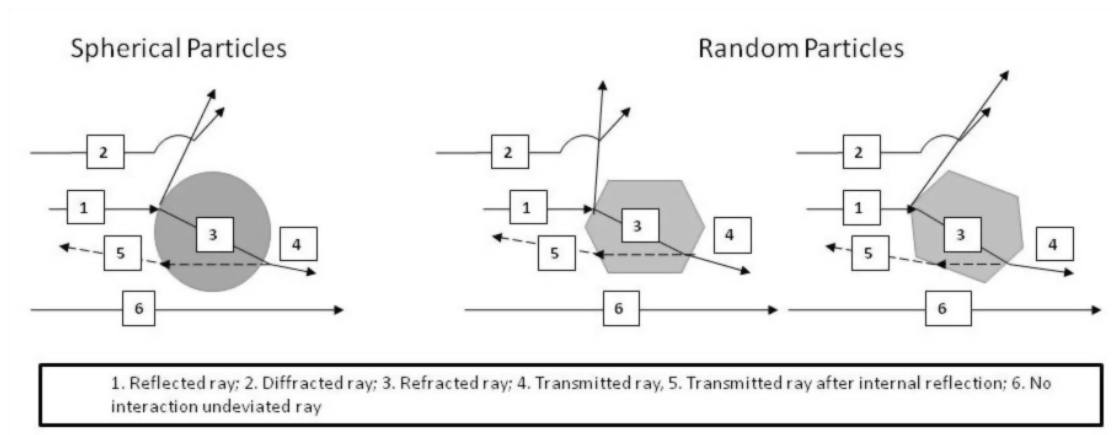


Figure 3.28: Light ray interaction with a particles

As the particles emitted during drilling of the PP and PA6 nanocomposites

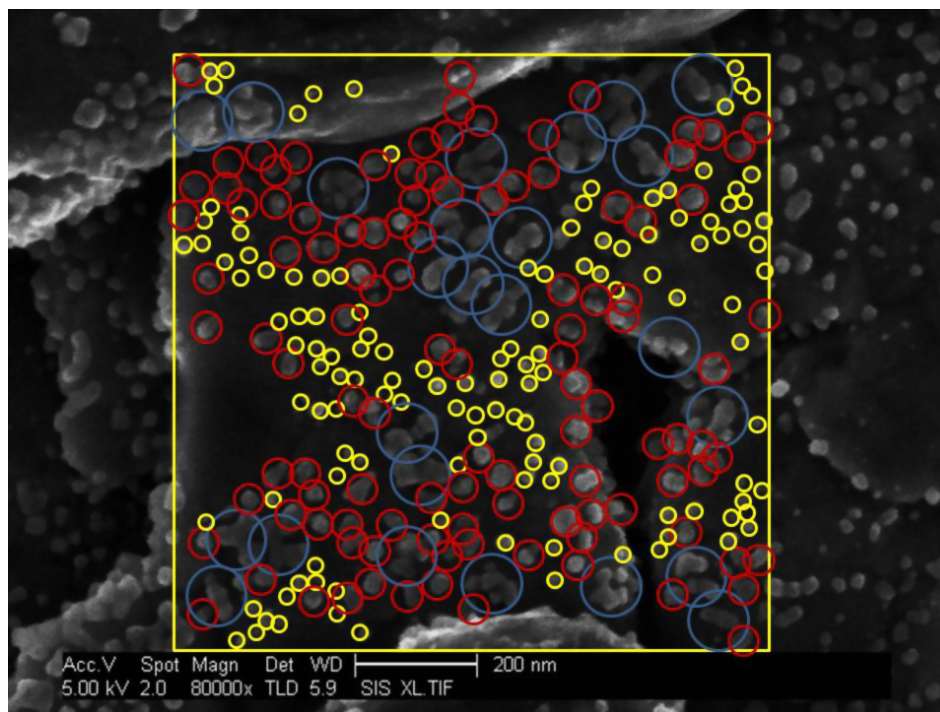


Figure 3.29: Particle analysis via SEM [particles with 25nm diameter (yellow), particles with 50nm diameter (red), particles with 100nm diameter and above (blue)]

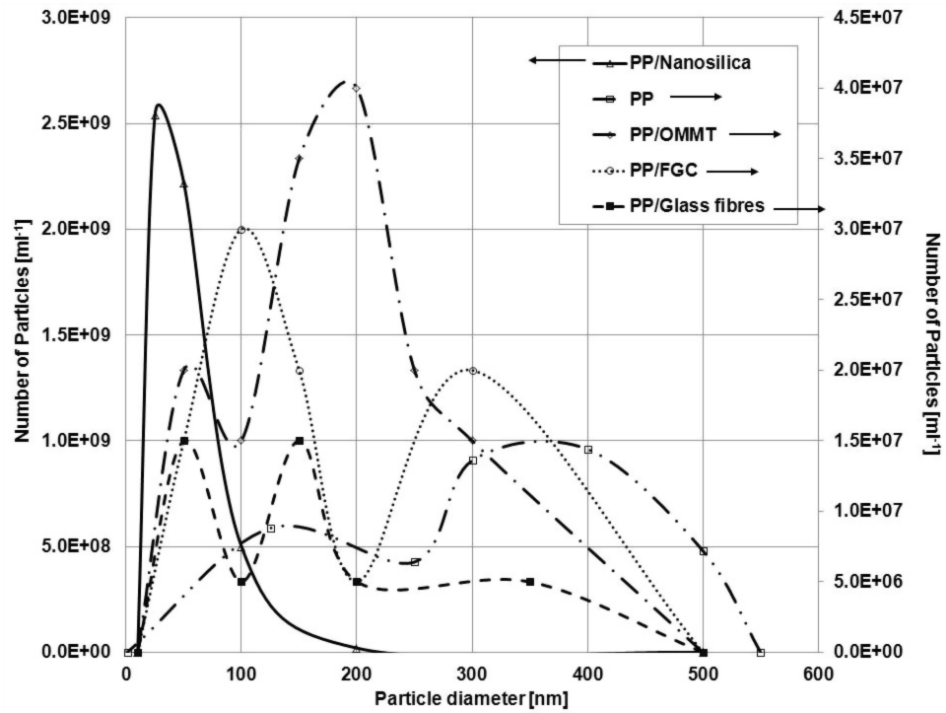
had random shapes and polydispersed size fractions the particles size distribution was additionally assessed through SEM micrographs analysis. The particle size distribution was determined by counting particle in a specific area according to their size, as shown in Figure 3.29. Particles in an area of $1 \times 1 \mu\text{m}$ on the SEM (magnification of 80000) were investigated, for the particles emitted by PP and PP composites. For PA6 and PA6 composites an area of $2 \times 2 \mu\text{m}$ on the SEM (magnification of 50000) was investigated. Particles were then classified according to their size. The total number of particles in this area was then used to calculate the total number of particles on the SEM substrate (area $10 \times 10 \text{mm}^2$) in dependence of the volume of liquid (1 drop = 0.05 ml).

Figure 3.30 shows the obtained size distribution of the particles emitted during drilling of PP and PA6 nanocomposites. The total number of particles emitted from the neat polymers were of similar values with $5.04\text{E}+07$ for the PP and $5.13\text{E}+07$ for the PA6 matrix. However, the total number of particles emitted by

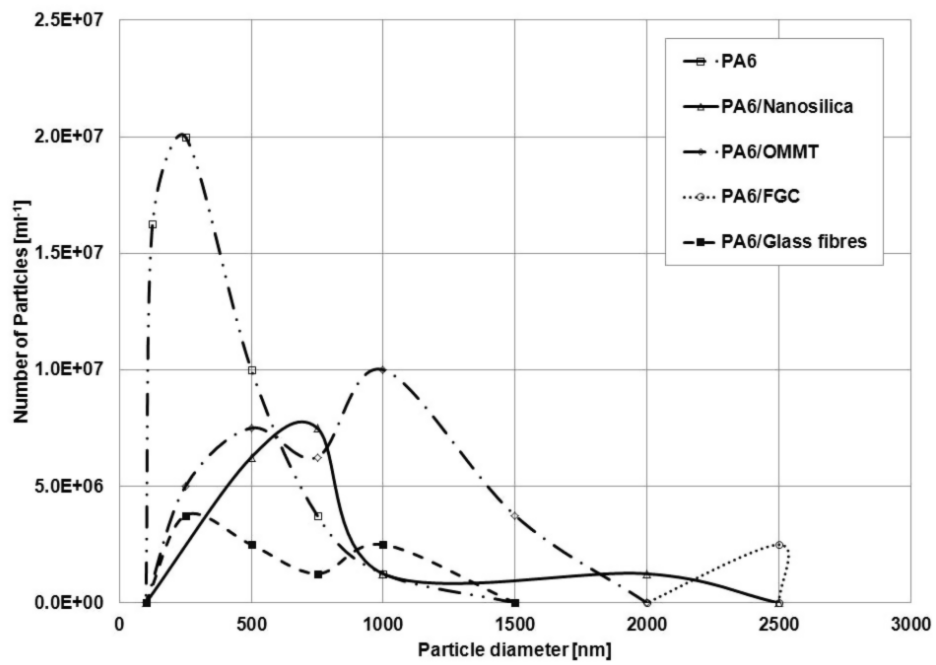
PP nanocomposites was 10 times higher for OMMT and FGC filled nanocomposites compared to the PA6 composites and 100 times higher for the nano-SiO₂ filled PP compared to the PA6 nanocomposite. Glass fibre filled composites behaved similar to the neat polymers.

3.3.5.2 Structure and morphology of deposited particles

Figure 3.31 and 3.32 shows the SEM micrographs of the nano-sized particles emitted by PP and PA6 nano composites during drilling of the solid material. Irregular shaped particles in the size range between 25-500 nm could be seen on the micrographs. While rather similar particles were found for PP/OMMT, PP/FGC and PP/glass fibres, the particles released by PP/nano-SiO₂ composite were clearly different, as the composite structure was still intact. Nano-SiO₂ particles in the size range of 10-80 nm could be found on the surface of the PP matrix. However, some of these particles might not be attached to the matrix and cause direct exposure. This scenario could not be found for the PA6 based composites, as shown in Figure 3.32. The particles released by the PA6 based composites were found in size ranges between 200-1000nm. The irregular shape of the particles seem rather similar for the nanocomposites and the PA6 matrix. However, for the PA6/GF and PA6/FGC, the particles seemed more angular and the particle surface was finer structured.



(a) Size distribution of PP composite



(b) Size distribution of PA6 composite

Figure 3.30: Particle size distribution of PP and PA6 composites emitted during drilling process of bulk composite panels

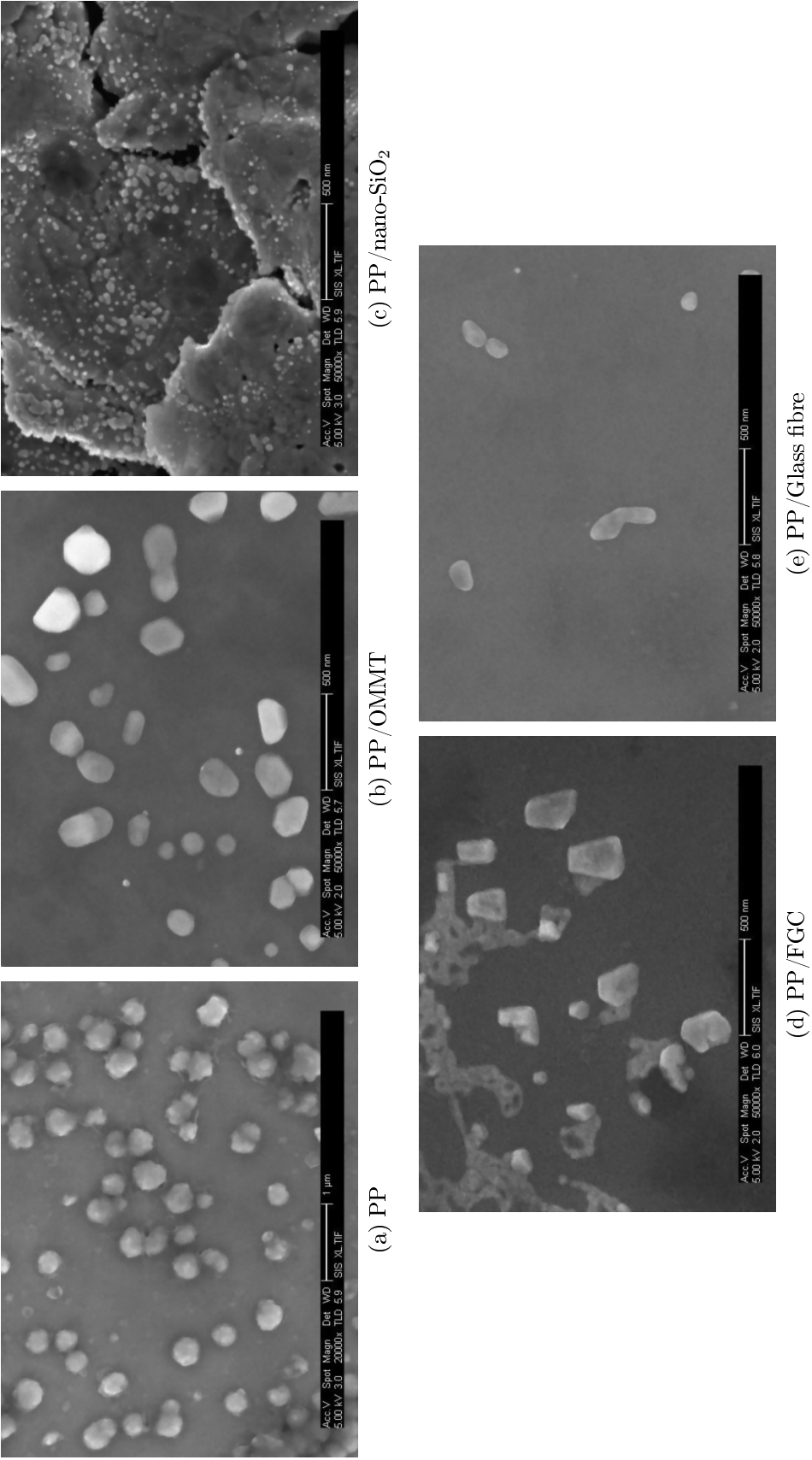


Figure 3.31: SEM micrographs of generated particles collected by ESP during the drilling process

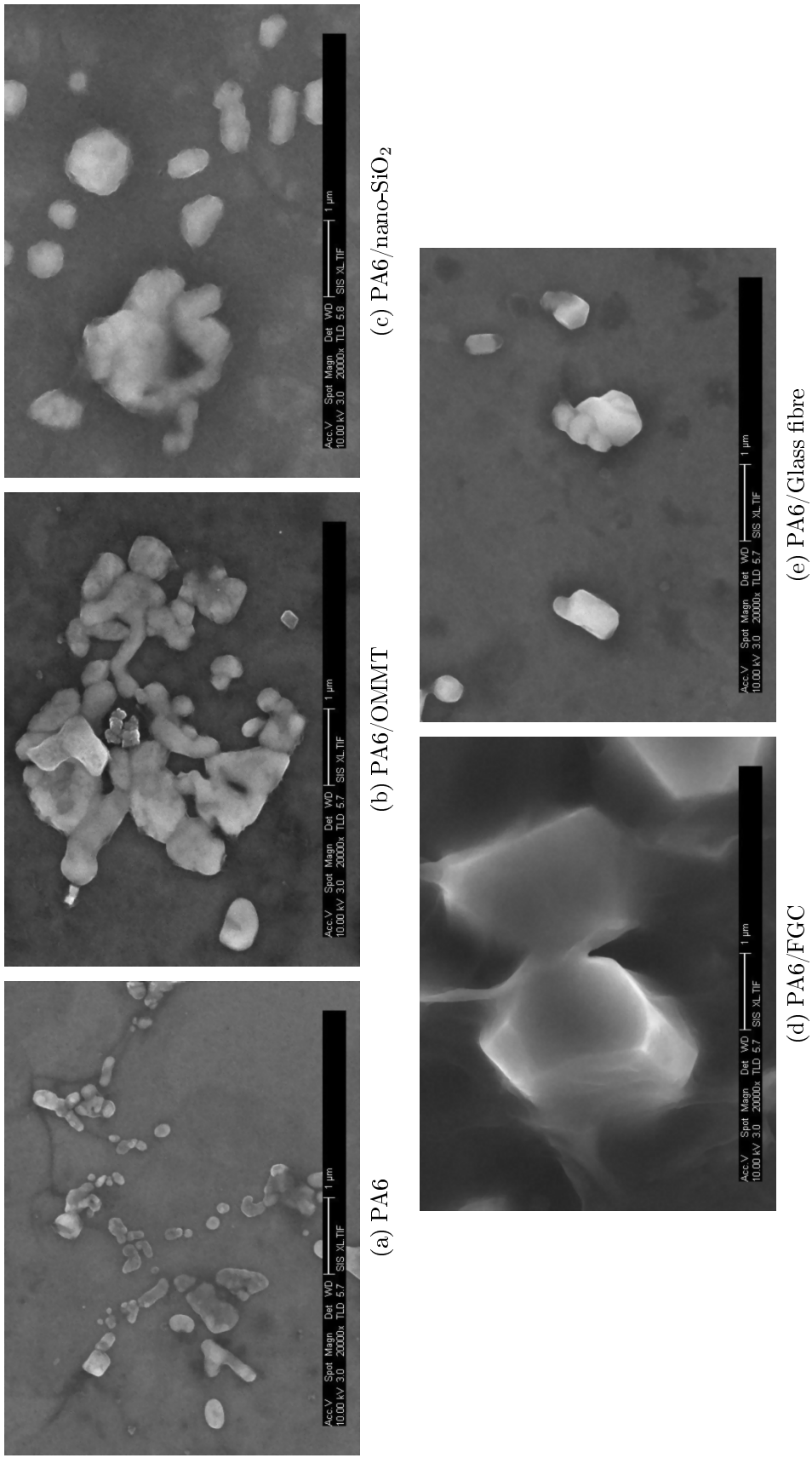


Figure 3.32: SEM micrographs of generated particles collected by ESP during the drilling process

Figure 3.33a shows the WAXD diffractograms of neat PP bulk matrix and dust generated from it during drilling. The main peaks at 14.05° , 16.75° , 18.4° and 21.2° correspond to the primary diffraction of the 110, 040, 130 and 111 planes of the α -phase crystals respectively. The peak at $2\theta = 15.95^\circ$ was associated with the 300 plane of β -phase crystals. Therefore, a blend of α -phase and of β -phase crystals was formed during manufacturing of the neat PP specimens. After the disintegration of material into dust particles, the diffraction peaks became weaker due to imperfection of the polymer crystals. Moreover, the peak associated to the β -phase crystals (around 15.95°) disappeared. The dominating morphological form of crystals in the PP dust was α -phase crystals. The diffractograms of PP/OMMT nanocomposites dust particles (Figure 3.33b) revealed similar effect of drilling on the crystal structure of PP in term of peaks position and relative intensity. It is important to notice that drilling caused further dispersion of OMMT nanoparticles since the peak at 6.5° , corresponding to the regularly arranged OMMT layers, was not occurring for the nanocomposite dust. It is also probable that dust was impoverished with OMMT. Drilling had the same effect on PP/nano-SiO₂ and PP/FGC structure as on neat PP. No significant changes of the dusts crystallographic structure was revealed by the WAXD study. Comparing PP/FGC bulk material to PP/FGC dust showed favoured formation of α -phase crystals due to the mechanical processing. Moreover, the diffraction peaks observed for the nanocomposite dust were less intensive than those of the neat PP dust indicating that mutual influence of glass fibres and mechanical forces disrupted the recrystallisation of PP and/or caused imperfections in the existing crystal fraction. Even stronger effect of crystal imperfection and lower content of crystal fraction was observed for PP/GF composite dust (Figure 3.33e). No additional peaks on the diffractograms for all dusts based on PP comparing to the bulk materials which indicated that no additional crystal forms of silicon dioxide were formed.

The diffraction pattern of the neat PA6 and its composites in bulk form and dust

particle emitted from these composites are presented in Figure 3.34. Polymorphic structures were formed under the action of mechanical force during drilling, since one strong peak corresponding to the γ -phase of PA6 in bulk form was weakened after breaking the solid material into dust and additional peaks at 20.05° and 23.35° occurred, showing the formation of α -crystal phase of PA6. Re-crystallisation of polymer matrix may be facilitated by the heat evolved during drilling of polymer materials. The diffraction patterns of the nanocomposite dust was very similar to that observed for PA6 dust and there are no premises that the presence of nanoparticles played significant role in polymer recrystallisation. Therefore, the changes in the polymer structure were mainly due to the action of physical factors during disintegration rather than the chemical composition.

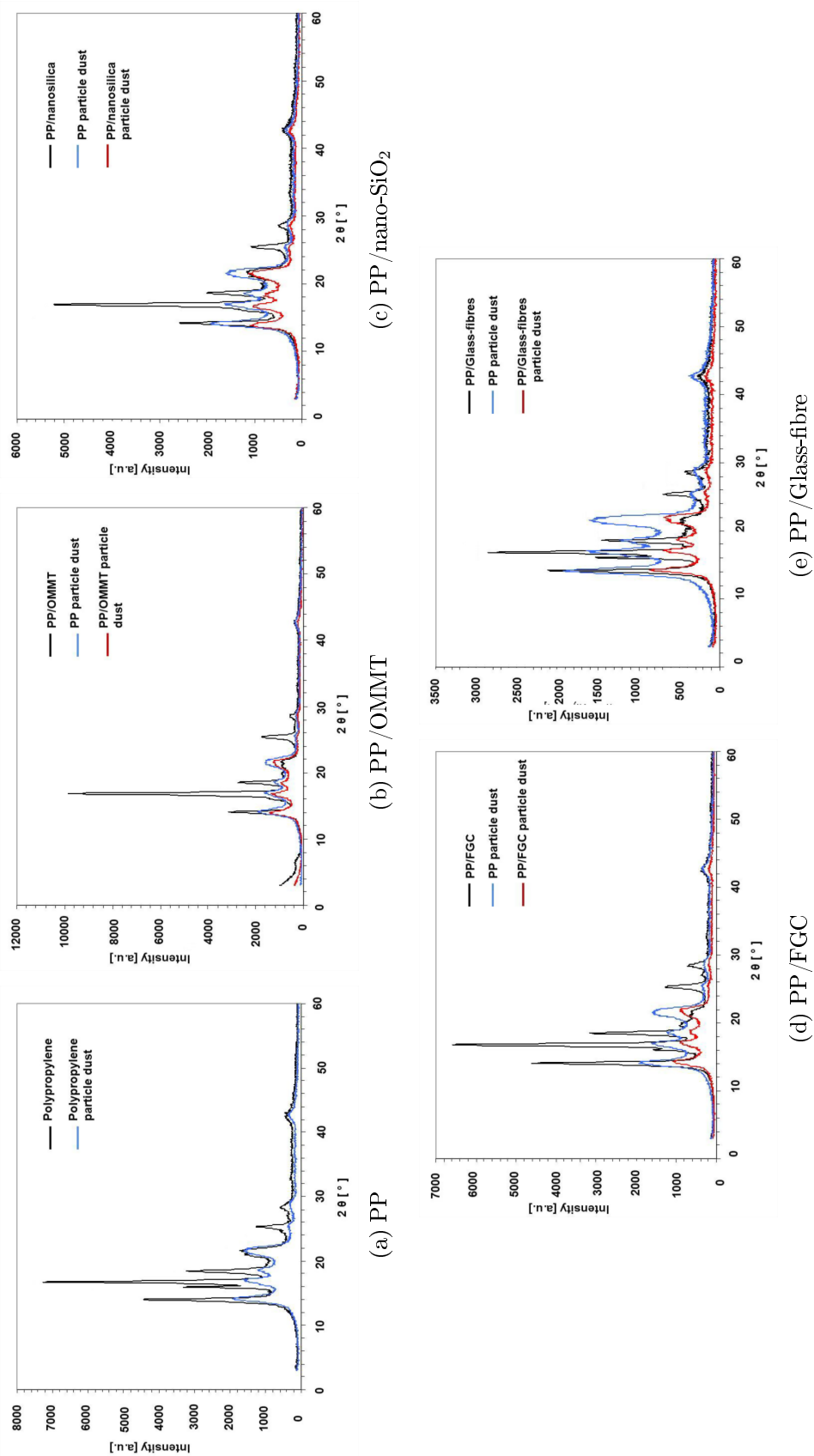


Figure 3.33: WAXD spectrum of bulk PP composite and spectrum of dust emitted from the bulk composites during drilling process

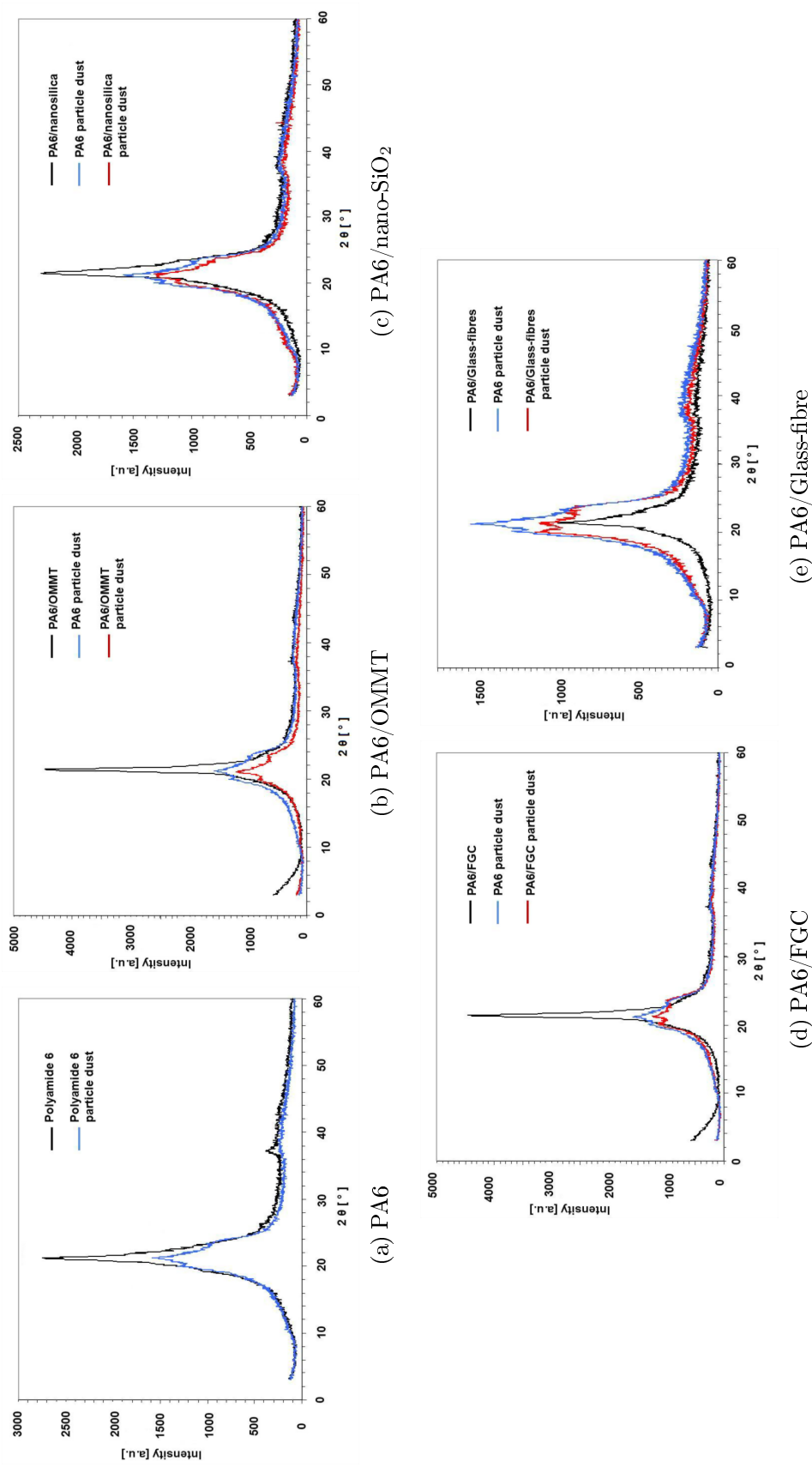


Figure 3.34: WAXD spectrum of bulk PA6 composite and spectrum of dust emitted from the bulk composites during drilling process

3.4 Conclusion

PP and PA6 based nanocomposites with four types of fillers: organically modified montmorillonite, fumed silica, foam-glass crystal material and glass fibres were obtained by direct melt mixing in a twin-screw extruder. The obtained granulate was then used for the nanocomposite manufacturing by compression moulding. The preparation of the polymeric nanocomposites involved a careful selection of components, processing techniques and conditions. In order to maintain a high dispersion of the nanofillers in both apolar (PP) and polar (PA6) matrices, selected nanofillers were used with appropriate surface modification providing good compatibility with both types of polymers. The presence of stable nanostructures in the polymeric matrices were confirmed by WAXD, SAXD and SEM analysis.

The DSC result showed that the nanofillers changed the thermal properties of the PP matrix. While an increase of melting temperature and crystallisation temperature was recorded, the degree of crystallinity decreased. It was evident that the fillers refined the size of PP spherulites of the nanocomposite considerably, confirming that the fillers act as nucleating sites for PP crystallisation. The nucleating agent enhances the crystallisation rate and promotes the formation of intercrystalline links.

TGA showed that all PA6 nanocomposites exhibited improved thermal stability in terms of initial temperature of degradation and temperature at maximum rate of mass loss. The profiles of TGA curves were slightly modified upon filler addition, indicating some changes in the degradation mechanism. The improvement in thermal stability in nanocomposites is sometimes considered as indication of high degree of homogenization and nanostructure formation. However, the difference in thermo-oxidative degradation of the nano- and microcomposites was smaller for the PA6 composites, in contrast to the PP based composites. Therefore, it can be assumed that the effect of the nanofillers on the thermal stability of the nanocom-

posite is less pronounced for PA6 matrices.

Further, the nano-sized particles emitted during drilling from these silica based nanocomposites were studied. Physical characterisation of the number concentration and size distribution of sub-micron particles from 5.6 to 512 nm was carried out. In general, nano and ultrafine airborne particles were emitted from all investigated materials, even from the neat polymer. However, composite based on PA6 polymer emitted 10 times higher particle concentration the composites based on PP. However, in both cases composites filled with nano-SiO₂ emitted the highest number of airborne particles and hence possessed the highest emission rates. Interestingly, integration of OMMT into the PA6 matrix reduced particle emission during drilling by 1.5 times compared with the neat PA6.

The characterisation of deposited particles showed that with decreasing airborne particle concentration the concentration of deposited particles increased and vice versa. In this case the total number of particles emitted by the PP based composites was 10-100 times higher than for the PA6 composites. For both matrices, nano-SiO₂ filled composites emitted the highest number of particles, whilst glass fibre filled composite did not significantly affect particle emission.

It can be summarised that the integration of nanofillers changes the behaviour of polymer matrices. While the thermal properties of the resulting nanocomposites were slightly effected, a significant effect on particle emission could be observed. Further studies, should focus on the benefit of these nanofillers on mechanical properties, ideally in larger structure for real life structural application should be investigated and the emission during mechanical testing should be reported.

Chapter 4

The effect of low velocity impacts on the emission of nano-sized particles from polypropylene and polyamide 6 nanocomposites

4.1 Introduction

Material used for crashworthy structural application, traditionally have been metals due to their plastic deformation characteristics, which enable them to absorb impact energy in a controlled manner. Polymer composite contrasting metals, do not typically exhibit plastic deformation. However, their stress-strain relationships may show signs of other types of nonlinearities, but they are superior to metals for specific energy absorption. Nanoreinforced polymers have focused the attention, because of their potential to exhibit impressive enhancements of material properties compared to the pure polymers. Therefore, polymer nanocomposites are manufactured commercially for diverse engineering applications and are used in many economic sectors.

Nanoclays, due to the ease of processing, enhanced thermo-mechanical properties, wide availability, and low cost have been found to be the ideal fillers for polymers. PMMA-epoxy-nanoclay composites^[165], polypropylene-nanoclay composites^[58], polyvinylidene fluoride-nanoclay nanocomposites^[166] and nanoclay-modified rigid polyurethane foam^[3;4;167] have exhibit improved thermo-mechanical properties when compared to their bulk polymer constituents and conventional micro-composite counterparts. Numerous studies have reported an improvement in energy absorption capacities for nanoclay/polymer nanocomposites^[3;4;118;168–170]. For example, John et al.^[171] have shown that the incorporation of 2 and 4 vol.% of nanoclay respectively improves the tensile modulus of cyanate ester syntactic foams by 6 and 80%. Further fumed silica nanoparticle have been used as filler for polymers. Polyamide 6/SiO₂ nanocomposite^[46], polystyrene/SiO₂ nanocomposite^[172], polyacrylamide/SiO₂ nanocomposite^[173] amongst others^[38] have been studied.

However, the increasing research, production and utilisation of nanoparticles for consumer goods and engineering applications, raises the question about their fate and behaviour. It is likely that, once nanoparticles are integrated into materials they will undergo mechanical and thermal stress situations which cause nano-sized particles to be detach as free nanofillers or hybrid particles. Therefore, the understanding of the exposure mechanism is crucial for the assessment of the potential environmental and health risks.

At present various research groups have investigated the release of nano-sized particles, from nanocoating and nanocomposites, during different mechanical stress situations such as shredding^[29], drilling^[25;94;97], sanding^[30;33], and abrasion^[26–28;31;32;34]. In general, only a very low amount of nano-sized particles were measured and no free pristine nanoparticle were detected. These findings raises the question on the release-ability of nanoparticles and the compatibility of the applied methods.

In order to release pristine nanofillers from a matrix, huge accelerations are nec-

essary to generate forces able to compete with van der Waals forces, for example through instantaneous shocks^[174]. However, larger nanofillers such as nanotubes or nanofibres are expected to be removed under lower acceleration from the matrix surfaces.

Hence, the aim of this study is to simulate mechanical shocks, through low velocity impact, of nanocomposite cones and to evaluate the particle released from the structures. For this purpose PP and PA6 nanocomposites cones were manufactured and their mechanical properties were analysed before subjecting the cones to low velocity impacts. Airborne particles emitted during impact test were measured and the results evaluated.

4.2 Experiments

4.2.1 Material selection and preparation of test samples

Polyamide 6 (Tarnamid T30, Azoty Tarnow, Poland) and polypropylene (Moplen HP500J, Basell Polyolefins) were used as matrix material for all composites (See section 3.2.2). As nanofillers the following materials were utilised (5wt.%); surface modified montmorillonite (DELLITE[®] 43B and 72T, Laviosa) and fumed nanosilica particles (AEROSIL[®] R 974 and 200, Degussa, Evonik Industries) (See Section 3.2.1). Nanofillers and polymers were compounded via extrusion to a master batch (Granulate 1 in Figure 4.1) as described in Section 3.2.2

Additionally, polyamide 6 with 30% glass fibres and 30% glass spheres (MM-PA I 1F30 MM-PA I 1K30, MacroMass Verkaufs AG, Germany) and polypropylene 30% glass fibres and 25% glass spheres (MM-PP BI 24 and MM-PP HE25, MacroMass Verkaufs AG, Germany) were used as secondary fillers. Further, glass fibres (GF) for PP and PA6 (Thermoflow 636/672, Johns Manville Fibres) compounding were integrated. This approach of melt blending was chosen to maximise nano and

micro particle distribution throughout the polymeric matrix, as well as the ease of handling the granulates. The recipes used for compounding of the final granulate for injection moulding and the extrusion parameters can be found in Appendix B.

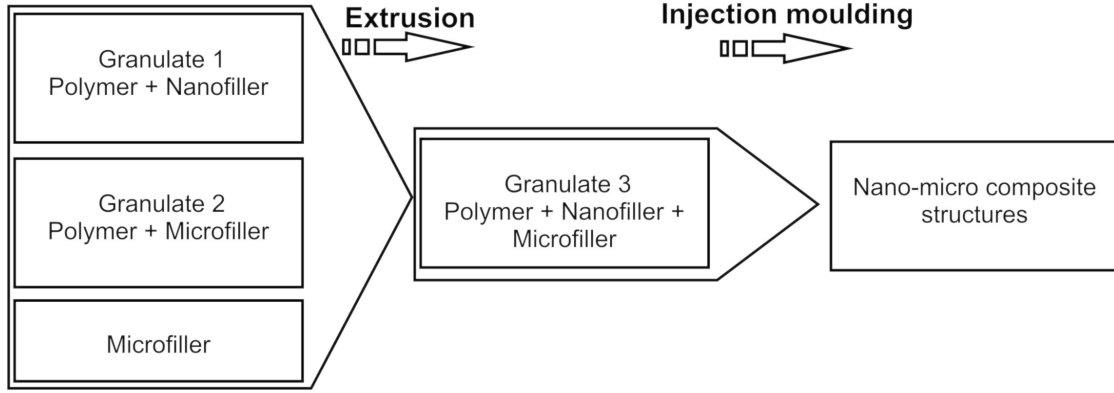


Figure 4.1: Three step manufacturing process of test specimen

Exploiting this recipe, fibre reinforced nanocomposites granulate were obtained for injection moulding of crash cones and tensile bars. Figure 4.2 shows the dimensions of the manufactured crash cones. Tensile bars had dimensions according to ISO 527 (Typ 1A). Injection moulding of the crash cones was conducted on a Ferromatik (K110, Ferromatik Milacron Europe) machine with a closing pressure of 1100kN, while tensile bars were manufactured on a Engel (ES200/60 HL ST) machine with a closing pressure of 600kN. All injection moulding parameters can be found in Appendix B.

4.2.2 Characterisation

The microstructure of the manufactured nanocomposites and resulting fracture surfaces were investigated by emission scanning electron microscope (SEM) and the crystalline structure of the manufactured nanocomposites was studied with help of powder X-ray diffraction (XRD) according to Section 3.2.3.

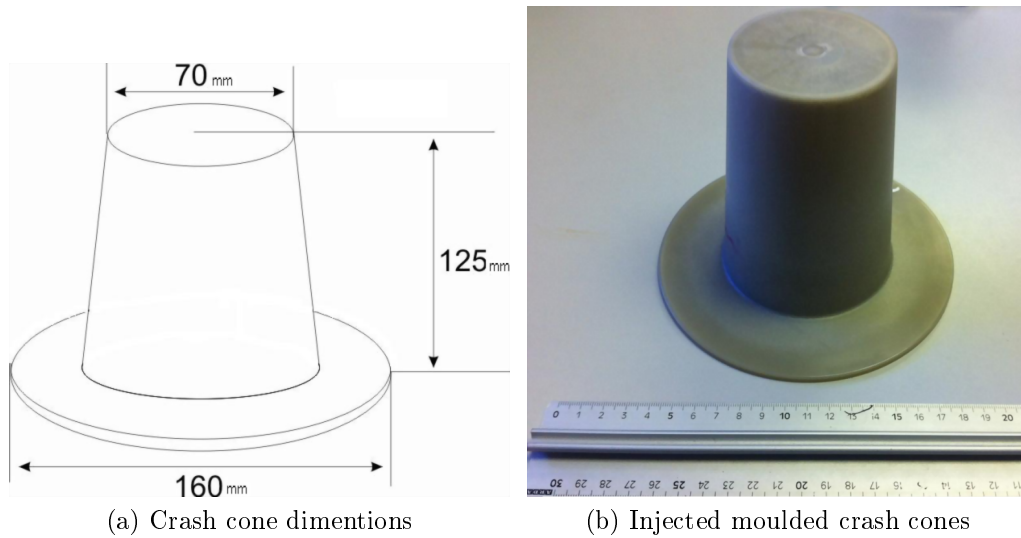


Figure 4.2: Manufactured crash cone dimensions form fibre reinforced nanocomposites granulate

4.2.3 Mechanical testing

4.2.3.1 Quasi-static tensile and compression test

Quasi-static tensile and compression tests were carried out using Instron 5500R electro-mechanical machine as shown in Figure 4.3. All tensile experiments were conducted according to ISO 527 standard. The tensile tests were conducted five times for each material, at a crosshead speed of 1 mm/min, while the load was measured using a 100 kN load cell.

Quasi-static compression test of the crash cones were conducted at a crosshead speed of 0.1 mm/sec. The load was measured using a 100 kN load cell and the displacement was measured using a built in crosshead displacement sensor. During the test the data was collected at every second, corresponding to a 0.1 mm displacement.

4.2.3.2 Drop weight impact test

Crash cones were impacted utilising a high energy capacity drop tower rig. This machine permits impact testing at up to 8 m/s velocity and maximum falling weight of 300 kg. External devices for measuring the load and displacement were

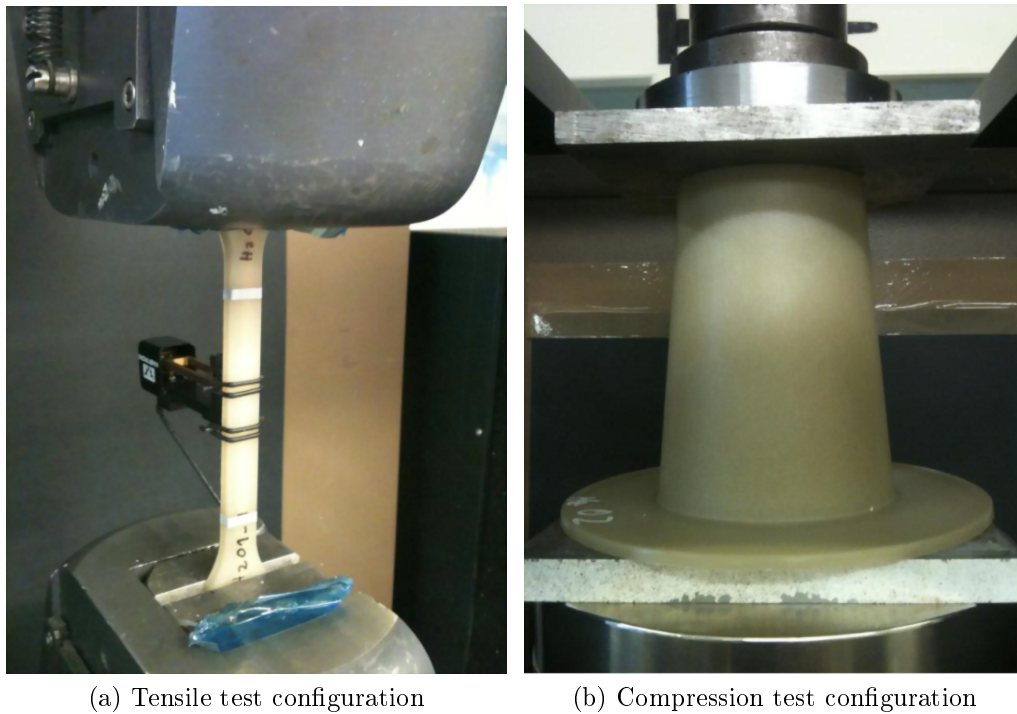


Figure 4.3: Quasi-static tensile and compression test conducted on Instron 5500R electro-mechanical testing machine

used. Both load cell and displacement transducer were connected to the data acquisition system (DAQ), which converted analog input into digital output signal. The signal from DAQ was converted and recorded as load and displacement every 0.05 ms. The low velocity impact tests were conducted at three different velocities 4.4, 6.2 and 7.7 m/s corresponding to 1, 2 and 3 metre drop heights. The experimental set up can be seen in Figure 4.4. The tests were performed by direct impact of the falling beam. The impactor mass of 54 kg was constant in all tests, giving the overall impact energies of 520 J, 1050 J and 1580 J. The load was measured using a 200 kN load cell, placed underneath the cones. In order to measure the beam displacement of the cones (shortening of cone), a linear variable differential transformer displacement transducer was used, with a precision of 0.01 mm and a maximum displacement speed of 10 m/s.

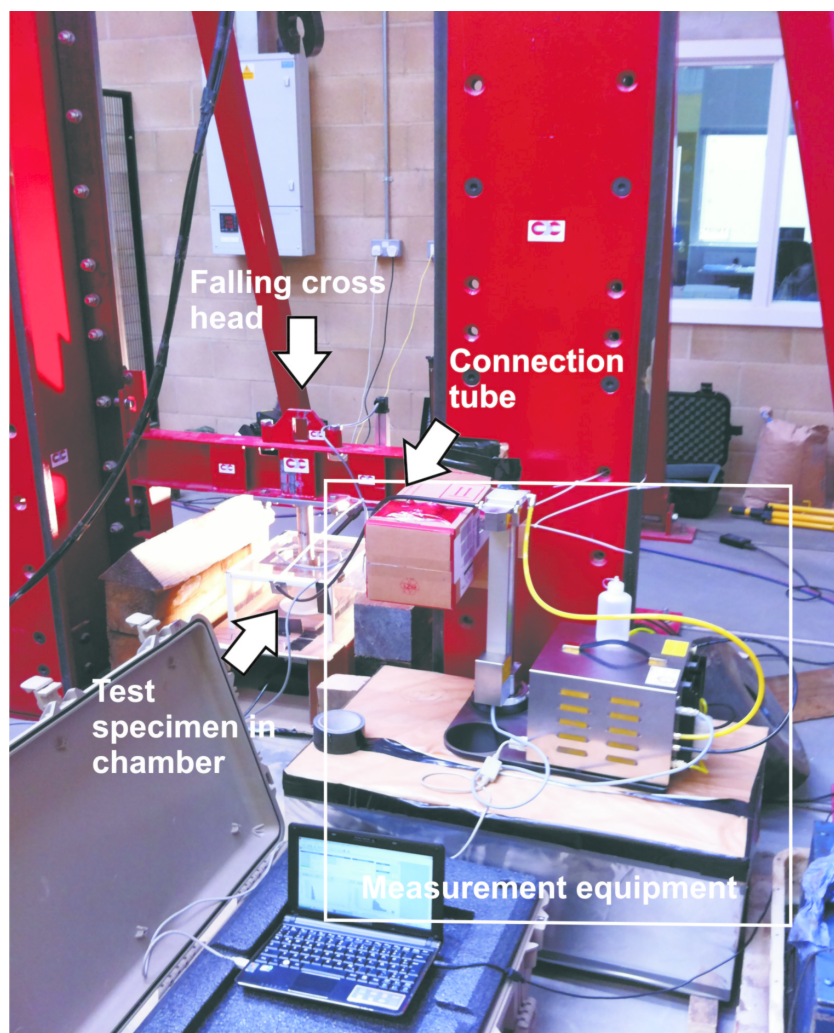


Figure 4.4: Experimental set up during drop tower impact testing of crash cones

4.2.4 Measurement of airborne particle number concentration and size distribution

To characterize the physical properties of particles generated during impacting, the crash cones were placed in a crash chamber, as illustrated in Figure 4.5. The particle emissions were measured using a condensation particle counter "CPC" 5.403 with classifier "Vienna"-DMA 5.5-U (SMPS+C, Grimm Aerosol, Germany). Prior to the measurements, the chamber was purged with laboratory air for about 20 min. Each sampling cycle comprised a 20 min background air monitoring in the chamber, and a 40 min post-impact period. The experiment was repeated 2

times for each composite material.

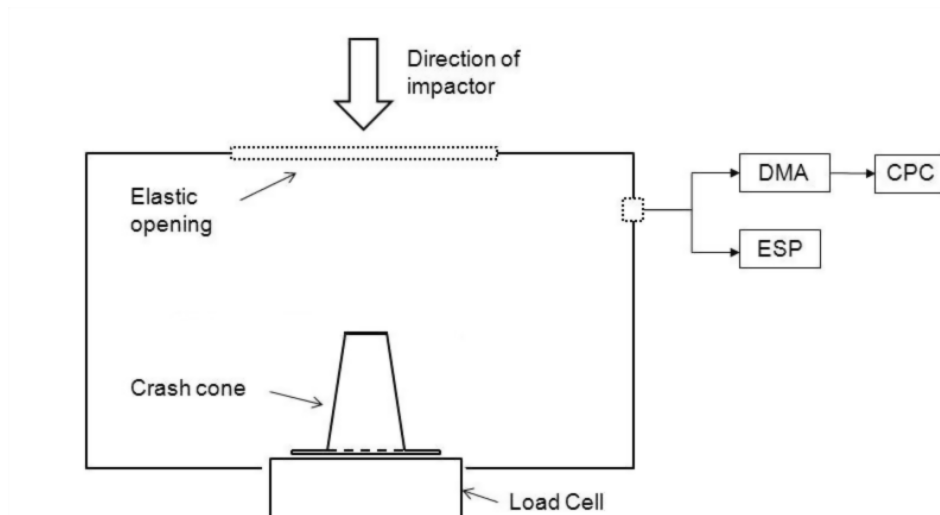


Figure 4.5: Schematic set up of crash chamber for measuring the particle emission from crash cones during impact testing

4.3 Results and Discussion

4.3.1 Morphology of nano and micro composites

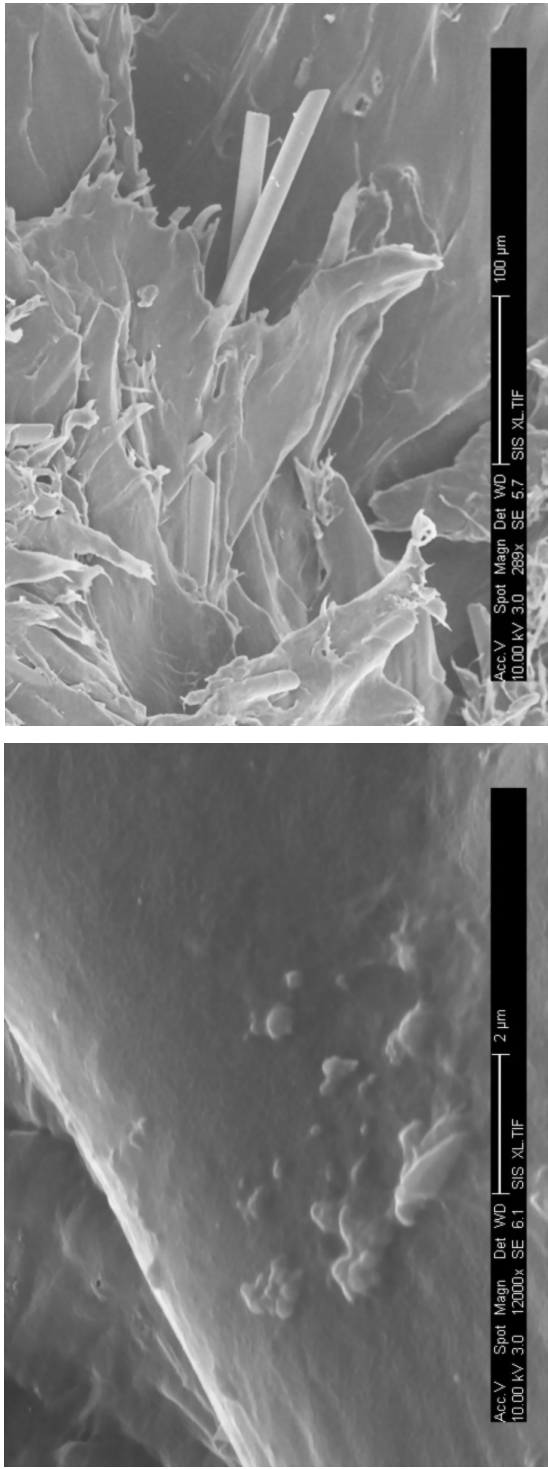
The composition of the manufactured crash cone and tensile bars can be found in Table 4.1. Glass fibre content was kept at 30 wt. % for all composites, while nanofiller loading accounted 1.6 wt.% and microfiller loading varied between 9 wt.% for the PP matrix and 10.7 wt.% for the PA6 matrix.

Figure 4.6 shows SEM micrographs of the nano- and micro-SiO₂, as well as OMMT filled PP composite. The silica micro-SiO₂-phase was found as rather large agglomerates (approx. 500 nm), mainly on the fibres. Micro fillers could be found distributed homogeneously throughout the matrix. Additionally, the SEM micrographs revealed that the micro-SiO₂ could be found in size ranges between 10-50 μ m. Nanoclays could not be seen during SEM investigations. For PA6 based composite the detection of nano- of micro-fillers was more challenges as shown in Figure 4.7). Glass fibres were found distributed homogeneously through out

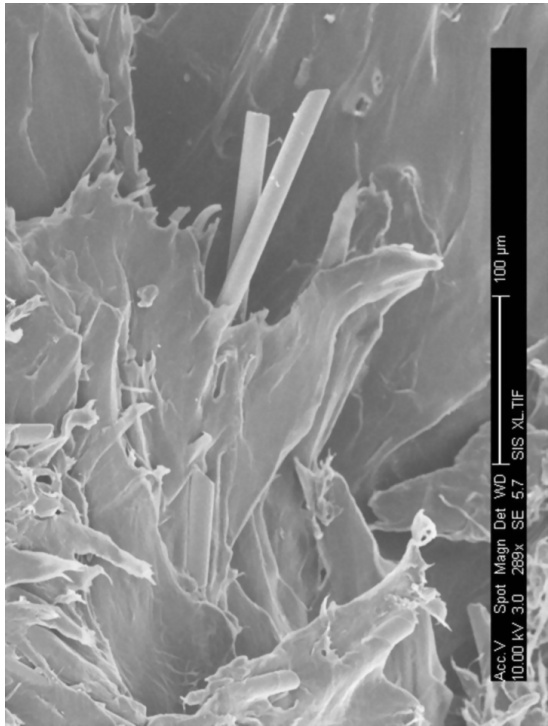
Table 4.1: Fibre reinforced nano and micro composite composition

Material	Matrix	Filler 1	Filler 2
PP-GF-nanoSiO ₂	PP	30 wt.% glass fibre	1.6 wt.% Nanosilica
PP-GF-OMMT	PP	30 wt.% glass fibre	1.6 wt.% Nanoclay
PP-GF-microSiO ₂	PP	30 wt.% glass fibre	9 wt.% Microsilica
PP-GF	PP	30 wt.% glass fibre	-
PA6-GF-nanoSiO ₂	PA6	30 wt.% glass fibre	1.6 wt.% Nanosilica
PA6-GF-OMMT	PA6	30 wt.% glass fibre	1.6 wt.% Nanoclay
PA6-GF-microSiO ₂	PA6	30 wt.% glass fibre	10.7 wt.% Microsilica
PA6-GF	PA6	30 wt.% glass fibre	-

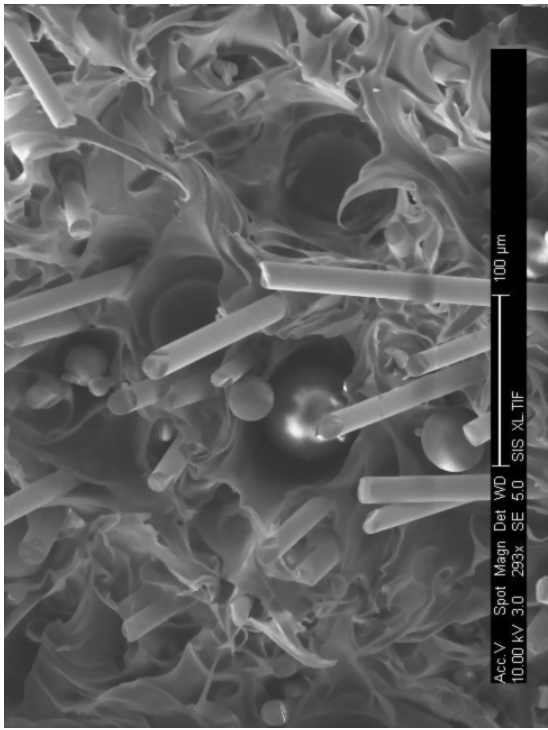
the investigated panels, indicating a good materials flow during injection moulding process. The results obtained during EDX analysis, illustrating the chemical composition of the composites, can be found in Appendix C. As the matrix in all samples was made from the polymer, carbon was mainly found. Investigation of the fillers showed existence of the elements such as: silicon, oxygen, sodium and calcium. An important difference between the nano-SiO₂ and micro-SiO₂ filled composites was observed by the existence of the silicon within the matrix of the nanocomposites, indicating dispersion of nanofiller inside the matrix. No silicon was found in the matrix of the micro-SiO₂ composites.



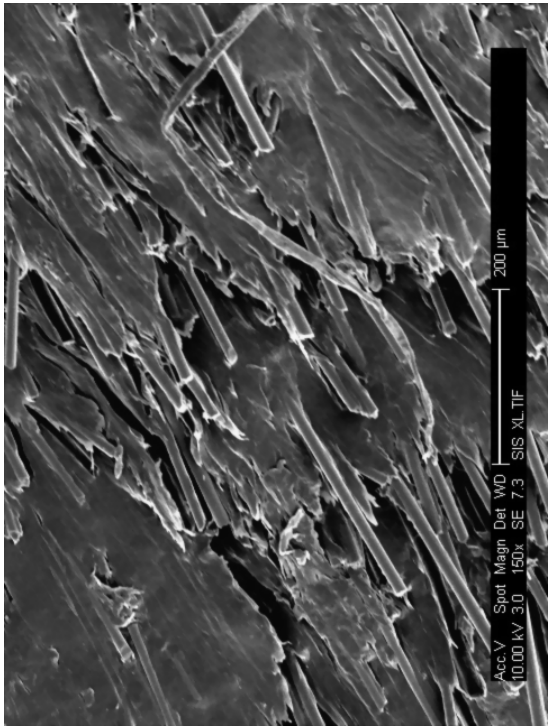
(a) PP-GF-nanoSiO₂



(b) PP-GF-OMMT

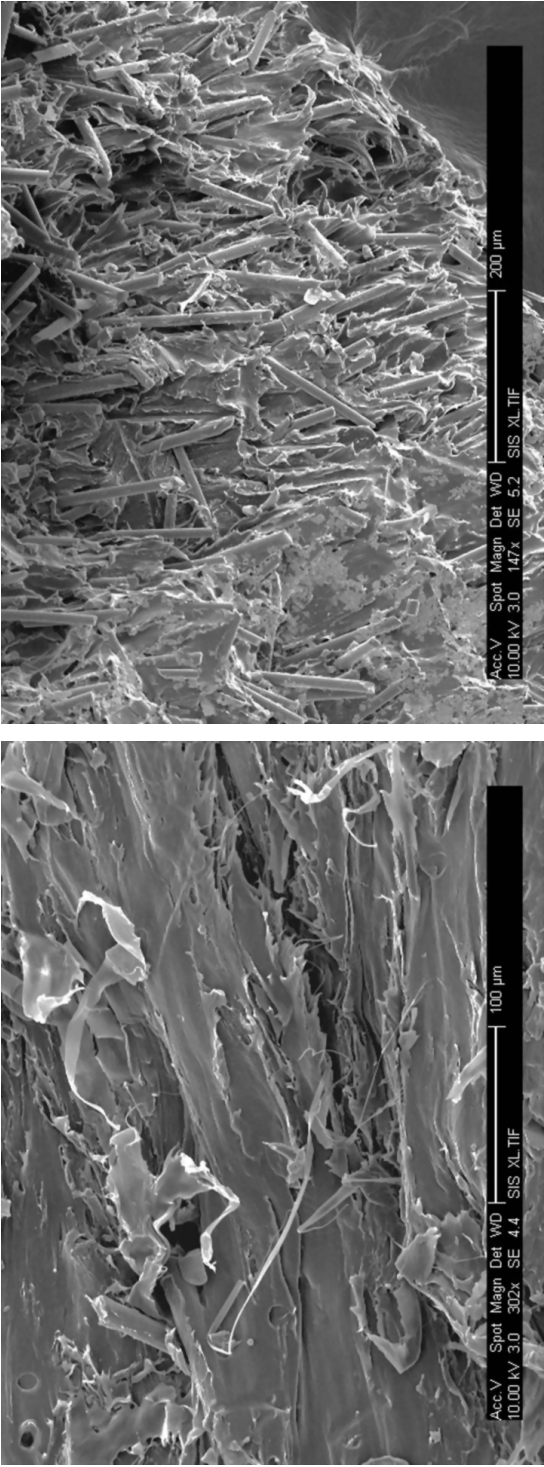


(c) PP-GF-microSiO₂

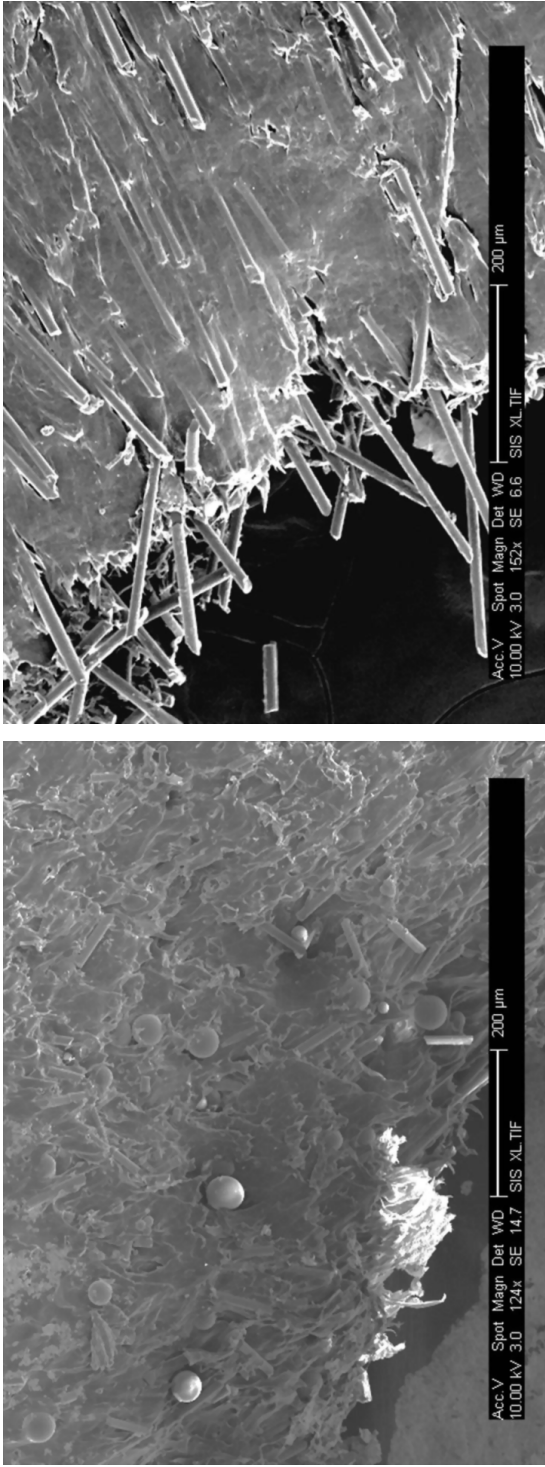


(d) PP-GF

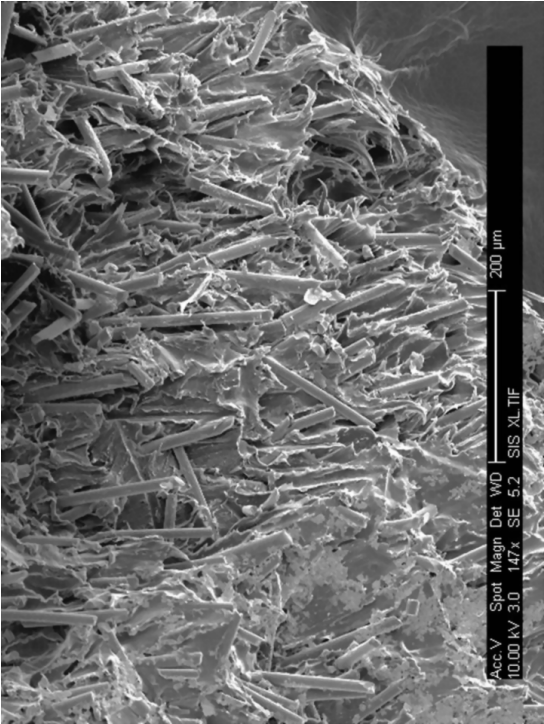
Figure 4.6: SEM micrographs of fibre reinforced PP nano and micro composite



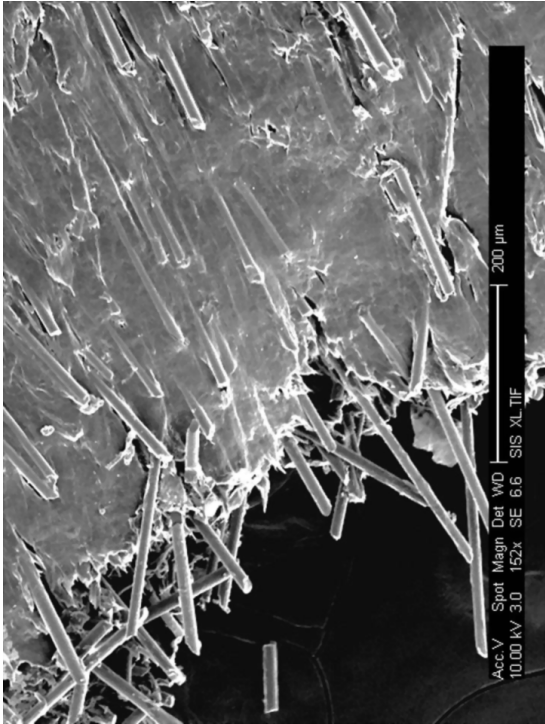
(a) PA6-GF-nanoSiO₂



(c) PA6-GF-microSiO₂



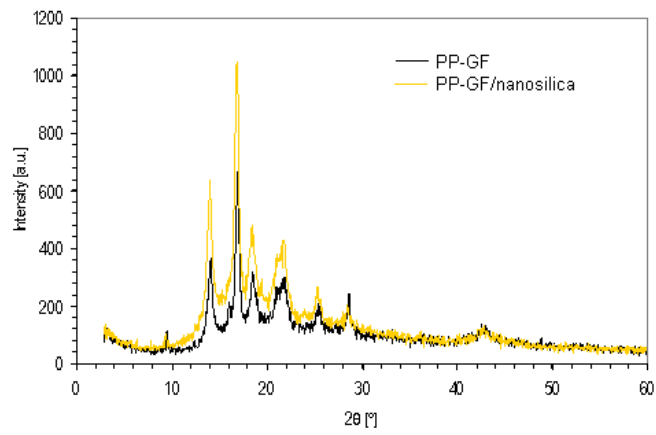
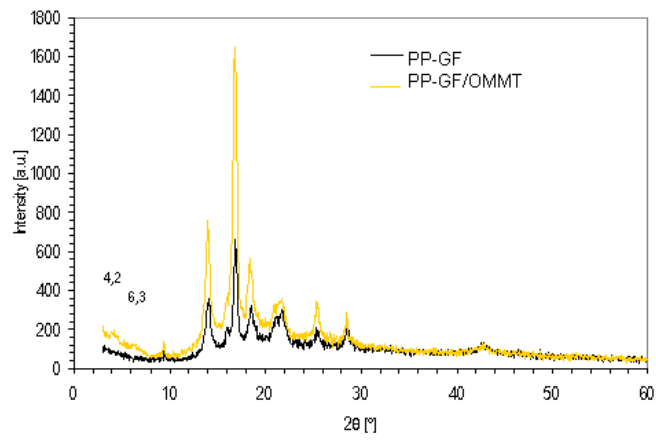
(b) PA6-GF-OMMT



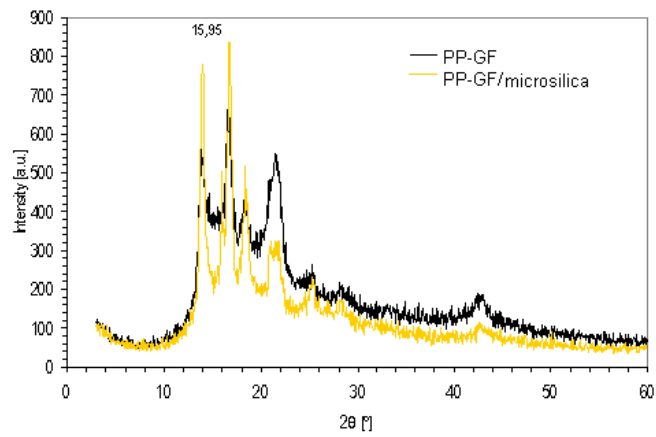
(d) PA6-GF

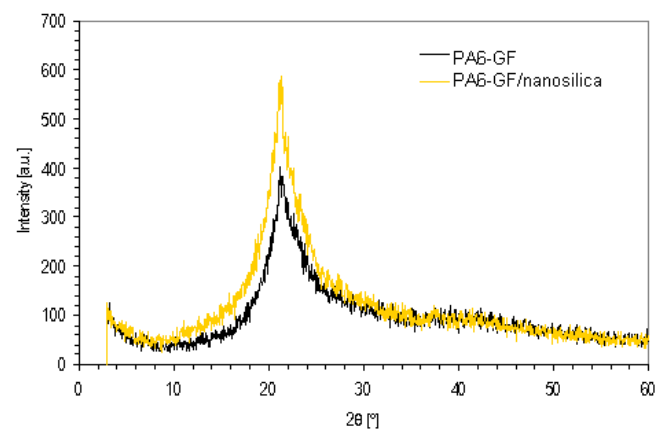
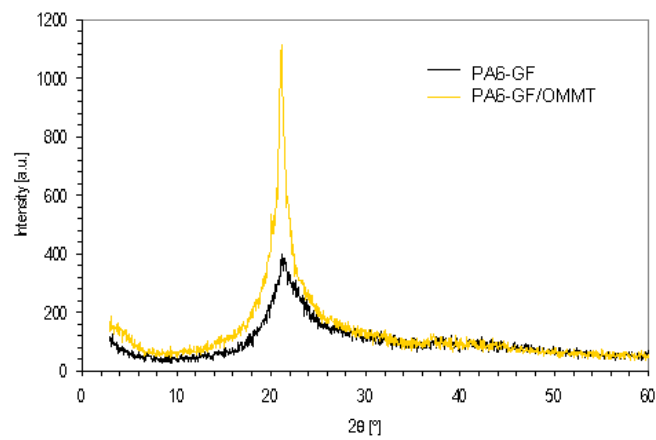
Figure 4.7: SEM micrographs of fibre reinforced PA6 nano and micro composite

Figure 4.8 shows the WAXD diffractograms of the manufactured PP composites. The diffraction peaks observed at the 4.2° and 6.3° for PP-GF-OMMT could be correlated with the presence of lamellar arranged OMMT. The crystal structure of PP was not significantly affected, however stronger peaks were observed for the nanocomposite panels indicating a higher content of polypropylene crystal phase. The WAXD diffractograms of the manufactured PA6 composites are shown in Figure 4.9. For the nanocomposite filled with OMMT, the peak derived from the γ -crystal phase of PA6 was strengthened indicating higher content of polymer crystalline phase. While for the micro and nano-SiO₂ composite, no changes in the diffractograms could be seen.

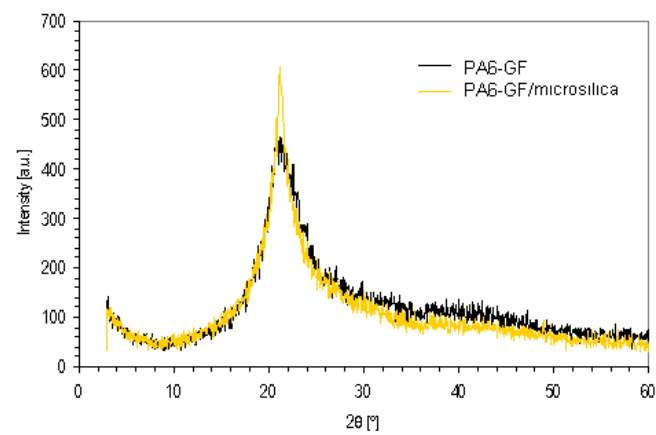
(a) PP-GF-nanoSiO₂

(b) PP-GF-OMMT

(c) PP-GF-microSiO₂**Figure 4.8:** WAXD diffractograms of fibre reinforced PP nano- and micro-composite

(a) PA6-GF-nanoSiO₂

(b) PA6-GF-OMMT

(c) PA6-GF-microSiO₂**Figure 4.9:** WAXD diffractograms of fibre reinforced PA6 nano- and micro-composite

4.3.2 Quasi-static tensile test

Table 4.2 illustrates the mechanical properties of the manufactured nano- and microcomposites. An increase in elongation to break could be found for the PP-GF-nanoSiO₂ composites. However, in general the results showed that by integration of nano- or micro-fillers the mechanical properties of the PP-GF matrix were reduced. PP does not have any polar groups in its chain^[50], which in general results in a significant adhesion problems between the hydrophilic filler and the matrix, creating poor bonds between matrix and filler^[50]. Even though the silica used for the manufacturing of specimens were surface modified it is possible that due to the temperatures involved in the compounding process, the modifier underwent degradation and hence, polymer/filler adhesion was reduced.

On the other hand, the mechanical properties of the PA6-GF matrix were improved by the integration of nano- and micro-fillers. In general the large fraction of nanoparticle atoms that reside at the interface, causes a strong interface interaction between filler and polymer and hence enhance the mechanical properties drastically. However, due to the high surface energy of the nanoparticles, nanoparticles tend to aggregate or agglomeration which leads to bad dispersion, and therefore a decrease of mechanical properties. Agglomeration of nano-SiO₂ particles could be seen on the SEM images. The agglomerate could be found in size ranges between 200 nm and 2 μ m. It follows that different studies reported dispersion of nanofillers can be improved by the utilisation of additives or modifiers^[46;175].

4.3.3 Impact behaviour

Dynamic axial crash test of the composite cones have been conducted by direct impact. The results obtained during the drop weight test of the cones subjected to an impact of 6.2m/s velocity, corresponding to an energy level of 1050J are given in Table 4.3. The amount of energy absorbed was similar for all material

Table 4.2: Mechanical properties of nano- and microcomposites

Composites	Modulus [GPa]	Strength [MPa]	Elongation [%]
PP-GF-nanoSiO ₂	6.18	60.9	3.18
PP-GF-OMMT	6.24	60.0	2.61
PP-GF-microSiO ₂	5.87	46.2	1.37
PP-GF	6.87	73.4	2.92
PA6-GF-nanoSiO ₂	8.04	120.1	4.98
PA6-GF-OMMT	8.72	124.0	3.73
PA6-GF-microSiO ₂	10.09	125.6	3.09
PA6-GF	7.84	125.2	4.22

combinations. However, the amount of specific energy absorption varied between the different materials. The difference in specific energy absorption is caused by the different crushing lengths, which were two times higher for PA6 composites than for PP composites. The value for the mean crushing load was much closer to the initial peak force, for all PP composites, which had a direct influence on the amount of energy absorbed by the structure. On the other hand, for the PA6 composites the mean crushing load was significantly reduced and the initial peak force increased.

Fibre reinforced nano- and micro-composites cones after impact testing are shown in Figure 4.10 and 4.11. Cones based on PP matrix showed more delamination than those based on PA6. For the PA6 matrix based cones less damage could be detected after integration of the fillers, especially the micro-SiO₂ filler changed damage behaviour. For the PP based composites a typical progressive crushing was observed. The material failed only in close proximity of the impactor, without visible cracks along the structure. As the displacement progressed the following sections of the cone became crushed. For the PA6 based composites the failure mechanism was different, as the material broke into large pieces and subsequently

Table 4.3: Impact properties of nano- and microcomposites

Composites	Crush length	Initial peak force	Mean crush- ing load	Energy ab- sorbed	Specific energy	Specific energy increase
	[mm]	[kN]	[kN]	[kJ]	[kJ/kg]	[%]
PP-GF-nanoSiO ₂	31.4	25.72	15.41	0.376	22.6	-4.2
PP-GF-OMMT	36.02	20.02	12.86	0.401	20.5	-13
PP-GF-microSiO ₂	35.03	26.28	13.52	0.403	20.7	-12.3
PP-GF	29.79	22.99	14.19	0.365	23.6	-
PA6-GF-nanoSiO ₂	57.56	26.51	8.98	0.432	9.8	+27
PA6-GF-OMMT	62.61	38.82	4.48	0.376	7.7	+0.1
PA6-GF-microSiO ₂	22.03	40.42	15.58	0.32	22.3	+188.5
PA6-GF	60.5	19.99	5.64	0.356	7.7	-

another part of the material was crushed. As the cones manufactured of neat PA6-GF (Figure 4.11a) and the PA6-GF-OMMT (Figure 4.11c) were significantly damaged at an impact velocity of 6.2 m/s, no further test at higher velocity were conducted.



(a) PP-GF

(b) PP-GF-nanoSiO₂

(c) PP-GF-OMMT

(d) PP-GF-microSiO₂

Figure 4.10: Macroscopic comparison of PP based crash cones subjected to 2m impact event

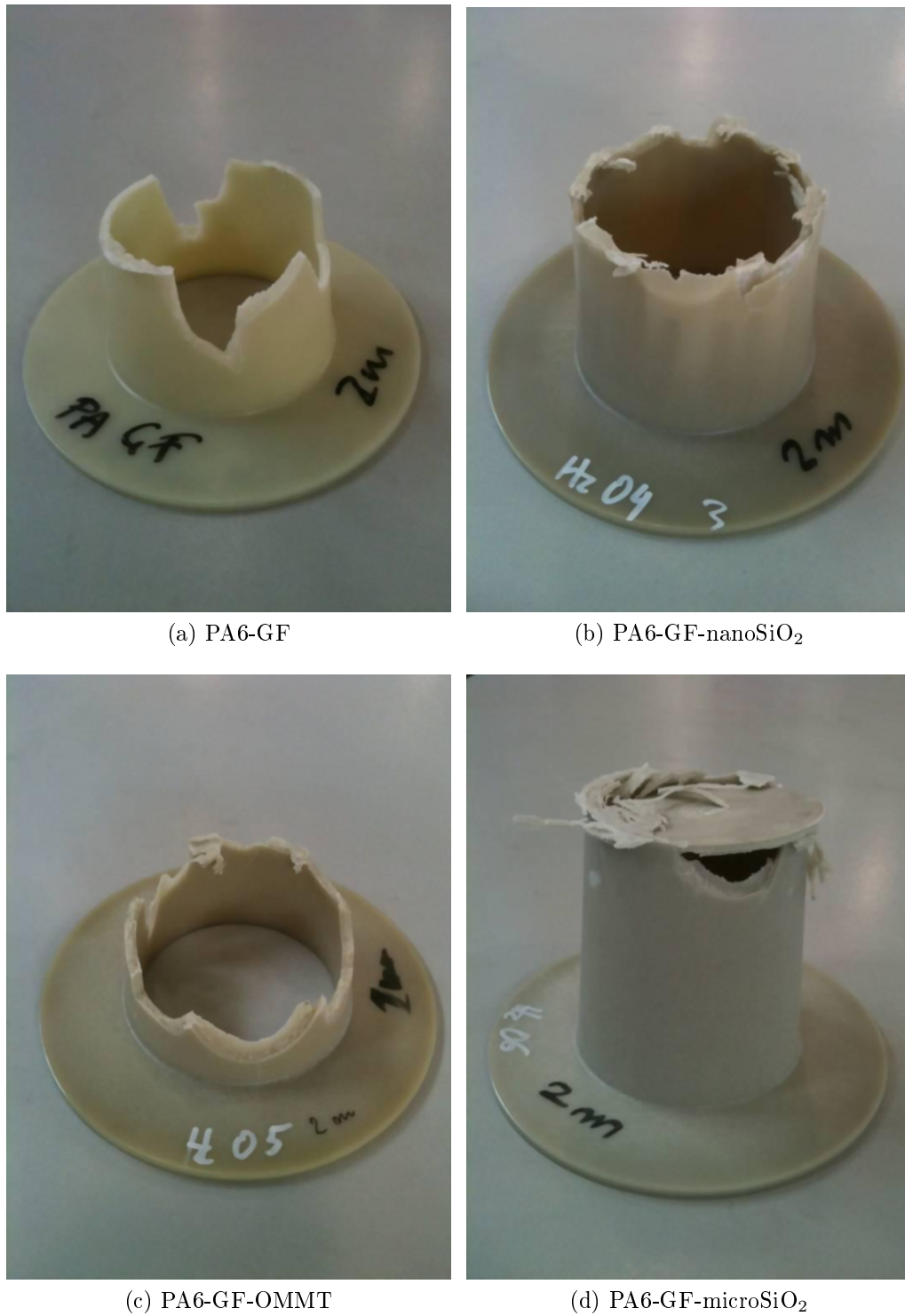


Figure 4.11: Macroscopic comparison o PA6 based crash cones subjected to 2m impact event

4.3.4 Airborne particle emission during low velocity impact tests

4.3.4.1 Sequential alteration of number concentration

The sequential alteration of the total number concentration of particles for a typical sampling cycle is shown in Figure 4.12. It consists of a 20-30 min background

measurement ($t \leq t_{max}$), the impact event ($t_0 = 0$), and a 30 min post-impact period ($t_0 \geq t_{max}$). Figure 4.12, shows that the total number concentration of particles was essentially constant with an average of 1500 particles/ cm^{-3} before impact. The maximum number concentration C_{max} was reached at time t_{max} ($t_0 \geq t_{max}$). Subsequently, the particle decay was observed with the concentration falling back to the original background level approximately after a post impact period of 20 min. To ensure that particles measured were released by the testing composite materials, a styropor *crash cone dummy* was manufactured and packed airtight. The *crash cone dummy* had the same dimensions as the crash cones and was used to determine the particles generated through the impact event as background noises. No increase in particles was measured during impacting of the *crash cone dummy*, hence particle measured during the experiments were not influenced by any background noises.

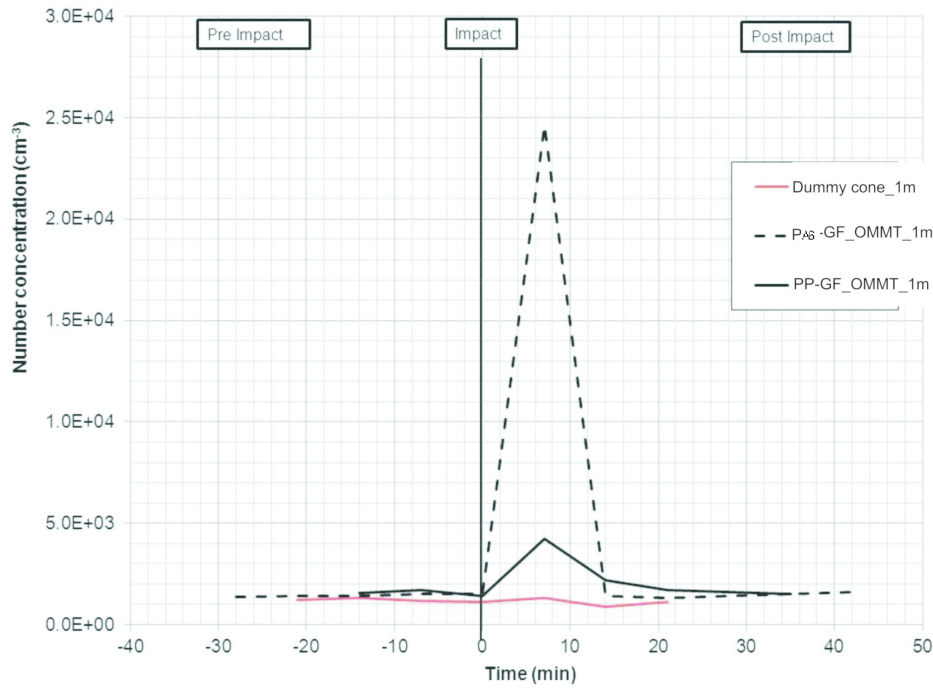
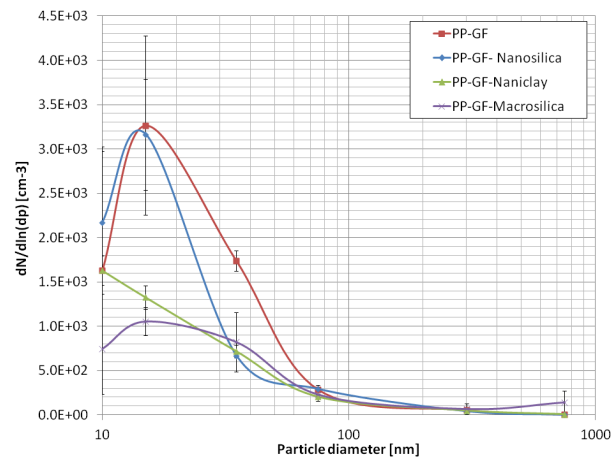


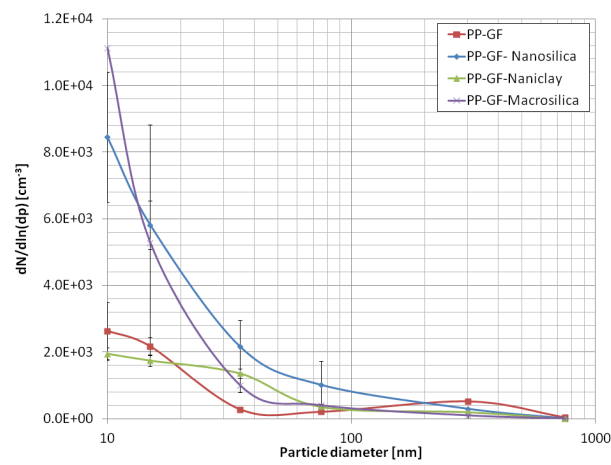
Figure 4.12: Sequential alteration of number concentration of a typical sampling cycle, consisting of a 20-30 min background measurement ($t \leq t_{max}$), the impact event ($t_0 = 0$), and a 30 min post-impact period ($t_0 \geq t_{max}$) for PA6 and PP glass fibre/OMMT cones for the 1m impact event (dummy represents the background noises generated by the impact event)

4.3.4.2 Airborne particle size distribution

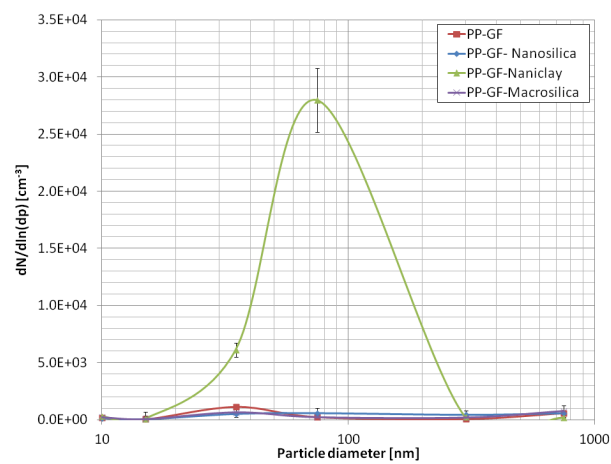
Figure 4.13 and 4.14 represent the particle size distribution of the airborne particles recorded after impacting for the different composite cones at different impact energies. The plots reflected particle size distributions at the time particle concentration reached its maximum. The plots present the normalised distribution with $\Delta N / \Delta \ln d_p$ versus the particle diameter d_p , where ΔN is the concentration of particles within a specified size interval and $\Delta \ln d_p$ is the difference in the natural logarithm of the largest and smallest particle sizes of that interval. From visual inspection of the graph, it can be noted that distinct modal diameters were obtained which appear to be filler dependent. Additionally, the impact velocity had a major influence on the particle size distribution. A major difference in peaks could be observed for the different impact velocities. Peaks moved from smaller particle sizes (10-15nm) for the 4.4 and 6.2 m/s impact towards larger particle sizes (50-80nm) for the higher velocity impact. The shift in size distribution showed that the integration of nanofillers changes the physical properties of the emitted particles. This could be observed for both PP and PA6 based materials. This results contradict with the results obtained in some recent studies^[27;30;31] that dealt with abrasion and sanding of surfaces and composites. In order to release nanofillers from a matrix, huge accelerations are necessary to generate forces able to compete with van der Waals forces, for example through instantaneous shocks^[174]. The difference in mechanical processing approaches could explain the alterations in the obtained results. Further, the normalised distribution varied depending on the used fillers. Highest values could be found for the OMMT filled cones for both PP and PA6 composites.



(a) PP - 4.4m/s impact

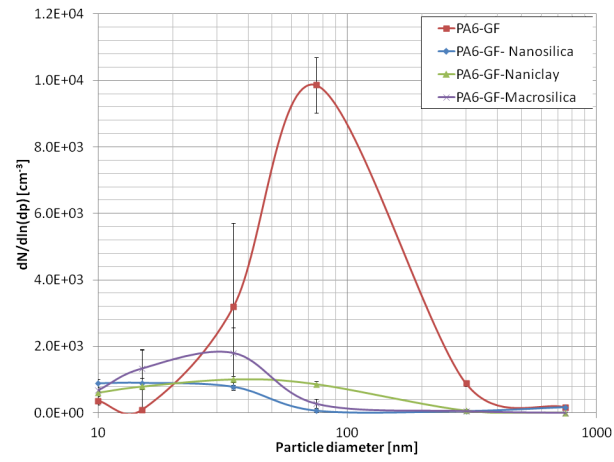


(b) PP - 6.2m/s impact

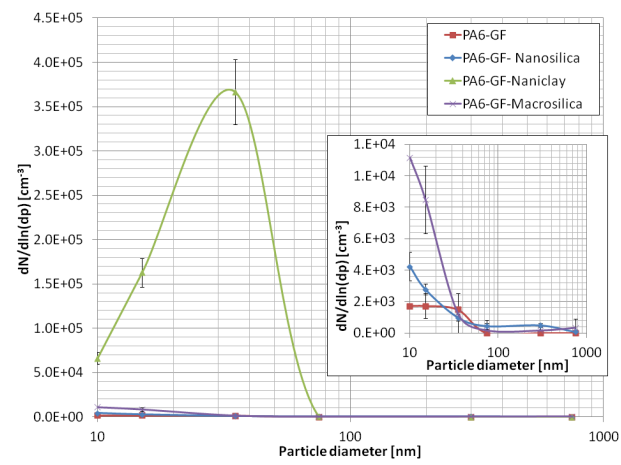


(c) PP - 7.7m/s impact

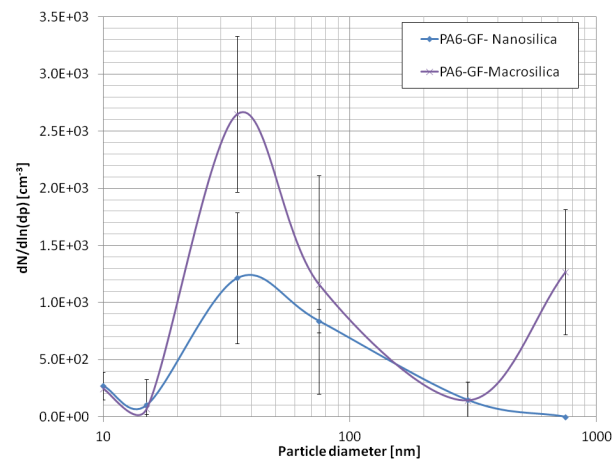
Figure 4.13: Normalised particle size distributions of PP based cones during 1, 2 and 3m impact events



(a) PA6 - 4.4m/s impact



(b) PA6 - 6.2m/s impact



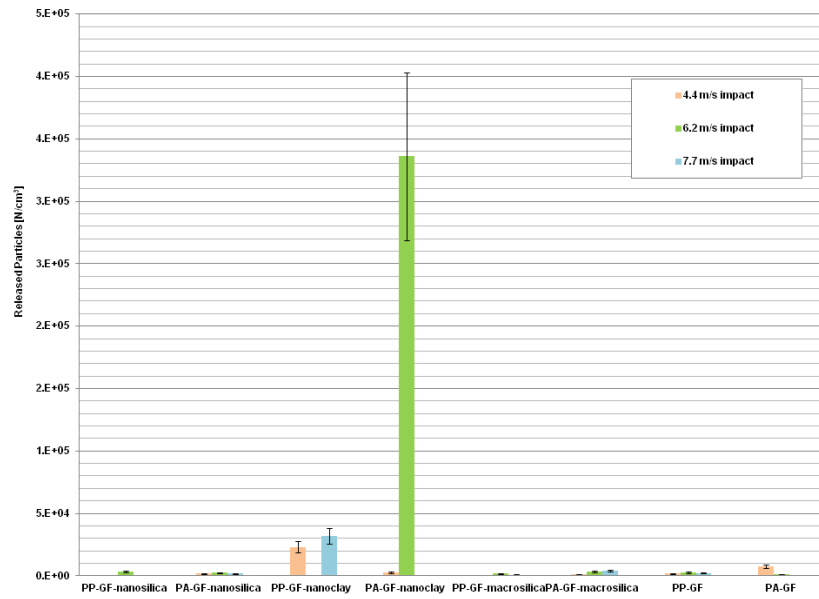
(c) PA6 - 7.7m/s impact

Figure 4.14: Normalised particle size distributions of PA6 based cones during 1, 2 and 3m impact events

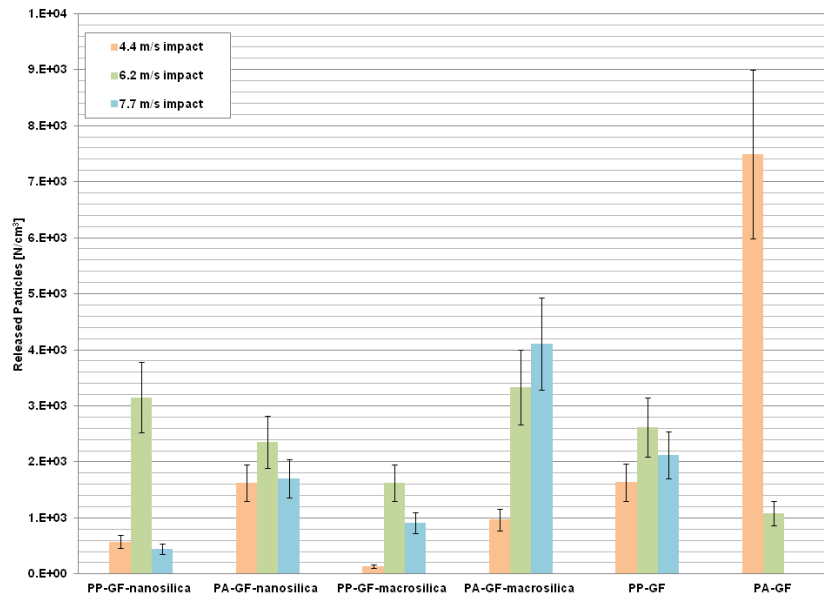
4.3.4.3 Particles emitted during impact

The number of particles emitted during crashing of the composite cones is represented in Figure 4.15. The error bars represent the standard deviation associated with the total emission rate of particles, in the size range of 11.1-521nm, resulting from the three replicate measurements. OMMT filled PP and PA6 composite generated the most particles throughout all impact tests. In general for the impact at 6.2 m/s the most particles were emitted, while impact at 4.4 and 7.7 m/s emitted similar amounts of particles, for all nanocomposites. The only exception was found for the PA6-GF-micro-SiO₂ composite where the number of particles emitted increased with increasing impact velocities. The cause of this behaviour can be explained by the fracture behaviour of the composite cones during impact test. While analysing the morphology of the fracture surfaces, different fracture mechanisms could be observed which could explain the particles emitted during impact.

Figure 4.16 shows the morphology of the fracture surfaces of PA6-GF composite and the PA6-GF-OMMT filled nanocomposite. A strong plastic deformation of the matrix could be seen for the PA6 composite, while the OMMT filled composite showed no plastic deformation and hence a very brittle failure behaviour. In addition a high number of fibre pull out and fibre/matrix debonding could be found. Brittle material behaviour results in fracture of material in many pieces and a low deformation. This mechanical characteristic is typical for polymer nanocomposites reinforced with silicate clays^[176;177]. For example large aggregates of clay observed in the material, serve as stress concentrators and lead to premature and brittle failure. Therefore, it can be assumed that the integration of the OMMT constrained the plastic deformation of the matrix. Further, this brittle behaviour led to an increase in particle emission.



(a) All composites



(b) Neat, nano and microsilica composites

Figure 4.15: Particles emitted during impact testing at different impact velocities and high

Additionally, it could be seen that the integration on nano-SiO₂ into the matrix did not influence the emission of particles drastically. Figure 4.17 shows the fracture of a fibre found on the fracture surface. It can be seen that some nano-sized particles can be found surrounding the fibre. It can be assumed that fibre fracture is the major source of nano-sized particle emission during impacting, as the emis-

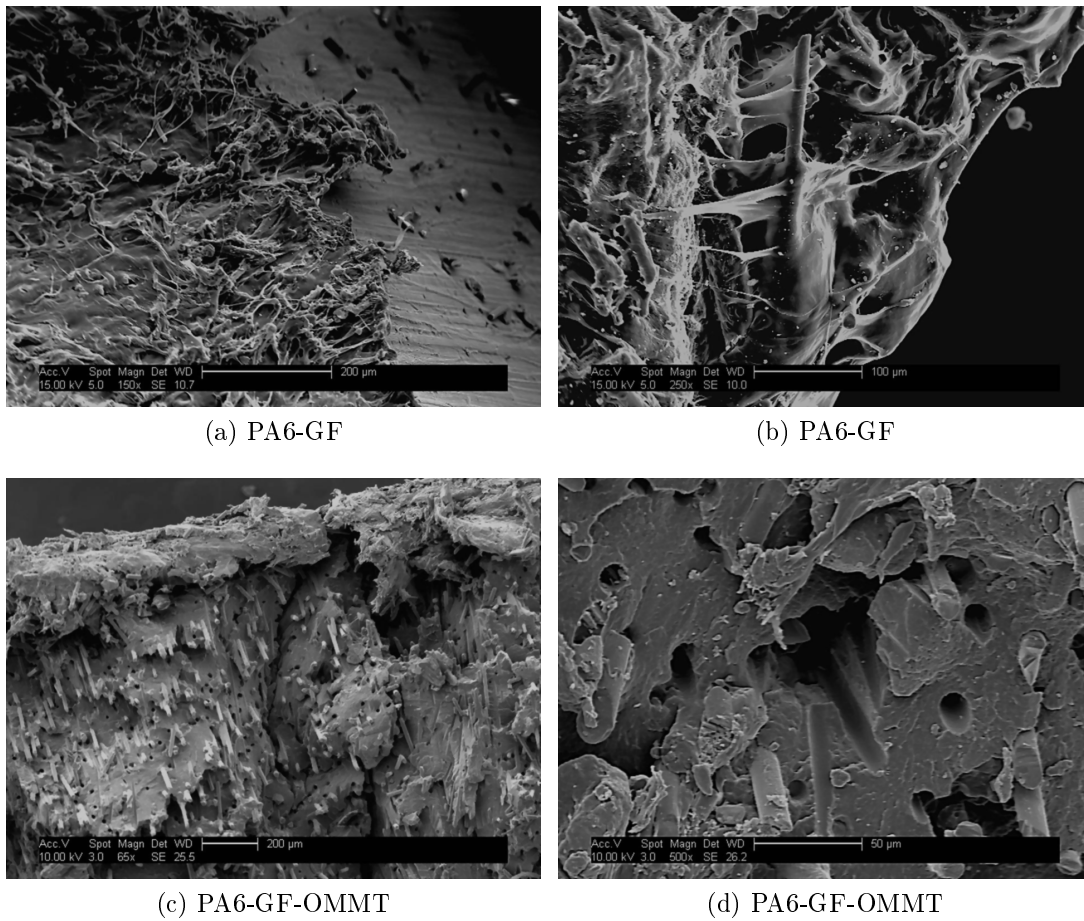


Figure 4.16: SEM micrographs of fracture surface of impacted crash cones

sion values for nano-SiO₂, micro-SiO₂ and neat PP-GF and PA6-GF composites were in the same range.

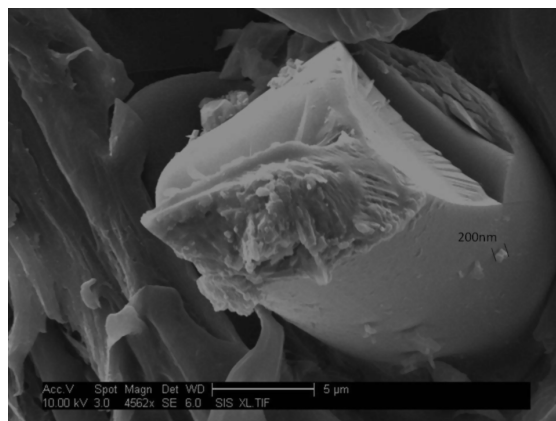


Figure 4.17: SEM micrographs of fractured fibre

4.4 Conclusion

Nano- and micro-reinforced crash cones have been manufactured throughout a two step extrusion process and final injection moulding of the nanogranulates. Quasi-static mechanical properties and crushing behaviour of the various polymer composites were studied. It was shown that addition of secondary filler into the glass-fibre reinforced polymer composites had significant influence on the mechanical behaviour of the material. It could be shown that by variation of the secondary fillers it is possible to change the micro-mechanism of a crash and therefore control the energy absorption characteristics of the composite. Especially for the PA6 composites the secondary reinforcement lead to an increase in mechanical properties such as strength, stiffness, and elongation to brake as well as energy absorption capabilities.

Particulate released from various silica based composites during impacting process were evaluated. Physical characterization of the number concentration and size distribution of nano-sized particles from 5.6 to 512nm was carried out, for the different composites. In general, nano-sized airborne particles were emitted from all investigated materials. However, composite filled with OMMT emitted higher amounts of particles than those filled with nano and microsilica. One reason for the increase of particle emission of the OMMT filled composites was the change of the failure behaviour of the matrix. OMMT induced a transition from ductile to brittle fracture. Brittle material behaviour results in fracture of material in many pieces and a localised deformation, and hence more particles were generated. However, obtained emission rates for both nano- and micro-SiO₂ filled composites did not vary significantly from the results obtained from traditionally reinforced glass fibres polymer composites.

Chapter 5

Influence of fracture at low velocity impacts on the nano-sized particle emission of sandwich structures with nanofilled foam cores

5.1 Introduction

High specific strength and stiffness, low weight, excellent thermal insulation, acoustic damping, and fire retardancy are just some of the excellent properties sandwich structures have to offer in structural applications. Hence, sandwich structures are commonly used in numerous economic sectors such as aerospace, marine, automobile, locomotive, windmills, building, consumer industries among others. Despite all these advantages, sandwich composites suffer sensitivity to impact loading damage and thus are limited in their function. Low energy impact can cause structural damage to the core material, whilst the face sheet remains undamaged. If the damage to the core material remains undetected, a potential risk for the application arises. This is imaginable for real life scenarios such as; tool dropping,

runway debris, bird strikes, hailstorms and ballistic loading. Therefore, it is crucial to improve the damage resistance characteristics of sandwich structures.

The damage initiation thresholds and damage size in sandwich structures primarily depend on the properties of the core materials and face sheets and the relationship between them. Honeycomb or foam have been classified as traditional core materials, to whom thin face sheets are bound for sandwich constructions. To decrease the damage, traditional core materials have been reinforced with nanofillers such as solid nanoparticles^[178;179], OMMTs^[1-4;168;180-182], and nanofibres^[179;183].

However, due to the ease of processing, enhanced thermal-mechanical properties, wide availability, and cost, OMMTs have been found to be the ideal filler for reinforcement of polyurethane (PU) foams. Hosur et al.^[3;4] and Njuguna et al.^[1;168;180;184;185] showed that by adding small amounts of OMMT to PU foams, major improvements in failure strength and energy absorption could be achieved. Further, it was reported^[3;4] that the integration of OMMT led to an increase of brittleness and hence an increase of dust generated during impact tests can be suspected. Building up on these previous studies^[1;168;180], the montmorillonite used in this study has been modified with a quaternary ammonium salt before integration in the PU matrix, as reported in the literature this could increase the degree of exfoliation in the structure^[186-188], and hence increase the mechanical properties. OMMT filled PU foams with a high degree of exfoliation were synthesised. This foams were used for core materials in sandwich structures and tested on energy absorption capacity during low-velocity impact and quasi static compression. Additionally, the thermal stability and degradation of the foams were analysed using thermogravimetric analysis. During impact of 5wt.% OMMT filled PU core material particles released were studied and the exposure of OMMT from foam cores evaluated.

5.2 Experiments

5.2.1 Synthesis of OMMT filled polyurethane foams

OMMT (Dellite®43B, Laviosa Chimica Mineraria S.p.A., Italy) was used as filler material. The preparation of the polyurethane foams with OMMT (0-10 wt.% loaded) consisted of three steps. In the first step, polyol (Rokopol RF551, PCC Rokita S.A., Poland) was stirred with the powdered OMMT. Rokopol RF551 was chosen as it is a general purpose sorbitol based polyether polyol recommended for the production of rigid polyurethane which features low viscosity, medium functionality and low reactivity and forms foams with excellent flow properties and good mechanical properties.

Then the catalyst (Polycat9, Air Products and Chemicals, Inc., UK), water and surfactant (SR-321, Union Carbide, Marietta, GA) were added in order to prepare the premix (component A). Polycat 9 catalyst was chosen as it is a low odour tertiary amine that provides a balanced promotion of the urethane and urea reactions in flexible and rigid foam applications.

In the next step, n-pentane as a physical blowing agent was added to component A. The diisocyanate compound was polyphenyl-polymethylene-polyisocyanate (polymeric MDI) with an average functionality of 2.6-2.7 acquired from Borsodchem Polska Sp. z o.o. under the trade name ONGRONAT® 2100. Which was added to component A and the mixture was stirred for 10 s with an overhead stirrer. Finally, the prepared mixtures were poured into a mould.

5.2.2 Fabrication of face sheet panels

Glass fibre reinforced polyamide 6 (MM-PA I 1F30, MACOMASS Verkaufs AG, Germany) and polypropylene (MM-PP-BI24, MACOMASS Verkaufs AG, Germany) were utilized as face sheet materials. From this granulates, plates of

160x160x4 mm³ were injection moulded and used as face sheets for sandwich fabrication. All injection moulding parameters are given in Appendix D.

5.2.3 Fabrication of sandwich structures

The face sheets were cleaned with ethanol prior application of the adhesive (DP8005 2 Part EPX Acrylic Adhesive, 3M). The adhesive was evenly distributed on the face sheet and pressed against the foam core, perpendicular to the foam growth direction. With help of clamps, the sandwich composites were kept under constant pressure for 12h during curing. The dimensions of the final sandwich structures were; height 38mm, width 60mm and depth 60mm and can be seen in Figure 5.1.



Figure 5.1: Manufactured foam composites

5.2.4 Foam characterisation

The synthesised PU/OMMT foam, intended as core materials were analysed by means of optical microscopy, X-ray Diffraction (XRD), fourier transform infra red spectroscopy (FTIR), scanning electron microscopy (SEM) with integrated energy-dispersive X-ray spectroscopy (EDX) and thermogravimetric analysis (TGA). SEM, XRD, EDX and TGA analysis correspond to the methods used in Section 3.2.3.

Optical microscopy analyses were performed using a PZO optical microscope equipped with vision track. To analyse the cell size and geometry, Aphelion software was used. FT-IR spectra of the prepared foams were recorded using a BIORAD FTS 165 spectrometer, operating in the spectral range of 4000-400 cm⁻¹. Nanofoams

were sliced by a rotary microtom (Leica, Microsystems Ltd.) and pressed against a spectral potassium bromide grade.

5.2.5 Quasi-static compression

Quasi-static compression tests of the sandwich structures, were carried out using an Instron 5500R electro-mechanical machine, in the same experimental configuration as reported in Section 4.2.3.1.

5.2.6 Low energy impact testing

Low energy impact tests were conducted using an instrumented falling weight impact device (drop tower). The device was equipped with data acquisition system to acquire force versus time data. Using this machine, impact energy and velocity can be varied by changing the mass and height of the dropping weight. The velocity of the falling drop mass was measured just before it stroke the specimen. The drop tower was also fitted with pneumatic rebound break, which prevents multiple impacts on the specimen. Two impactors were utilised, a flat (70 mm diameter) for surface load impact and a hemispherical (15 mm diameter) for localised point load impact. The energy level was kept at 15 J for all impacts. Figure 5.2 shows the location of the specimen in the crash chamber. Crash test occurred against foam growth direction. The samples were placed and adjust according to the striker in the crash chamber.

By impacting the nanofilled foams, fragments were obtained and sampled in the crash chamber. The chamber was filled with 250ml of double deionized water, to suspend the particles in solution. The solution was the removed by mean of a sterile syringe through the designed opening and stored in a glass vial. The solution was first filtered with general purpose filtrate paper (Whatman Standard Grades, 11 μm) and then ultrafiltrated (Vivacell 250 ultrafiltration system, Sartorius Sted-

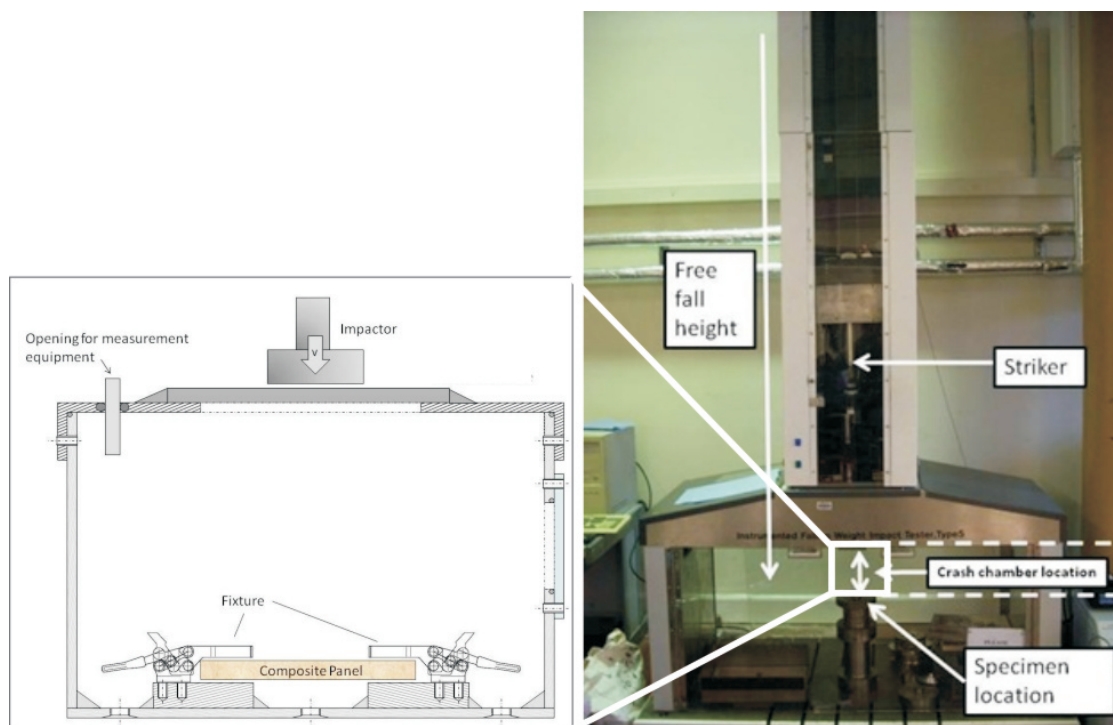


Figure 5.2: Schematic diagram of designed crash chamber for particle collection (left) and drop tower configuration (right)

imBiotech GmbH, Germany) for size fractionation. Filters with a molecular weight cutoff of 5000 were used under 3.5 bar pressure. Additionally, airborne size distributions were measured in the chamber with the help of a SMPS+C, according to Section 4.2.4.

5.2.7 Characterisation of emitted dust particles

The microstructure of the emitted dust particles were investigated by emission scanning electron microscope (SEM) and transmission electron microscope (TEM), according to Section 3.2.3. Particle size distribution was measured by dynamic light scattering (Zetasizer nano zs, Malvern Instruments Ltd.), according to Section 3.2.5.

5.3 Results and Discussion

5.3.1 Morphology

The cell structure of the synthesised foams are represented in Figure 5.3 and 5.4. Due to the anisotropic structural properties of the materials, which was a result from the forced growth of the foam, the materials were characterised in parallel and perpendicular directions. Mean area and number of foam cells were determined, and can be found in Table 5.1. Further, an apparent density of 40.7, 38.7, 40, 39.6 and 39.2 kg/m³ was measured for the 0, 2.5, 5, 7.5, and 10 wt.% filled foams.

An increase of anisotropy index in parallel direction to the foam growths, could be found for the PU/OMMT foam. It has to be noted that for the given amount of OMMT content the amount of modifier were already incorporated in the given value. The highest anisotropy index could be detected for the foams with 5 and 10 wt. % of OMMT loading. The incorporation of OMMT resulted in smaller number of cells with higher dimensions and higher anisotropy index for the parallel cross-sections. In the case of perpendicular direction, an increase of number of cells with smaller dimensions was observed. The choice of foaming method affected the foam cell structure, particularly the mould shape and dimensions. The amount and distribution of nucleation agents were also crucial factors for obtaining foam cells with a controlled structure and uniform distribution^[189;190]. The effect of OMMT dispersion on the cells' structure has been studied in the literature^[191–193]. It was shown that the exfoliated polyurethane/OMMT foams achieved a much higher nucleation rate than the intercalated nanocomposites, hence a more uniform cell distribution. Once the OMMT was better dispersed (at the same nominal particle concentration), the effective particle concentration was higher and thus a more heterogeneous nucleation sites was available. Further, the effect of OMMT on the cell size was studied^[194]. It was reported that the cell size was reduced with the presence of OMMT. The reduction of cells was caused by the increase of

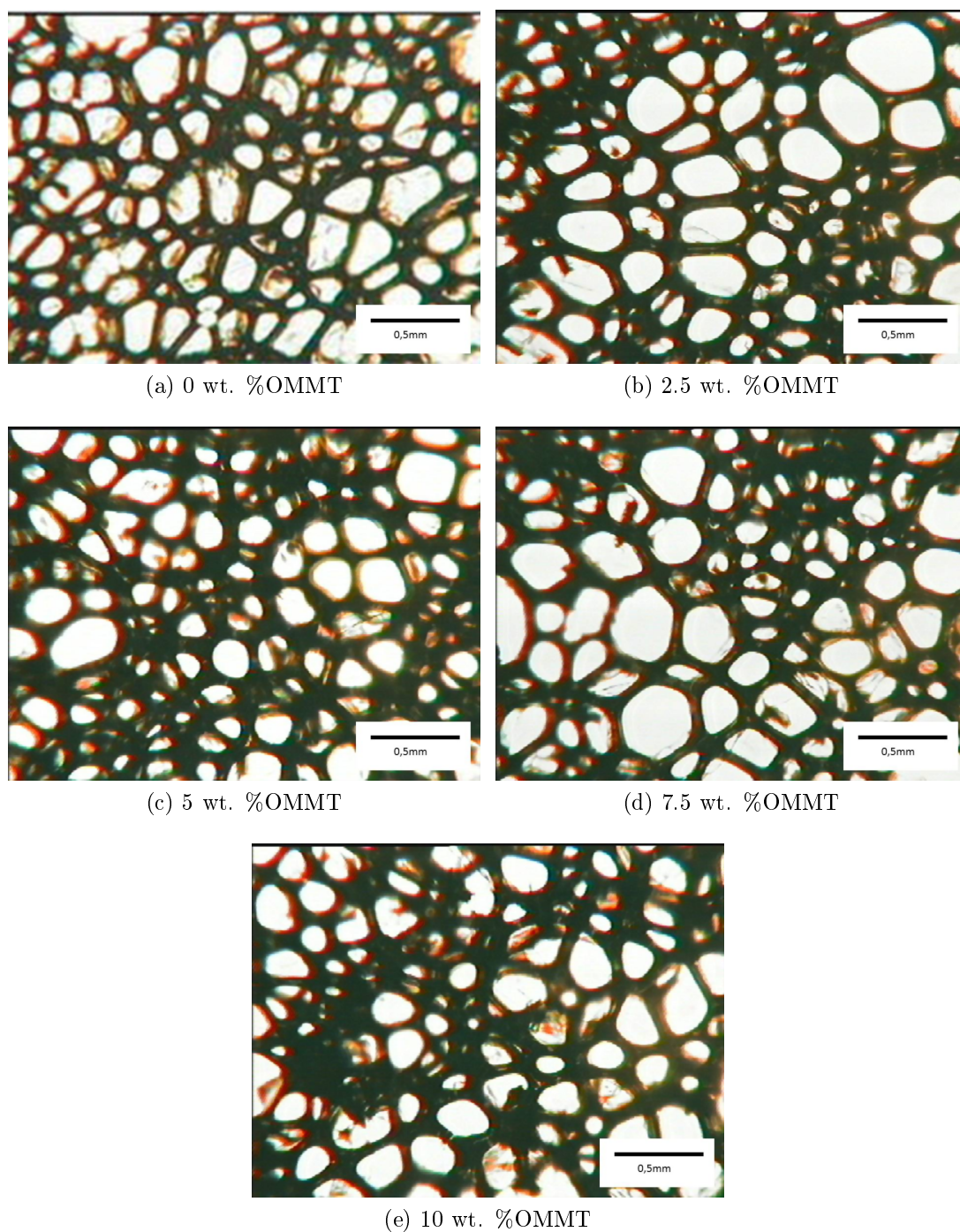


Figure 5.3: Cell structure of modified PU/OMMT foamed materials parallel to the direction of foam's growth

bubbles that start to concurrently nucleate which caused less amount of gas to be available for cell growth. The surface chemistry of the OMMT had an effect on the nucleation efficiency in the polymer clay foaming agent system. The interactions

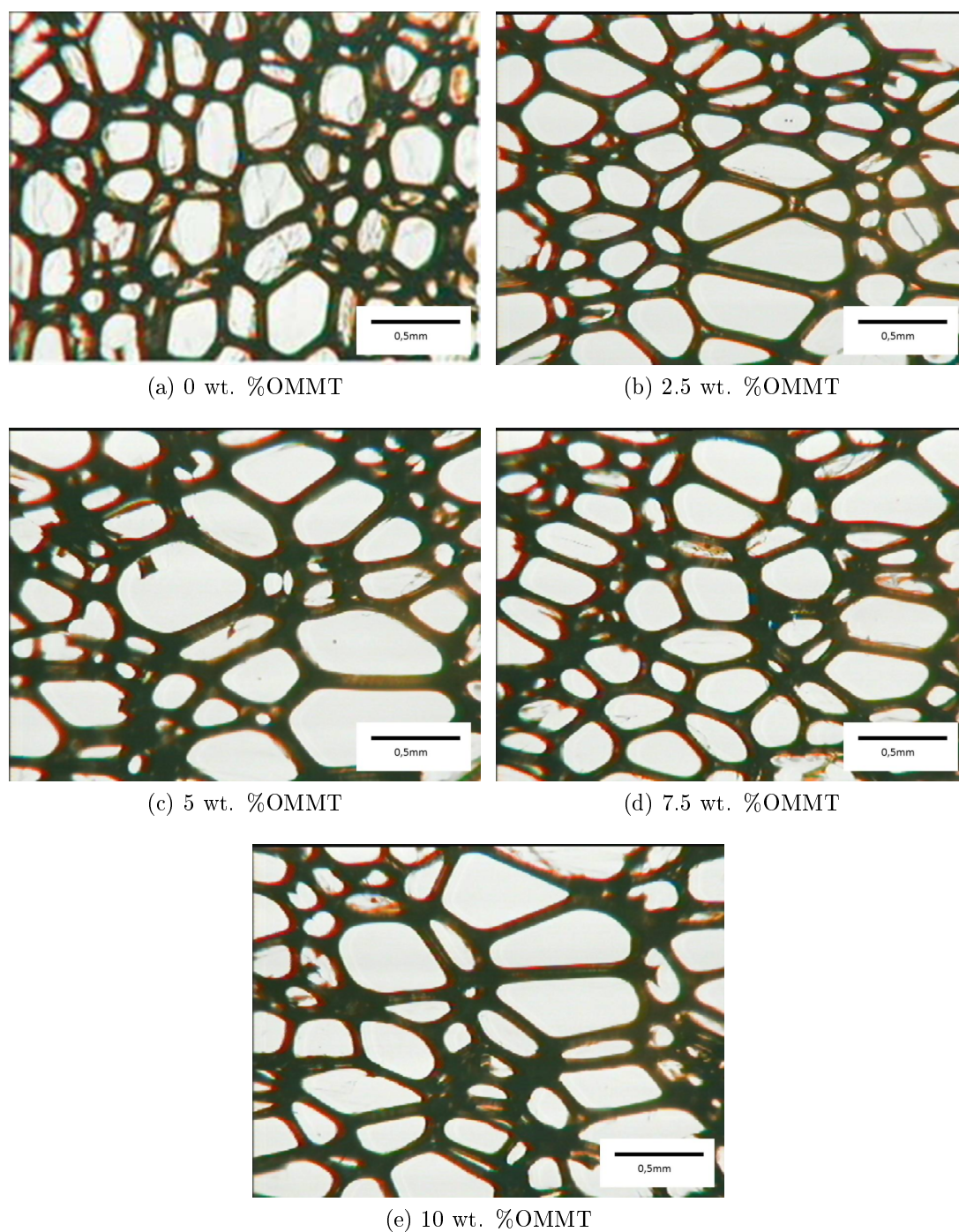


Figure 5.4: Cell structure of modified PU/OMMT foamed materials perpendicular to the direction of foam's growth

of CO₂ with the interfacial region between OMMT and polymer, had a dramatic impact on the resulting foam morphology^[192].

Additionally, the foam morphology and the chemical composition of the foams

Table 5.1: Structural properties of the PU/OMMT foamed nanofoams

	OMMT content [wt. %]	Average num- ber of cells	Average sur- face of cells [mm ²]*10 ⁻³	Anisotropy coefficient
Parallel to direction of foam growth	2.5	84	9.4	1.45
	5	66	12	1.5
	7.5	78	10	1.41
	10	66	13	1.53
Perpendicular to direction of foam growth	2.5	89	8.3	1.21
	5	102	7.1	1.08
	7.5	98	7.6	1.07
	10	94	8.1	1.08

were investigated by SEM and EDX. Figure 5.5 shows the surface of the neat PU foam and PU foam loaded with 10wt.% OMMT and the corresponding EDX spectra. As the investigated specimen were gold sputtered, the peaks for gold can be neglected in the spectra. From the EDX spectrum the presence of OMMT could be proven, as 70.95 wt.% carbon, 21.88 wt.% oxygen, 0.47 wt.% sodium, 0.36 wt.% magnisium, 1.26 wt.% aluminium, 4.56 wt.% silicon and 0.53 wt.% calcium could be identified. While the chemical analysis for the neat foams indicated only the presence of carbon and oxygen.

5.3.2 FTIR and WAXS analysis of PU modified with OMMT

The FTIR analysis of PU-based materials showed the formation of bands characteristic for polyurethane, and can be seen in Figure 5.6. The following bands were identified from FTIR measurements; absorption bands at 3345 cm⁻¹, due to the N-H stretching, and bands around 2946, 2911 and 2871 cm⁻¹ due to the C-H stretching in -CH₂- groups. The bands at 1717 and at 1507 cm⁻¹ were connected with the stretching vibrations of C=O in urethane and allophanate groups (I amide band) and to the deformation vibrations of N-H bond (II amide band),

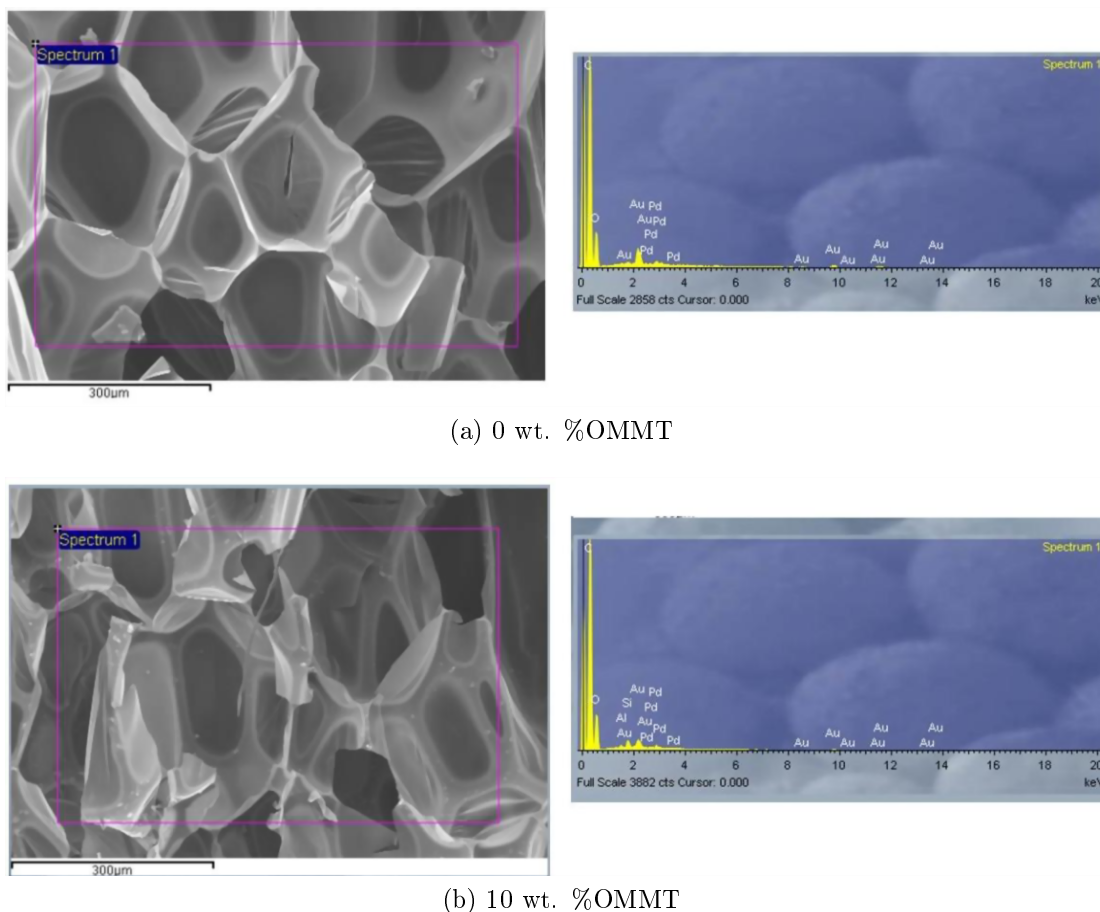
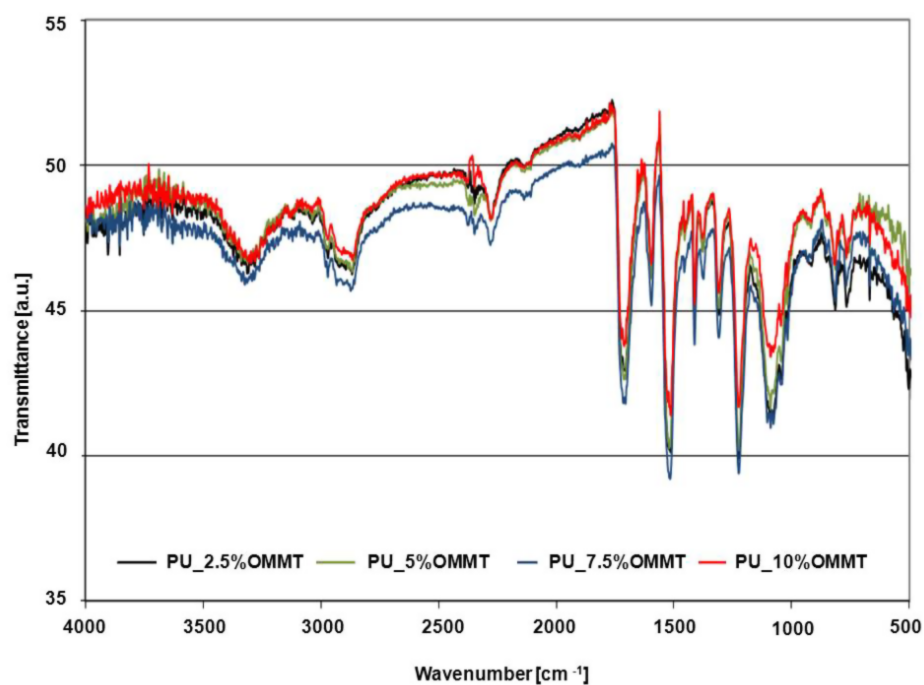


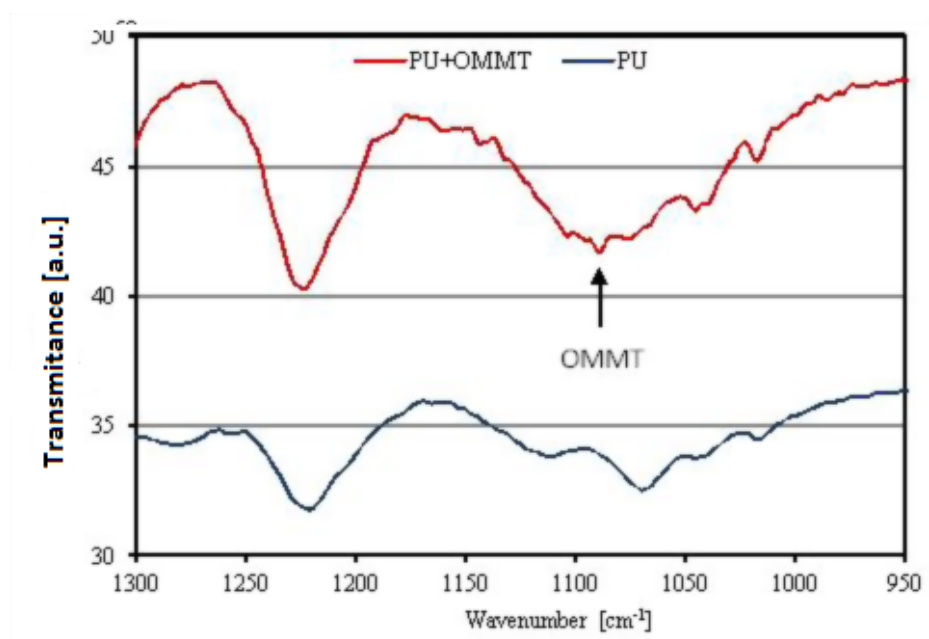
Figure 5.5: SEM micrographs of modified PU/OMMT foamed core materials, for foams neat foams and foams with 10wt.% OMMT and EDX spectra of these foams

respectively. C-H stretching vibrations were reflected in the absorption band maximum at 1596 cm^{-1} . Another possible origin of that band are the deformation vibration of N-H in urethane group. The bands at 1412 cm^{-1} were known to origin from the carbonyl of urethane group forming a hydrogen bonding, allophanate and biureth bond. Bands at 1285 , 1223 and 1071 cm^{-1} were due to the polyethers used. The FTIR analysis confirmed the formation of polyurethane in the presence of OMMT. The band characteristic for OMMT was observed in a range of 1000 - 1100 cm^{-1} . A broadening of the absorption band which correspond to the ether bound was observed, as shown in Figure 5.6b.

The nanoinduced foams were submitted to WAXD analysis in order to assess the structure of the polymeric composite and the regular arrangement of the

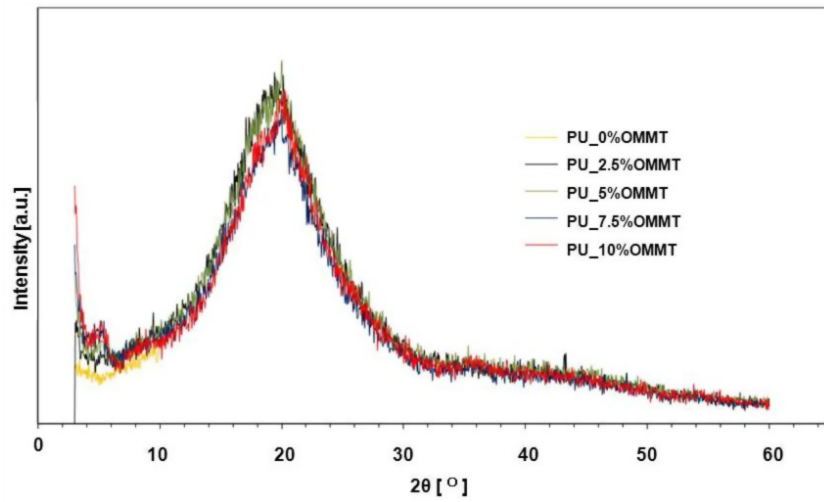


(a) Full spectrum

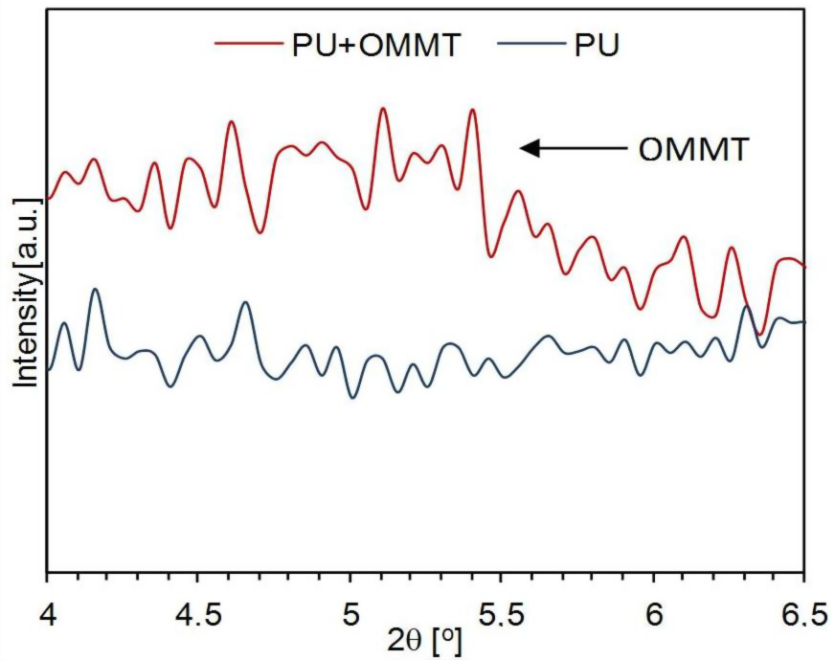
(b) Spectrum between 950-1300 cm^{-1} **Figure 5.6:** FTIR spectrum of PU/OMMT nanocomposites

OMMT. The diffraction pattern of the neat PU sample did not reveal any crystalline phases in the material. Figure 5.7a displays the diffractogram of PU/OMMT nanocomposite with a diffraction angle 2θ between 3 and 60°. The structure of

the PU and PU/OMMT foam specimen was completely amorphous. Since the raw materials were multifunctional a cross-linked polymer was formed without the ability to form a crystalline structure. The lamellar arrangement of OMMT was maintained in the nanocomposite as evidenced by the diffraction peak at $2\theta = 5.5^\circ$, which was assigned to the (001) lattice spacing of the OMMT and can be seen in Figure 5.7b.



(a) 2θ between 3 and 60°



(b) 2θ between 4 and 6.5°

Figure 5.7: WAXD diffractogram of PU/OMMT

5.3.3 Thermal stability

The results of the thermogravimetric analysis of the modified PU foams can be found in Figure 5.8. The degradation of the PU/OMMT foams ran in one distinct stage with a maximum of mass loss around 345°C. The degradation process was only slightly influenced by the presence of OMMT by shifting the degradation slightly towards higher temperatures. The shift of degradation towards higher temperatures was caused by the suppression of the molecular mobility of polymer chains by the OMMT layers (Figure 5.8b). As no thermal stabilisers were used, the following effects may have influenced the nature and extent of the thermal decomposition; (i) specific intermolecular interactions via hydrogen bonding, (ii) crystallinity, and (iii) the presence of chemical cross-linking. For instance, Wang et al.^[195] postulated that the degree of phase separation and specific interactions play a major role in the decomposition of polyurethanes. The extent of inter-urethane hydrogen bonding, arising from incomplete phase separation between the soft and hard segments, was found to influence the thermal stability of PU's under investigation. In a different work, Ferguson et al.^[196], have shown evidence for the mutual stabilisation effect of soft- and hard-phase based on a protection function of soft segments through different functional groups and hydrogen bonding. Integrated absorbance data showed that the hydrogen-bonding behaviour in polyurethanes was insensitive to crystalline transitions within the hard segment microdomains, but that it reflected the morphological transitions in a block copolymer that were associated with intersegmental mixing^[197].

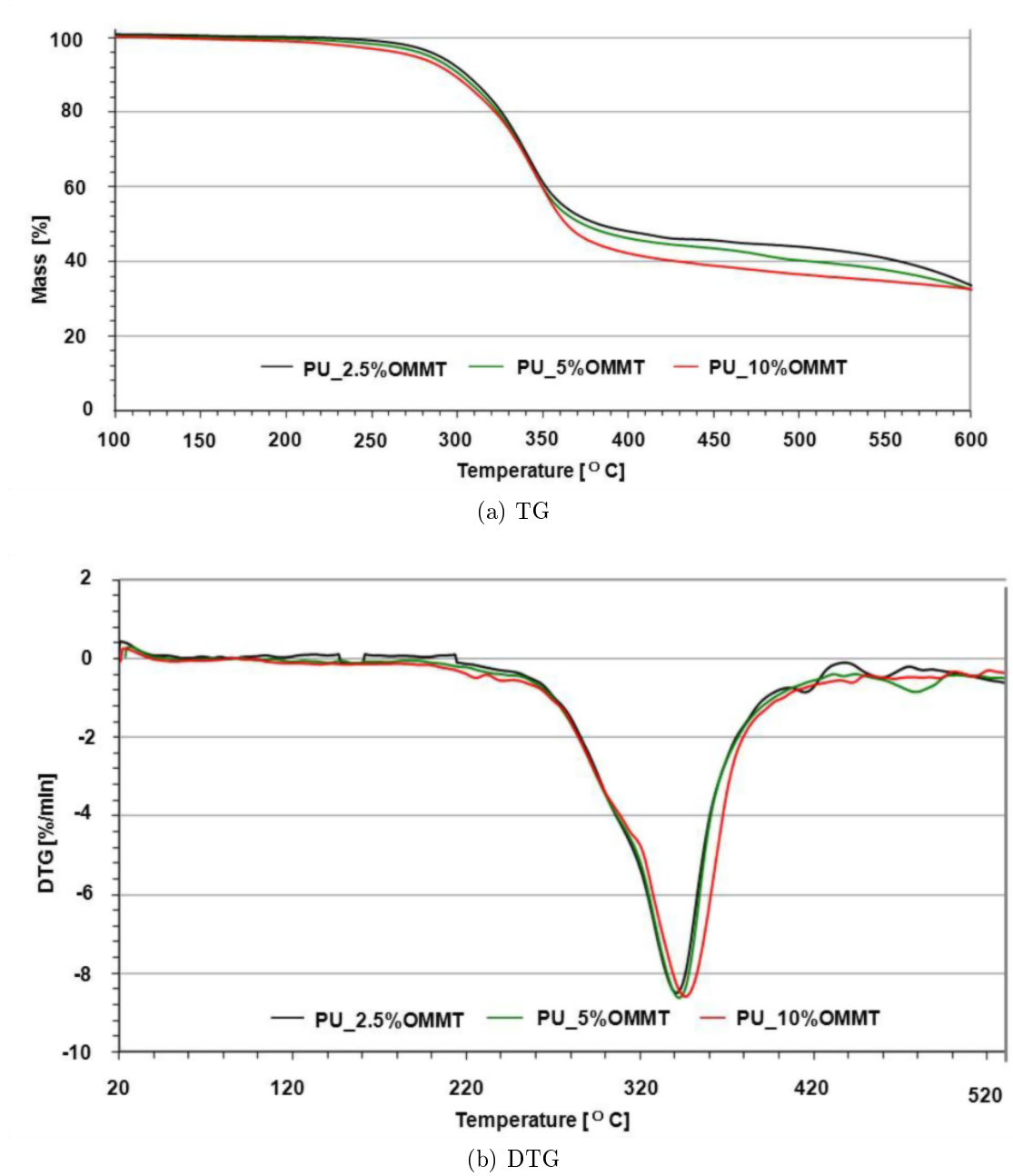


Figure 5.8: TG and DTG curves of PU/OMMT composites

5.3.4 Quasi-static compression behaviour

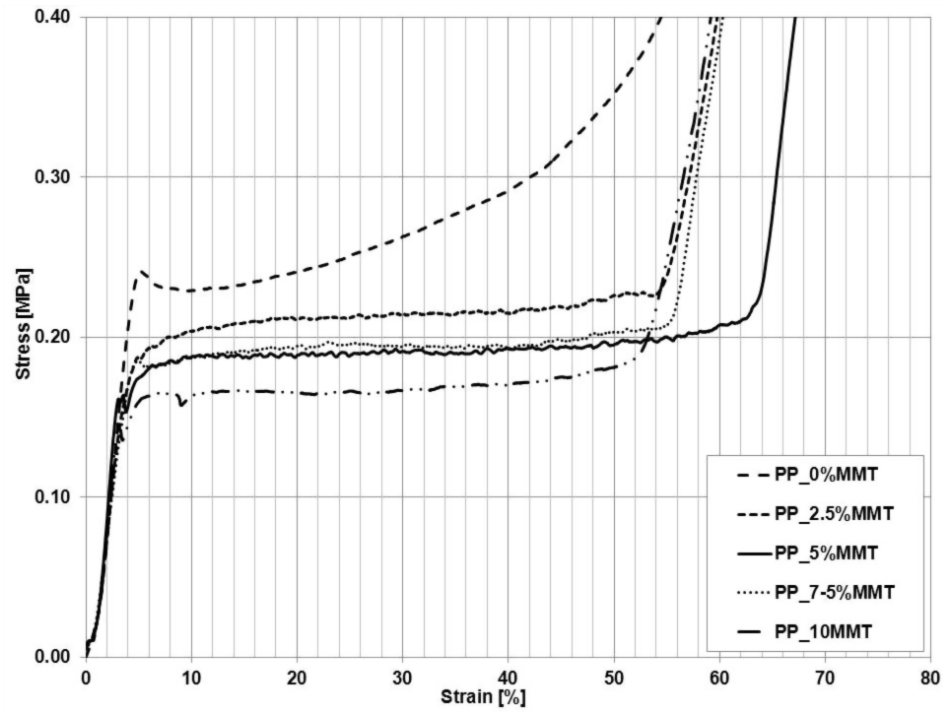
Compressive properties of the tested sandwich panels have been calculated according to BS ISO 844:2004 and are presented in Table 5.2. Compressive strength, with corresponding relative deformation were calculated and compressive stresses at 10% relative deformation were calculated as the material yielded before com-

pletion of the test but still resisted increasing force. The stress-strain relationship for the sandwich panels can be found in Figure 5.9. For all manufactured sandwiches a decrease in compressive properties was measured. Compressive strength and stress (at 10% relative deformation) decreased with increasing filler loading. A variation in compressive stress, for the different face sheets could be identified for lower deformations. However, once 10% relative deformation was reached the sandwiches with different face sheets resulted in the same compressive stresses. Nevertheless, an increase in compressive modulus could be achieved for the PA6 face sheet sandwiches.

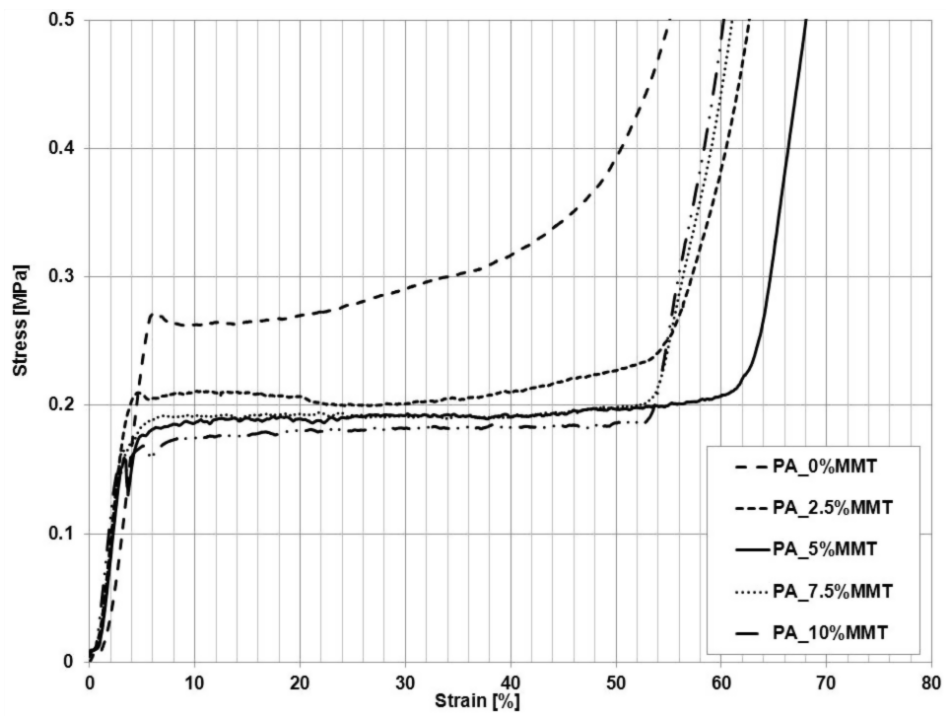
Table 5.2: Quasi-static properties comparison

Material	Compressive strength	Relative deformation	Compressive stress (at 10% ϵ_m)	Compressive modulus
	[MPa]	ϵ_m [%]	[MPa]	[MPa]
PP_PU/0%OMMT	0.236	4.76	0.229	4.55
PP_PU/2.5%OMMT	0.186	4.75	0.202	3.92
PP_PU/5%OMMT	0.160	3.02	0.187	5.30
PP_PU/7.5%OMMT	0.183	4.56	0.185	4.01
PP_PU/10%OMMT	0.139	4.56	0.162	3.05
PA6_PU/0%OMMT	0.270	6.53	0.263	4.137
PA6_PU/2.5%OMMT	0.206	4.14	0.209	4.98
PA6_PU/5%OMMT	0.157	3.82	0.184	4.10
PA6_PU/7.5%OMMT	0.163	2.99	0.189	5.45
PA6_PU/10%OMMT	0.149	2.63	0.172	5.67

Figure 5.10 shows the dependency of energy absorption during compression in relation to the filler loadings. Energy absorption increases with higher filler loadings respectively. An increase of up to 40% could be measured for both PP and PA6 facesheets, for the 10 wt.% OMMT loaded foam. The decrease of compressive strength, stress and energy absorption properties of the 5 wt.% OMMT loaded sandwiches can be explained by the high number of cells which result in



(a) PP-PU/OMMT sandwiches



(b) PA6-PU/OMMT sandwiches

Figure 5.9: Stress-strain relationship for manufactured sandwiches panels during quasi-static compression test

the smallest average cell surface area. According to Cao et al.^[198], the overall compressive performance of PU nanocomposite foams depends on the competition between the positive effects of clay on polymer reinforcement and foam morphology, and the negative effects on H-bond formation and network structure. The strength and the modulus of PU foams was dependent on the H-bond formation among urethane groups. PU molecules were grafted onto the clay surface through the reaction between -NCO- groups on the clay, so that the clay could interfere with the H-bond formation in the PU. Which resulted in a negative effect on the compressive properties of the PU nanocomposite foams. Similar results were reported by Harikrishnan et al.^[182] where no significant increase in the compressive strength was found with the addition of clay. The authors^[182] stated that with higher clay loading, compressive strength showed a decreasing trend which was caused by the weakening of foam structure due to formation of large voids. Kim et al.^[7] explained the decrease of compression strength in OMMT reinforced PU foams with the decrease of foam density with increasing clay content.

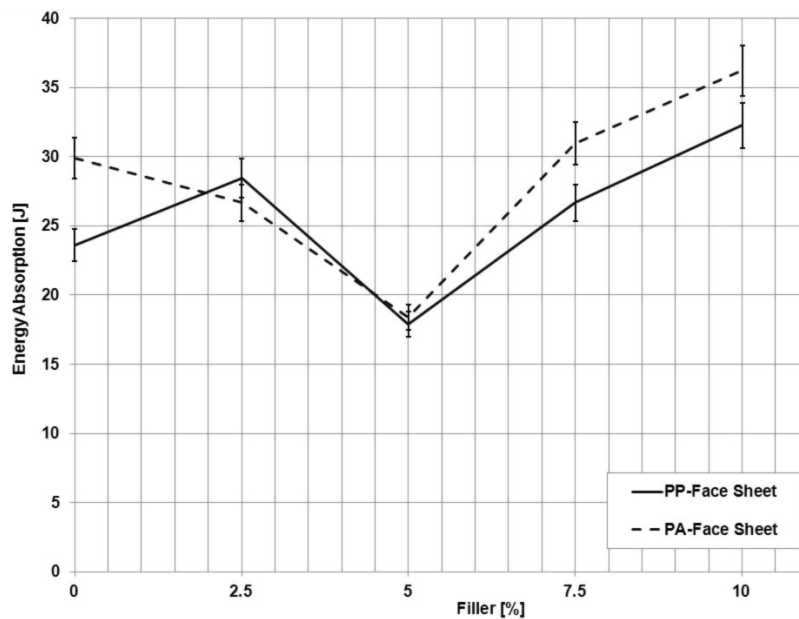


Figure 5.10: Energy absorption vs. composite loading for manufactured sandwich structures

5.3.5 Low energy impact behaviour

Manufactured sandwich panels were subjected to low energy impact test. Samples of each set were tested at a energy level of 15J with a hemispherical and a flat striker. Data was collected for each impact, which included time, load, energy, velocity and deflection, and is represented in Table 5.3. While the usage of different face sheets has showed little difference for the quasi static compression tests, once the sandwiches were subjected to low energy impact tests the PA6 face sheet shown superiority over the PP face sheet. Further, the result indicates that the integration of OMMT did not increase the peak force absorbed by the material, however an increase in deflection could be measured. The deflection at peak load and the maximum deflection were qualitative indication of the stiffness of the material. The deflection at peak load varied between $\pm 1mm$ for the sandwiches subjected to point impact, and increased by approx. 2.5-3 times for the surface impacted sandwiches, compared to the neat PU foams. The increase of absorbed energy could be calculated, respectively. Energy was absorbed in an initial stage by elastic deformation of the material, however once the maximum elastic deformation was reached the structure dissipated the excess energy in form of plastic deformation or through various damage mechanisms.

Table 5.3: Impact performance properties of manufactured sandwich structures

Material and impact type	Peak load [N]	Deflection at peak load [mm]	Absorbed energy [J]	Max. deflection [mm]	Impact velocity [m/s]
PP_0%OMMT_Point	1075.27	6.71	3.73	8.9	3.47
PP_2.5%OMMT_Point	917.21	8.72	5.76	12.90	3.57
PP_5%OMMT_Point	779.66	8.89	6.25	14.74	3.57
PP_7.5%OMMT_Point	848.16	6.96	6.69	12.94	3.57
PP_10%OMMT_Point	733.77	7.51	6.36	15.30	3.57
PA6_0%OMMT_Point	1407.1	6.69	5.2	9.46	3.47
PA6_2.5%OMMT_Point	963.07	5.96	6.54	12.15	3.57
PA6_5%OMMT_Point	825.49	6.60	6.43	13.89	3.57
PA6_7.5%OMMT_Point	836.95	6.15	6.61	12.99	3.57
PA6_10%OMMT_Point	928.67	5.49	6.97	14.09	3.57
PP_0%OMMT_Surface	1586.69	6.73	5.04	9.48	3.11
PP_7.5%OMMT_Surface	755.24	18.10	6.38	18.10	2.64
PP_10%OMMT_Surface	869.67	17.54	5.82	17.54	2.64
PA6_0%OMMT_Surface	1495.15	5.91	5.55	9.37	3.11
PA6_2.5%OMMT_Surface	675.13	16.13	6.79	16.57	2.64
PA6_5%OMMT_Surface	766.68	16.76	6.50	16.76	2.64
PA6_7.5%OMMT_Surface	789.56	17.28	6.59	17.29	2.64
PA6_10%OMMT_Surface	892.55	16.36	6.16	16.36	2.64

The introduced damage to the sandwich structures due to the different energy absorption mechanism of the nanoreinforced foams can be seen in Figure 5.11. The loads induced during the impact are directly correlated with the fracture mode and propagation of the cracks. Neat foams showed no signs of plastic deformation while the OMMT filled foams clearly showed signs of fracture damage. With increased percentage of filler loading, the degree of fracture increased as well. Brittle fracture with progressive crashing and medium fragmentation was observed. The characteristics for this fracture mode were, that axial cracks, initiated at the early stage of the impact event and stopped quickly after the formation. Therefore, the size of the generated debris was significantly smaller than the debris size observed for elastic deformation of the neat PU foams. Therefore, this led to the conclusion that the utilisation of OMMT leads to changes in the energy absorption mechanism of the PU studied. Further, with increasing clay content the core material got more brittle. With increasing OMMT loadings there were increasing cracks and plastic deformation on the surface of the foam cores along the length of the structures.

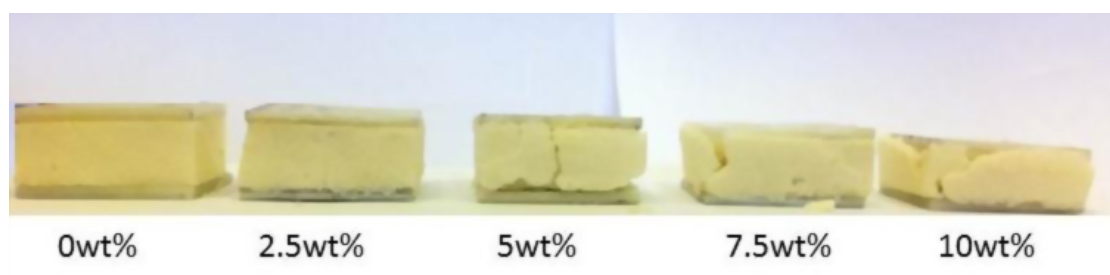
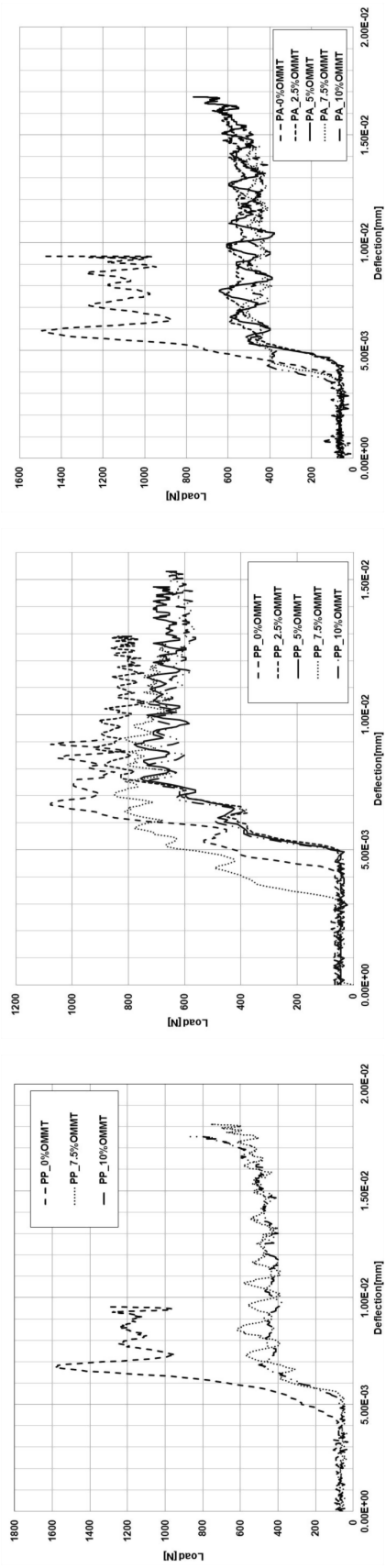


Figure 5.11: Energy absorption of neat PP facesheet/PU-OMMT cores with increasing filler loading for 15J point impact

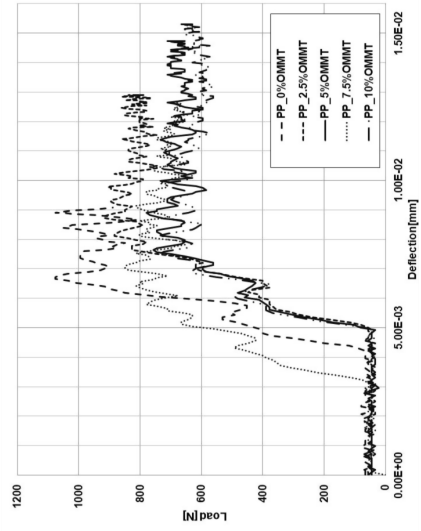
PA6 face sheets absorbed relatively more impact energy, compared to the PP sandwich structures. The improvement in energy absorption utilising nanofoams, was between 66-92% for PP face sheet sandwiches and 23-34% for the PA6 face sheet sandwiches under point load. Load-deflection graphs are shown in Figure

5.12. It should be noted that all the specimens reported in Figure 5.12e (a-d) did not show any perforation during the impact and hence the force returned to zero for each test carried out as shown on in Figure 5.12e. However, to ease the reading of the graphs it was decided to plot only the load subjected to the specimen. The percentage of filler loading did not have significant influences on the specific energy absorption capacities.

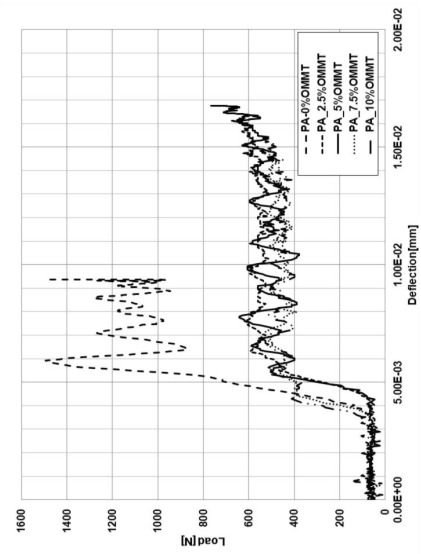
The results obtained in this study conflicted with results obtained by Hosur et al.^[3;4] and Njuguna et al.^[1;168;180] who reported an increase of peak load for OMMT filled foams. Nevertheless, it should be noted that the morphology of the PU/OMMT nano foams utilised in^[1;168;180], were very different from the one used in the present study. The utilised foams had twice the number of cells in perpendicular and parallel direction, which resulted that the average cell surface area was half the area detected in the present study.



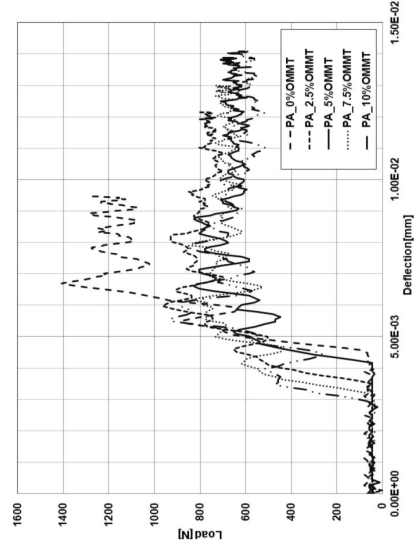
(a) PP Surface Impact



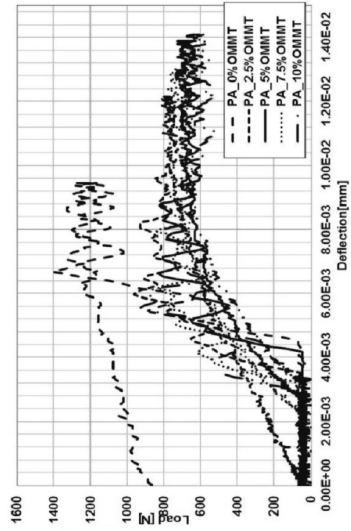
(b) PP Point Impact



(c) PA6 Surface Impact



(d) PP Point Impact



(e) PA6 Surface Impact

Figure 5.12: Load-deflection graphs for point load and surface impact of manufactured sandwich structures

5.3.6 Dust emitted from PU/OMMT foam cores

5.3.6.1 Airborne particles

PU/OMMT (5wt.%) foam cores were impacted directly (surface impact) with 15J energy and dust emitted from the material was measured, sampled and analysed. Airborne particle concentration was measured pre-, during and post impacting of the specimen. The corresponding particle size distribution in each stage is represented in Figure 5.13. It can be seen that the particle size distribution of pre-impact and laboratory air are very similar. However, after impact the number of particles in the size range of 20-50nm had doubled. The average particle concentration before impact was approx. 5000 cm^{-3} , and increased rapidly after impact to the doubled value. Once the maximum concentration was reached the particle concentration declined and after approx. 35 min reached the initial value of 5000 cm^{-3} .

5.3.6.2 Deposited particles

Figure 5.14 shows the SEM micrographs of un-filtrated solution obtained by diluting the PU/OMMT fractures in deionized water. An overview of the substrate surface is given in Figure 5.14a. Characteristic for the surface area were particles, which were enclosed by OMMT as shown in Figure 5.14b. The utilised OMMT had a highly hydrophilic nature, hence was found to be dissolved OMMT. The OMMT which was set free during impact dissolved in water and agglomerated due to favourite bonding to other OMMT particles. Figure 5.14c shows a particle surrounded by an atoll of OMMT. This configuration was caused by the drying process of the sample solution on the SEM substrate. During drying larger particles deposited on the surface due to sedimentation which reduced the surface tension of the substrate and promoted agglomeration of smaller particles.

Figure 5.15 shows the micrograph made from the solution after the first fil-

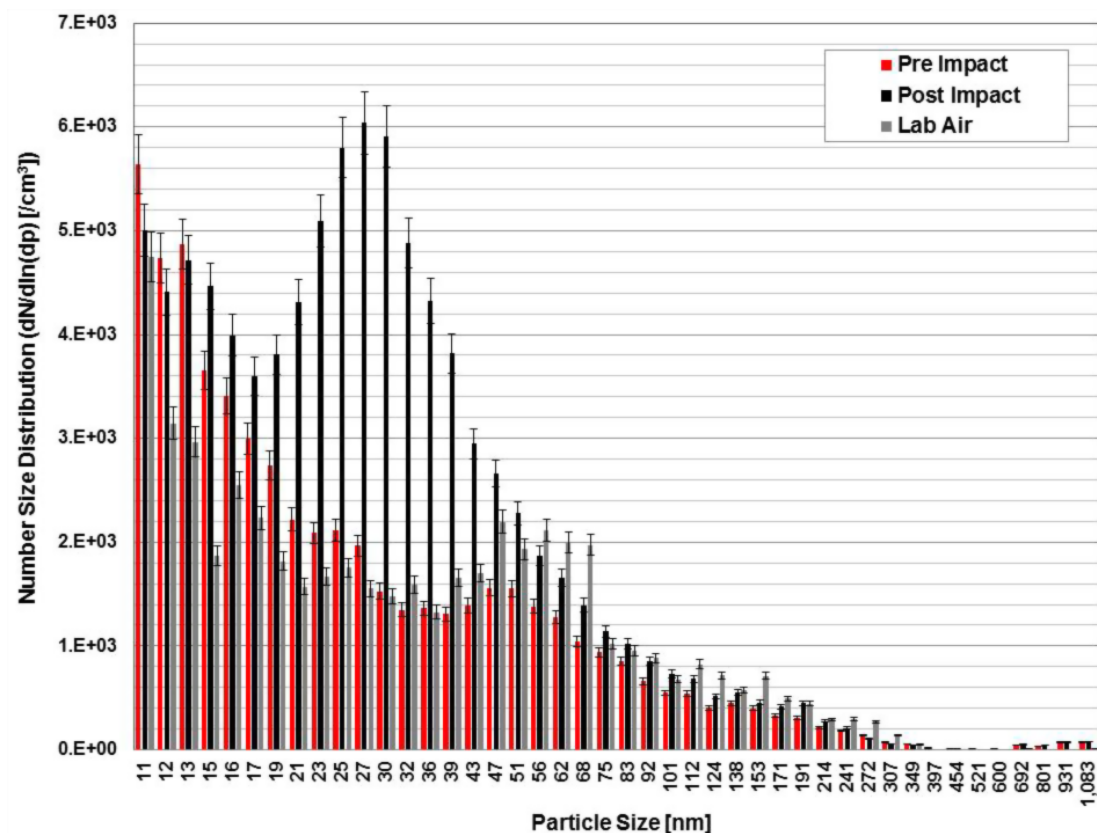


Figure 5.13: Normalized particle size distributions of generated particles during impact of sandwich structures

tration step ($< 11\mu\text{m}$). Similar to the micrographs obtained from the unfiltered solution, particles were enclosed by dissolved OMMT matter, however from a visual investigation the concentration of dissolved OMMT matter increased after the filtration step. Further, smaller particles could be detected as shown in Figure 5.15b, which consisted of the same material as the bulk PU/OMMT nanocomposites before impact.

The SEM micrographs obtained from the solution after the second filtration step ($< 1\mu\text{m}$) are shown in Figure 5.16. Figure 5.16a shows that the concentration of dissolved OMMT matter increased, compared to the unfiltered solution and the solution after the first filtration step. However, it could not be excluded that smaller particles were embedded in the OMMT matter. Hence, transmission electron microscope was used to investigate this option. For TEM investigation

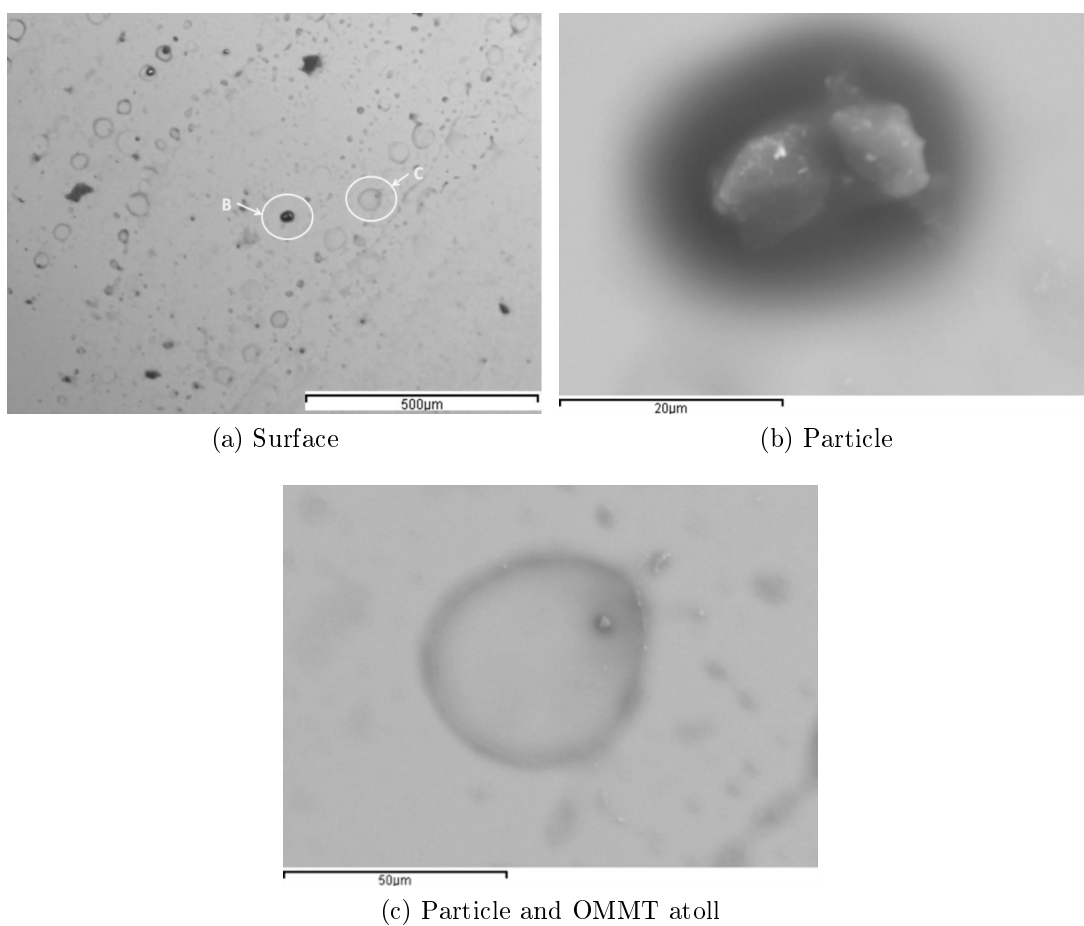


Figure 5.14: SEM images of un-filtrated solution of collected particles from the impact event

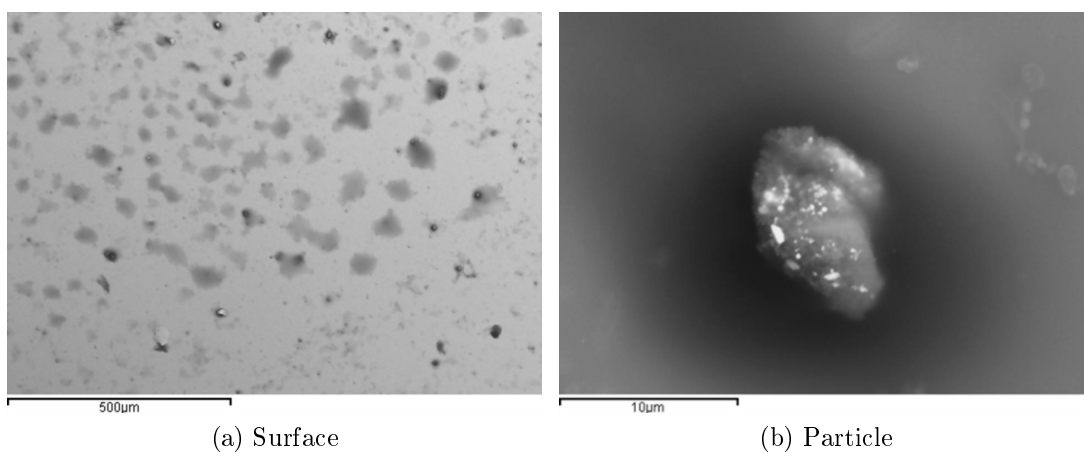


Figure 5.15: SEM images of filtrated solution $< 11 \mu\text{m}$ of collected particles from the impact event

the solution was sonicating for 2 hours. A drop of this suspension was then placed on a carbon-coated copper TEM grid and left to dry in air.

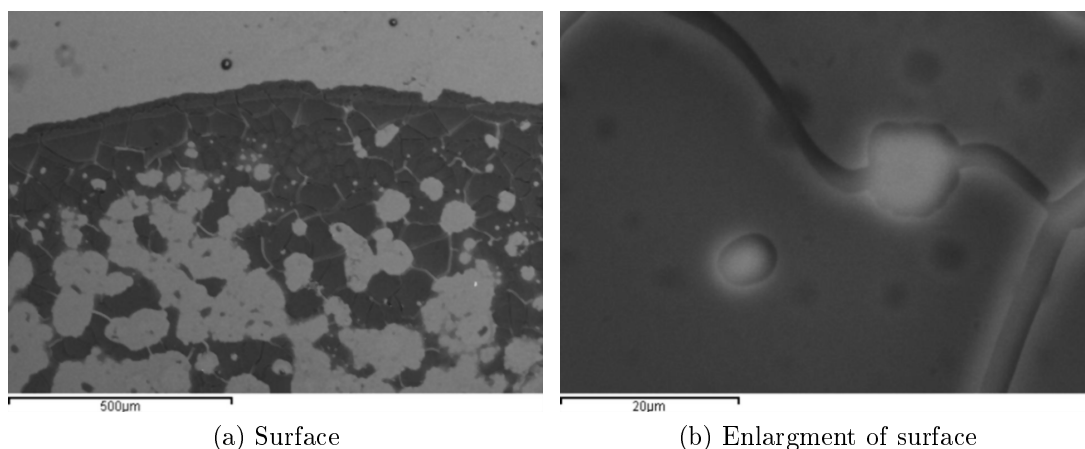
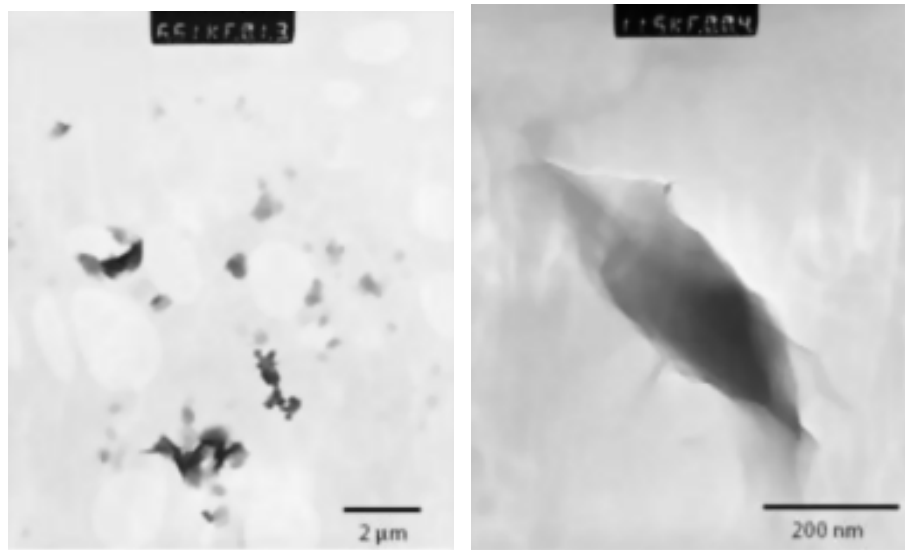


Figure 5.16: SEM images of filtrated solution $< 1 \mu\text{m}$ of collected particles from the impact event

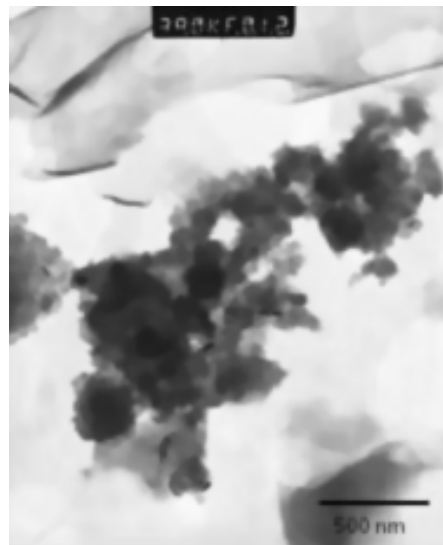
The TEM micrographs are shown in Figure 5.17a. As previously shown on the SEM micrographs, the OMMT matter was also detected by TEM. However, the enlargement of the OMMT matter showed two types of particles, which can be seen in Figure 5.17b and 5.17c. Single OMMT structures could be found, which kept their layered pattern and had an elliptical form with a mean semi-major axis size of 360 nm and a mean semi-minor axis of 120 nm (Figure 5.17b). This finding indicates that some of the incorporated OMMT did not bond or were fully intercalated with the matrix, so that they could be released during the low velocity impact test. Beside pristine OMMT, composite particles could be found as shown in Figure 5.17c. Hybrid nano-sized particles indicate that the intercalated structure of PU/OMMT nanocomposites endured impact testing.

Additionally, DLS analysis was conducted to analyse the particle size distribution. DLS analysis detected particles in the size range of 255-458 nm, as shown in Figure 5.18. The results indicate that by filtration of the solution the frequency of smaller particles increases. By filtration of the origin solution and increase of the 255 nm sized particles could be measured from 1.1% to 9.9%. The results of the DLS correlates well with the investigations conducted via SEM. Further, the DLS results showed that the highest frequency could be found for particle with a geometric mean size of 342 nm, within all solutions. However, it has to be kept in



(a) PU/OMMT fractures

(b) OMMT particle



(c) PU/OMMT particle

Figure 5.17: TEM images of filtrated solution $< 1 \mu\text{m}$ of collected particles from the impact event

mind that DLS analyse is based on the theory that the investigated particles are perfect spheres, as discussed in Section 3.3.5.1.

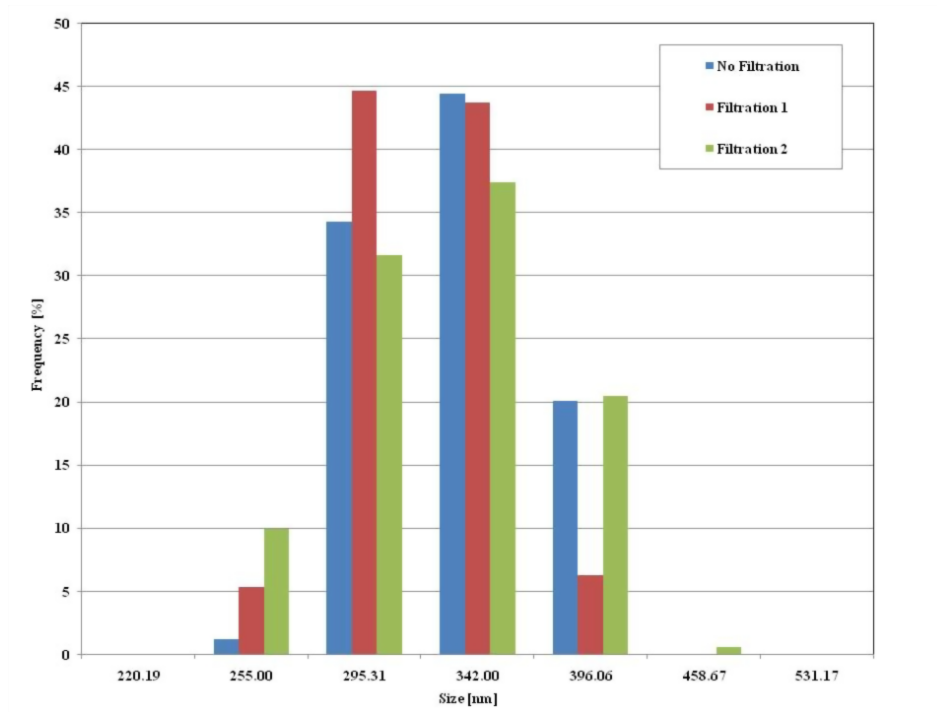


Figure 5.18: DLS analysis of suspensions of collected particles from the impact event

5.4 Conclusion

Sandwich panels were fabricated with PU/OMMT foam cores and glass fibre reinforced PA6 and PP face sheets. Cell structure of the different loaded foams were found to be rather similar in parallel and perpendicular direction to the foam growing direction. The degradation rate of the PU foams was slightly enhanced by the presence of OMMT. Further, the addition of OMMT increased the energy absorption capacity during compression and low energy impact tests. However, lower values for compressive strength and peak load were recorded. The usage of different face sheets has showed little difference for the quasi static compression tests. However, once the sandwiches were subjected to low energy impact tests the PA6 face sheet shown superiority over the PP face sheet.

This study has shown that by impacting PU/OMMT nanocomposites via low- energy impact test, nano-sized particle can be release and generated in unbounded and bounded state. Measurement of the released airborne particles have shown

that during impact mainly particles in the size range of 20-50 nm are generated. Further, investigation of the deposited particles has shown that after the second filtration step ($< 1 \mu\text{m}$), mostly agglomerated OMMT could be found. However, through further dilution and sonification of the suspension, two types of particles could be detected on the TEM micrographs, elliptical (350x 120 nm) OMMT layers and hybrid PU/OMMT particles. This result indicates that although the nanocomposites had an intercalated structure not all of the OMMT was bond to the polymer, and therefore could be released during drop tower impact test. Furthermore, nano-sized particles, consisting of composite material could be detected.

Chapter 6

Overall discussion

6.1 Experimental evidence of effects influencing particle emission during different release scenario

Today, examples in the open literature have shown that a variety of mechanical techniques such as abrading^[27;28], sanding^[27;93], sawing^[26], drilling^[26;94;97], and scratching^[34] can release nano-sized particles contained in coatings and composite matrices. Exposure studies in laboratory, as a consequence of the approach of exposure measurements, can provide basic data about the ability and/or the quantity of nano-sized particle release due to simulated treatment processes.

These studies however miss a crucial point. The quantity and properties of particle released from a nanocomposite or coating is not only being influenced by the pristine filler particles, but by more complex interaction between particle/matrix and furthermore the arising nanocomposite properties. Hence, these studies failed in developing any effective assessment of the nanocomposite used, but rather just studied individual material systems.

Within the scope of this thesis PP and PA6 based nanocomposites with different types of fillers: organically modified montmorillonite, fumed silica, foam-glass crystal material, glass spheres and glass fibres were obtained by direct melt mixing

in twin-screw extruders. Further PU/OMMT foams were prepared. The preparation of the polymeric nanocomposites involved a careful selection of components, processing techniques and conditions. Further, it was crucial to manufacture the nanocomposite utilising no additives or modifiers to clearly identify the sources of particle release.

Two release scenarios were studied; a drilling process to simulate a continuous release scenario and a low velocity impact test as a quick and sudden release scenario. In the following the influence of matrix material, filler type, and filler size, on the particle emission will be discussed.

6.1.1 Effect of matrix type on particle emission

During drilling of the composite panels a significant difference in particle emission could be measured depending on the polymeric matrix used. Airborne particle emission rates for the PA6 based composite were 10 times higher than emission rates for the PP based nanocomposites. However, the characterisation of deposited particles showed exactly the opposite particle behaviour. In this case the total number of particles emitted by the PP based composites was 10-100 times higher than those of the PA6 composites. This fact leads to the conclusion that the studied PP based composite generated particles that agglomerates quicker and hence promote particle deposition. This could have been caused by the form of integration of the fillers in the matrix. The interfacial interactions between filler and matrix were the main driving forces for the formation of nanocomposites. Formation of nanostructures were eased when both polymeric and inorganic filler had similar polarity e.g. PA6-based matrix with Si-based fillers. However, these interactions were much harder to achieve for the PP based composites. Nevertheless, presence of stable nanostructures in compatibilized PP matrix were confirmed by WAXD, SAXD and SEM analysis. However, for PP/OMMT nanocomposite only an intercalated structure could be found while for PA6/OMMT composites a

higher degree of exfoliation could be found.

It is likely that the different thermal properties of the matrix materials, have direct influence on the particle emission, during drilling. The integration of OMMT and nano-SiO₂ lead to a change in the thermal properties of the PP and PA6 matrix, as discussed in Section 3.3.3. It is very likely that these changes influence the rate of particle emission during drilling of nanoreinforced composites as shown in Figure 6.1. With increasing melting temperatures, the particle emission rate increased respectively. Hence, a correlation between thermal properties of the working material and dust emission can be made.

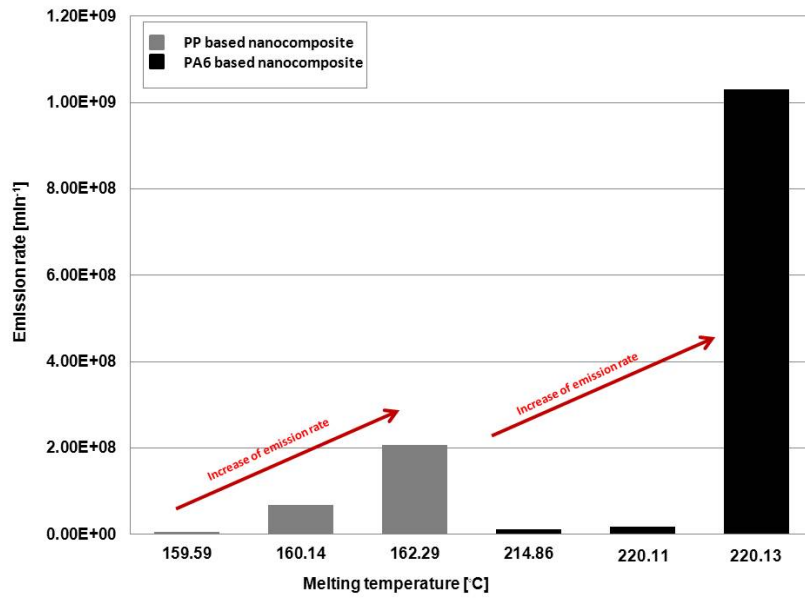


Figure 6.1: Dependency of emission rate on the temperature

The result have shown that there is a dependency between thermal properties and dust generation of nanofilled thermoplastics. Similar results were observed on the nanoscale dust emission during machining of metal and metal alloys^[135;199;200]. For instance, Songmene et al.^[199] identified five different sources for particle emission during drilling of solid material: i) shearing action of chips; ii) deformation and friction; iii) deformation and friction on the tool-chip interface; iv) friction on tool-workpiece; v) and friction of chips in drill flutes as shown in Figure 6.2.

Further, the authors also recognized the difficulty of isolating each source for a separate study. Songmene et al.^[199] reported that heat treatment of the material

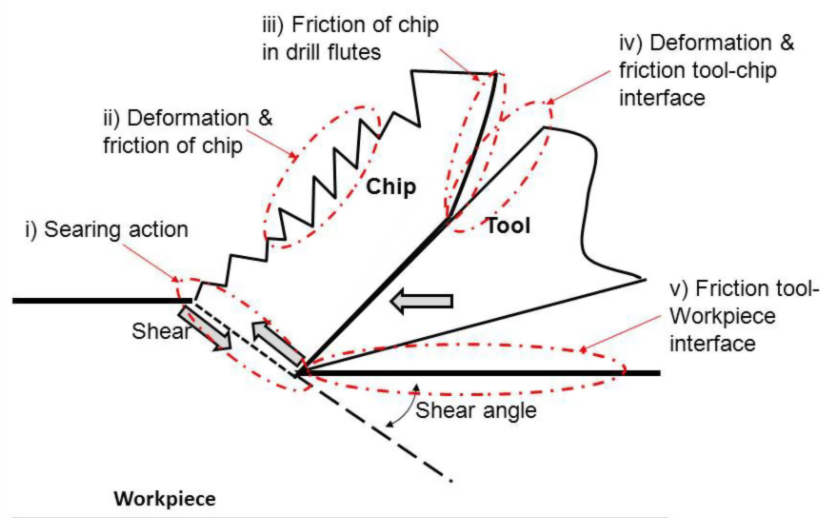


Figure 6.2: Schematic representation of possible sources of particle emission during machining

influenced the mechanical properties, and consequently, the quantity of particles emitted. However, the authors concluded that the quantity of particles emitted depended on the workpiece materials conditions.

For low velocity impact test, no significant effect of the matrix materials on the particle emission could be found. In general PA6 generated 4-8 times more airborne particles than PP based composites. A pronounced difference in energy absorption between the composites made of PP and PA6 matrices, was observed. All PP composites absorbed more impact energy compared to the PA6 composites. It was discovered that all PP composites fail in a progressive and stable manner, whereas the PA6 composite in a brittle and unstable manner. This behaviour can be directly associated with the mechanical properties of the matrix/fibre interaction. In general, PP is a ductile material with relatively low strength, whereas PA6 is a brittle material which possessed a high stiffness. The brittleness of the material caused larger cracks and fragmentation, reducing the energy absorption capabilities of the material. In case of PP nanocomposites the matrix cracks and

failure were localised in a close proximity of the impact point and they were no crack propagation along the structure. Delamination and debonding of the fibres increase the effectiveness of the energy absorption, and at the same time avoided the weakening of the non-crashed section of the structure. As impact on PP based composite only caused localised failure and not complete failure of the composite, it can be assumed that the emission rate of particles during impacting can be influenced slightly, depending on the matrix materials.

Increasing OMMT loading in PU foams, affected the brittleness of the composites structure. PU/OMMT specimen subjected to the same impact energy showed difference in energy absorption mechanism. While the neat foams showed signs of plastic deformation the nano filled foam clearly showed signs of severe fracture damage. In general the degree of deformation decreased and the degree of fracture increased with increasing filler loads. The increase of brittleness in relation to OMMT filling was reported previously by Yang et al.^[46] and Zoukrami et al.^[175]. In general, an increase in fracture promotes particles generation. Therefore, the results obtained suggest, but do not prove, that an increase of OMMT loading leads to an increase of particle emission. As shown for the example of the PU foam with 5 wt.% loading, two types of particles were released during impact test; elliptical (350x 120 nm) OMMT layers and hybrid PU/OMMT particles. This result indicated that although the nanocomposites had an intercalated structure, not all nanoclays were intercalated and therefore were released during drop tower impact test.

6.1.2 Effect of nanofiller type on particle emission

During drilling of the composite panels a significant difference in particle emission could be measured depending on the nanofiller type. In both matrices, composites filled with nano-SiO₂ emitted the highest number of airborne particles and hence possessed the highest emission rates. Additionally, nano-SiO₂ filled com-

posites emitted particles with the smallest geometric mean sizes. Nano-SiO₂, in its pristine form, was the filler with the smallest particle size and highest bulk density. Indeed, very small (approx. 20nm) particles were detected during SEM investigation of the airborne particles. Therefore, it can not be excluded that the sampled nano-sized particles were of pristine nature. Further, integration of OMMT decreased particle emission in PA6 nanocomposite in comparison to the neat polymer. Similar results were obtained by Raynor et al^[29] while, assessing the potential nano-sized particle released during nanocomposite shredding of a thermoplastic nanocomposites (18CPP091-Forte Nanocomposite manufactured by Noble Polymers (Grand Rapids, Mich.)). The authors measured lower particle emission for the OMMT filled composites than for the neat resin. Further, the measured particles were all in smaller size ranges than those of the pristine nanofiller, hence the released nano-sized particles must have been generated by process related mechanism, other than the direct release of pristine nanofillers.

In this study a significant different in nano-sized particle released by nano-SiO₂ and OMMT filled polymer nanocomposites was measured. Therefore, it can be concluded that the type of filler used for composite fabrication has a major impact on the amount and type of nano-sized particle released during a drilling process.

A significant influence of the nanofiller type used on the particle emission could additionally be identified for low velocity impact tests. OMMT filled PP and PA6 composite generated the most particles throughout all impact tests. This behaviour can be explained by the fracture mechanism of the composite cones during impact test. The incorporation of nano-SiO₂ particles did not increase the impact strength of the material, however changed the fracture mechanism. The brittleness of the material was significantly reduced, which was observed as an increase in elongation to break, determined in the tensile tests. However, the opposite behaviour was observed for the OMMT filled nanocomposites. In this case the impact strength of the material was increased but at the cost of reduced ductility.

Hence, the strain reached the maximum allowable limit and the crack propagated along the structure, leading to a complete failure of the structure. As a result the energy absorption capability of the material remained on the same level, in spite of the increase in quasi-static strength and stiffness.

Damages due to low-velocity impact events weaken the structure of composite materials, due to a continuous service load. In every material, energy is absorbed in two ways (i) deformation of material and (ii) fracture of material. As material deformation is limited to the material properties, the fracture of the material in smaller and smaller pieces is the direction towards higher energy absorption capacities. In recent studies^[5] it has been reported that the impact behaviour and related properties (energy absorption capacity) of polymer matrices can be engineered by adding nano-scale fillers. Figure 6.3 shows the basic principal behind the increase in fracture pieces due to nanofillers. In a micro- and macro-filled composite (6.3 a-c), cracks will propagated from one filler particles to the other. The same principle is valid for nanocomposites, however the distance between particles is reduced and therefore the material breaks in smaller pieces, resulting in a brittle material behaviour and hence more particles are emitted.

6.1.3 Effect of filler size on particle emission

As shown in the literature^[75;76] and by the results obtained in this study, the utilisation of nanofiller over microfiller in an identical matrix material led to higher degree of property enhancement. As reported in Chapter 4.3.2 the tensile modulus differed by 0.31 GPa by using nano-SiO₂ instead of micro-SiO₂ particles in PP matrix. Additionally, the specific energy absorbed during impact test increased from 20.7 kJ to 22.6 kJ by using nano-SiO₂ alternative to micro-SiO₂ particles. Hence, it could be assumed that these changes in mechanical properties would directly affect the quantity and properties of the nano-size particles released.

However, comparing the quantity and geometric mean size of particles released

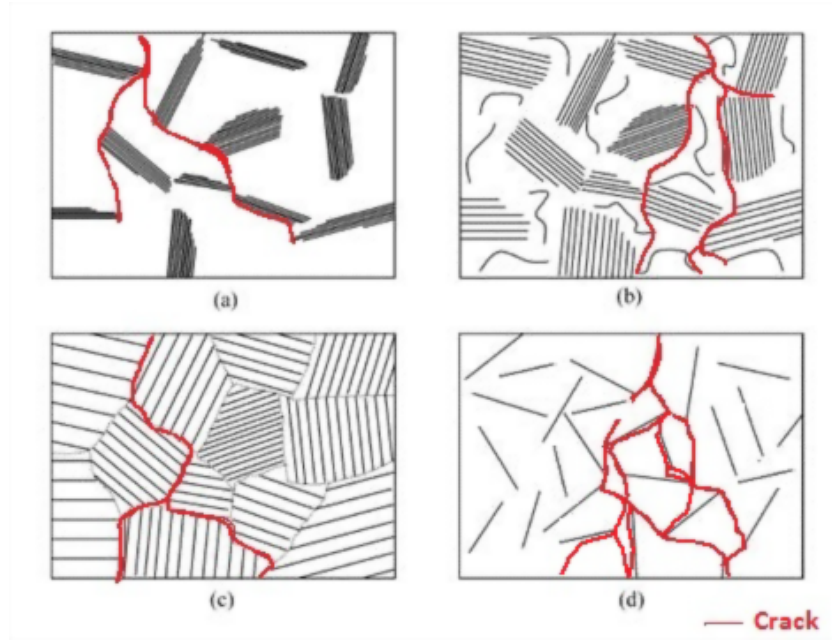
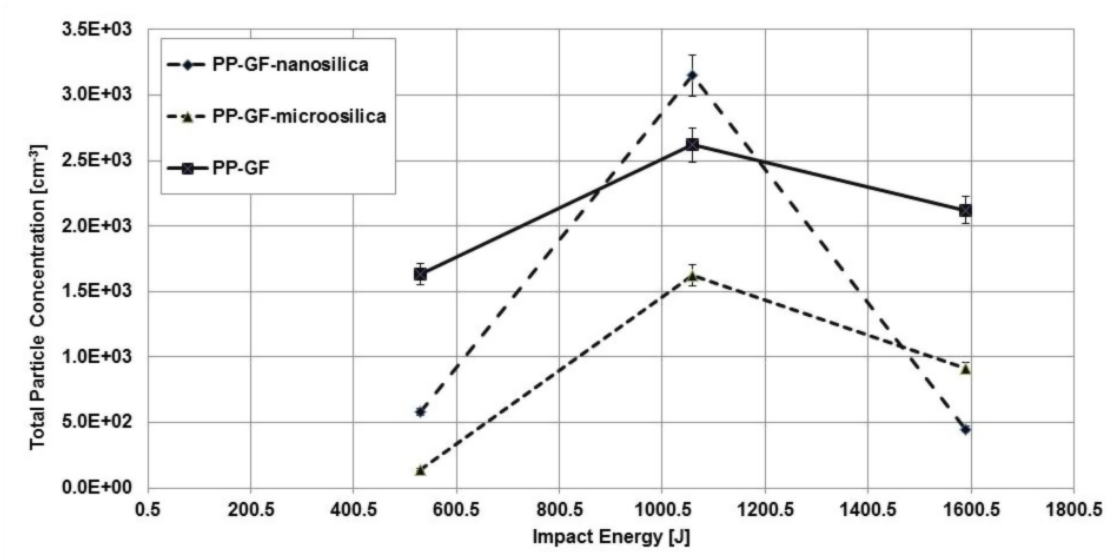
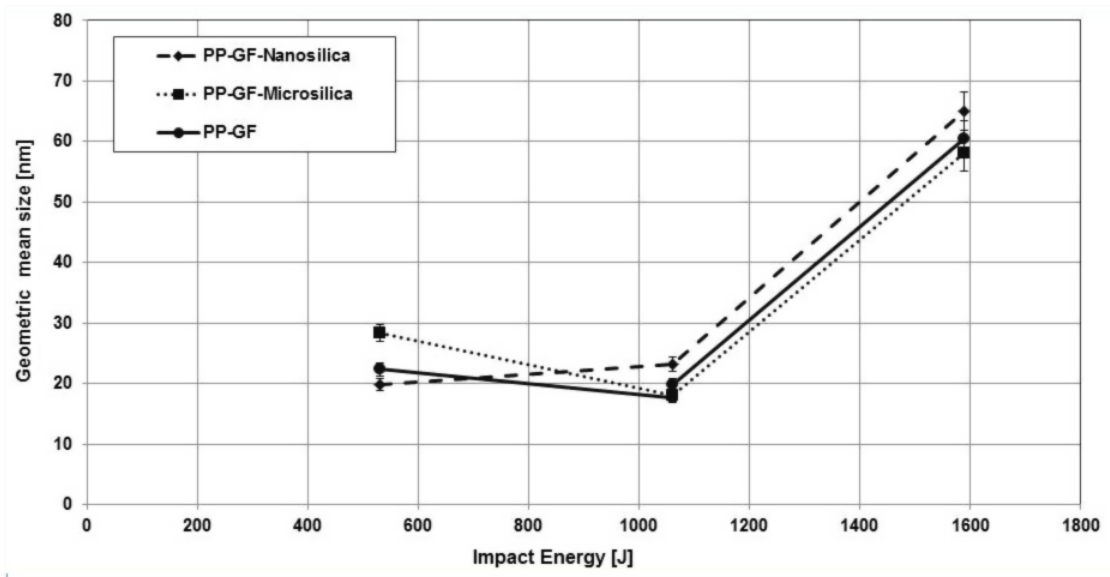


Figure 6.3: Difference in fracture behaviour depending of the degree of exfoliation

during different impact test (Figure 6.4) it could be seen that there was a clear pattern. While there was a maximum peak of particles concentration for the impact at 1050J energy level, the particles geometric mean size was at a minimum peak. Further, the released quantity was similar and significantly lower for the 530J and 1560J impact. However, particle size increased significantly depending on the impact energy. The geometric particle size increased from approx. 25 nm for the 530 J to approx. 60 nm for the 1560 J impact. Nevertheless, this behaviour was observed for all PP and PA6 reinforced with conventional glass fibre, and the composites containing nano-SiO₂ or micro-SiO₂ as a secondary filler. Therefore, it can be concluded that the particle size of the secondary reinforcement is not necessarily affecting the particle emission during impact testing, even though it significantly influences the mechanical properties of the composite material.



(a) Total particle concentration vs impact energy



(b) Geometric vs impact energy

Figure 6.4: Comparison plot of nano-SiO₂ and micro-SiO₂ fillers on particle emission for PP composites

6.2 Summary and recommendations

Within the scope of this thesis two release scenarios for nano-sized particle exposure were studied. A drilling process to simulate a continuous release scenario and a low velocity impact test as a quick and sudden release scenario. The results obtained suggest, that the particle emission rate and the properties of the released

particles depend strongly on the type of matrix and filler used. No real dependency of filler size on the particle emission during impact testing could be found.

The following important points can be noted:

- Nanocomposites based on PA6 matrix generated more nano-sized particles than those based on PP matrix, during drilling and low velocity impacts.
- Nanocomposites filled with nano-SiO₂ emitted the highest number of airborne particles and hence possessed the highest emission rates, for both PA6 and PP matrices during drilling.
- No significant different in particle generation between nano and micro-SiO₂ filled PP and PA6 nanocomposite could be found during impact tests.
- OMMT integrated into PU foams, was released in bound and unbound state during low velocity impact tests.

Chapter 7

Conclusion and future work

In this study different silica based nanofillers (organically modified montmorillonite and nanosilica) as well as silica based microfillers (foam-glass crystal material, glass spheres and glass fibres) were introduced into polypropylene, polyamide and polyurethane matrices. The preparation of the polymeric nanocomposites involved a careful selection of components, processing techniques and conditions. The nanocomposites based on PP and PA6 were prepared by direct melt mixing in an twin-screw extruder, while the PU/nanocomposites were produced by in situ polymerisation. The formation of nanostructures was eased when both polymeric and inorganic filler had similar polarity e.g. PA6-based matrix with Si-based fillers. However, these interactions were much harder to achieve for the PP based composites. In order to maintain a high dispersion of the nanofillers in both apolar (PP) and polar (PA6) matrix, selected nanofillers were used with appropriate surface functionalisation providing good compatibility with both types of polymers. The presence of stable nanostructures in compatibilised PP matrix were confirmed by WAXD, SAXD and SEM analysis.

In addition to the pure nanocomposite based on PP and PA6, nanocomposites based on PP-30% glass-fibres and PA6-30% glass-fibres were fabricated using direct melt mixing in a twin-screw extruder. These composites were subjected to

different mechanical process, to not only identify their properties but more fundamental to understand their behaviour in terms of structural integrity. In other words, the interest laid in the understanding of particle release mechanisms. To understand the exposure mechanism during different mechanical processes, airborne and deposited particles were systematically characterised. Further, some correlation between material properties and particle emission were built. From the results obtained in this study it can be concluded that:

- Nanoparticles are released from all materials studied, whether they had nanoparticles integrated or not. In some cases the pure polymeric matrix emitted more airborne particles than the nanofilled composite. It was found that two major effect influence the particle emission; matrix material and filler type.
- Nanoparticles released are not all free ENP but also hybrid particles consisting of matrix/nanofiller material. In some cases the measured particles were all in smaller size ranges than the pristine nanofiller, hence the released particles must have been generated by a mechanism e.g. chopping, other than the direct release of pristine nanofillers.
- It was shown that addition of secondary filler into the glass-fibre reinforced polymer composites had significant influence on the mechanical behaviour of the material. It could be shown that by variation of the secondary fillers it was possible to change the micro-mechanism of a crash and therefore control the energy absorption characteristics of the composite. Especially for the PA6 composites the secondary reinforcement led to an increase in mechanical properties such as strength, stiffness, and elongation to brake as well as energy absorption capabilities.
- The incorporation of nano-SiO₂ particles did not increase the impact strength of the material, however changed the fracture mechanism. The brittleness of

the material was significantly reduced, which was observed as an increase in elongation to brake, determined in the tensile tests. However, the opposite behaviour was observed for the OMMT nanocomposites. These changes in mechanical fracture behaviour had direct impact on the particles emission rates.

- The impact velocity had a major influence on the particle size distribution. A major difference in particle emission could be observed for the different impact velocities. Peaks moved from smaller particle sizes (10-15nm) for the 4.4 and 6.2 m/s impact towards larger particle sizes (50-80nm) for the higher velocity impact. The shift in size distribution showed that the integration of nanofillers changes the physical properties of the emitted particles.

Future studies, should focus on the benefit of these nanofillers on the mechanical properties of larger structure for real life structural application and further, the emission during the mechanical testing should be reported and compared with the results obtained in this study. Future research also needs to include ageing of the nanocomposites and the changes induced to the material properties and hence particle release, due to different ageing factors.

Additionally, it could be shown that the ability to measure nano-sized particles is still challenged e.g. results obtained by DLS vs. NTA, and that measurement devices need to be adapted/developed to analyse particle in this size ranges in a reliable and reproductive manner. Equipments to identify the chemical composition of the released particles need to be developed for full particle characterisation. The main possibility for nano-sized particles to be uncontrollably released into the environment is during the use, recycling and disposal nanocomposites, therefore future studies should focus on methods to control the release of nano-sized particles throughout these processes e.g. by the modification of additives and modifiers. Further, the data collected within this study can be used as a starting point for

future risk assessment, as well as for life cycle analysis for the considered materials, in order to meet the society trends and customers demands to improve ecology, safety and comfort.

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Achievements

Journal papers

1. S. Sachse, F. Silvia, H. Zhu, K Pielichowski, J. Njuguna, A. Irfan, A. Leszczynska, V. Ermini, M. Blazquez and O. Kuzmenko. Physical characteristics of nanoparticles emitted during drilling of silica based polyamide 6 nanocomposites. *IOP Materials Science and Engineering*, 40, 012012, 2012
2. S. Sachse, F. Silvia, H. Zhu, K Pielichowski, J. Njuguna, A. Irfan, A. Leszczynska, V. Ermini, M. Blazquez and O. Kuzmenko. The effect of nanoclay on dust generation during drilling of polyamide 6 nanocomposites. *Journal of Nanomaterials*, Volume 2012, Article ID 189386, 8, 2012
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Conference papers/presentations

1. S. Sachse, F. Silva, K. Pielichowski, A. Leszczynska and J. Njuguna. Compression strength and low-velocity impact performance of nanocored sandwich composites. *International Conference on Mechanics of Nano, Micro and Macro Composite Structures*, Politecnico di Torino, Italy, 18-20th June 2012
2. S. Sachse, F. Silva and J. Njuguna. Mechanical properties and impact-energy absorption of injection moulded nanocomposite structures. *European Conference on Composite Materials - ECCM15*, Venice, Italy, 24-28th June 2012.
3. A. Irfan, S. Sachse, J. Njuguna, and H. Zhu. In vitro assessment and characterization of silica nanoparticles toxicity in human lung A549 cells. *Nanoforum 2012: Safety and Health Effects of Nanoscale Materials -Towards Sustainable Safe Nanomaterials*, Barcelona, Spain, 28th May - 1st June 2012.
4. J. Rose, M. Auffan, P. Chaurand, J. Labille, D. Borschneck, A. Masion, H. Miche, C. Geantet, E. Puzenat, P. Afanasiev, E. Lecelrc, J. Garric, F. Manuela, B. Vollat, P. Noury, K. Abbaci, K. Pielichowskiaze, A. Leszczynska, S. Michalowski, J. Njuguna, S. Sachse and J. Y. Bottero. Environmental exposure to Nanomaterials and their by-products through their life cycle *NANOLCA 2012: Safety issues and regulatory challenges of nanomaterials*, San Sebastián, Spain, 3rd-4th May 2012.
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6. S. Sachse, A. Irfan, S. Michałowski, K. Pielichowski, O. Kazmina, V. Ermini, H. Zhu and J. Njuguna. The effect of nanofiller during machining of

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Conference posters

1. S. Sachse, F. Silva, H. Zhu, A. Irfan, A. Leszczyńska, K. Pielichowski, V. Ermini, M. Blazquez, O. Kuzmenko and J. Njuguna. Nano dust emission from polyamide 6 nanocomposites: A case study on a mechanical drilling process. *NANOLCA 2012: Safety issues and regulatory challenges of nanomaterials*, San Sebastián, Spain, 3rd-4th May 2012.
2. A. Irfan, S. Sachse, J. Njuguna and H. Zhu. In vitro analysis of nanoparticles released from polyamide nanomaterial composites during drilling process. *2011 Annual UK Review Meeting on Outdoor and Indoor Air Pollution Research*, Cranfield, UK, 10-11th May 2011.
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Conference proceedings

1. Editor: IOP Materials Science and Engineering, 2012, 40
2. Editor: Nanostruc2012 International Conference on Structural Nano-Composites-Abstract Book, 2012

Work reports

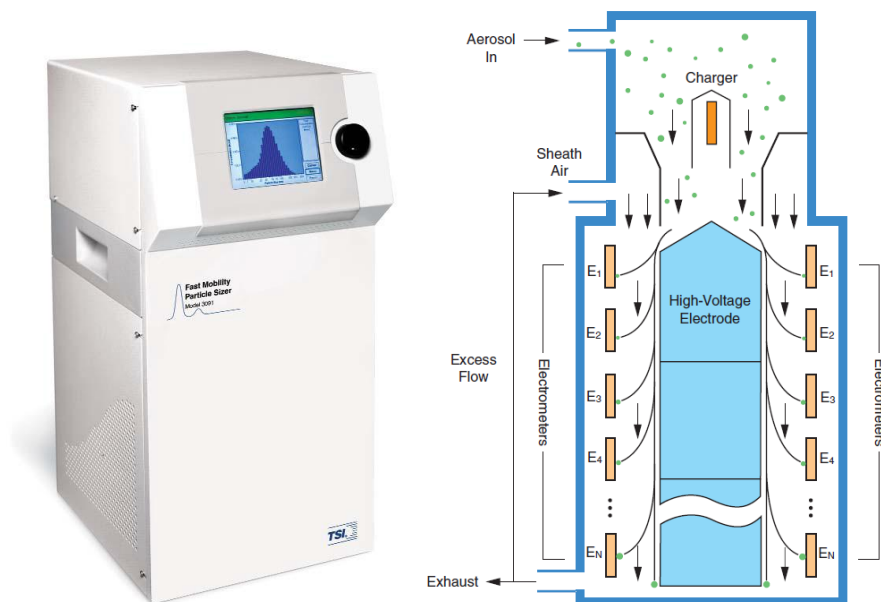
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Appendix A

Air monitoring instruments

Fast Mobility Particle Sizer™ (TSI, USA)

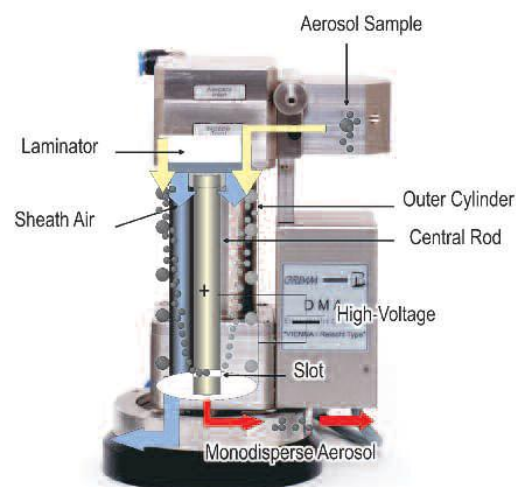


Specifications

3091 Fast Mobility Particle Sizer™ Spectrometer

Particle Size Range	5.6 to 560 nm
Particle Size Resolution	16 channels per decade (32 total)
Electrometer Channels	22
Charger Mode of Operation	Unipolar diffusion charger
Inlet Cyclone 50% Cutpoint	1 μ m
Time Resolution	1 size distribution/sec
Flow Rates	
Aerosol	10 L/min
Sheath Air	40 L/min
Inlet Aerosol Temperature	10 to 52°C
Operating Temperature	0 to 40°C
Storage Temperature	-20 to 50°C
Atmospheric Pressure Correction Range	70 to 103 kPa (700 to 1034 mbar)
Humidity	0 to 90% RH (noncondensing)
User Interface	Rotary knob and display
Front Panel Display	6.4-inch color VGA LCD
Data Averaging	2 to 60 sec (selectable)
Computer Requirements	Pentium® 4 processor, 2 GHz speed or better, at least 512 MB RAM
Operating System Required	Windows® XP or better
Communications	9-pin RS-232
Electrical Inputs	
Analog	Two analog input channels, 0 to 10 V
Trigger	Two trigger input channels, potential-free contact closure or 3.3 V pulled to GND
Electrical Outputs	Trigger output channel, potential-free contact closure
Dimensions (LWH)	70.4 × 34.3 × 43.9 cm (27.7 × 13.5 × 17.3 in.)
Weight	32 kg (70 lb)
Aerosol Inlet	3/8-in. OD (without inlet cyclone)
Cyclone Inlet	3/8-in. OD
Exhaust/Outlet	3/8-in. OD
Power Requirements	100 to 240 VAC, 50/60 Hz, 250 W

Scanning Mobility Particle Sizer (SMPS+C, Grimm Aerosol, Germany)



GRIMM SMPS+C Systems

Size Range	5.4 – 358 nm (M-DMA), 11 – 1110 nm (L-DMA)
Concentration Range	See data sheet of connected CPC
Size Resolution	44 channels, as standard. Optionally up to 255 channels. Logarithmic spacing.

Air Flow System

Flow Rates of Sample Air	0.3 L/min
Flow Rate of Sheath Air	3.0 L/min
Flow Control	Through differential pressure sensors across a heated orifice. Insensitive against variations in ambient temperature and pressure
Aerosol Carrier Gas	Air and inert gases

Liquid System

Working Fluid	1-Butanol (Reagent-grade p.A.) for activation of hydrophobic and hydrophilic particles
Condensate Removal	Continuous drain with a micro-pump into drain bottle

Communications

RS-232	9-pin D connector, ASCII based command set
Memory Card ¹⁾	PCMCIA SRAM 4MB
Analog Inputs	Port for 3 optional analog climatic or gas sensors, plug and play

Operating Conditions

Ambient Temperature	10 to 35°C (50 to 95°F)
Ambient Humidity	0 to 95% RH, noncondensing
Pressure	± 50 mbar to ambient pressure
Power Requirements	85-264 VAC wide range power supply, 47-440 Hz, or 120-370 VDC

GRIMM U-DMA Vienna Type Differential Mobility Analyzer

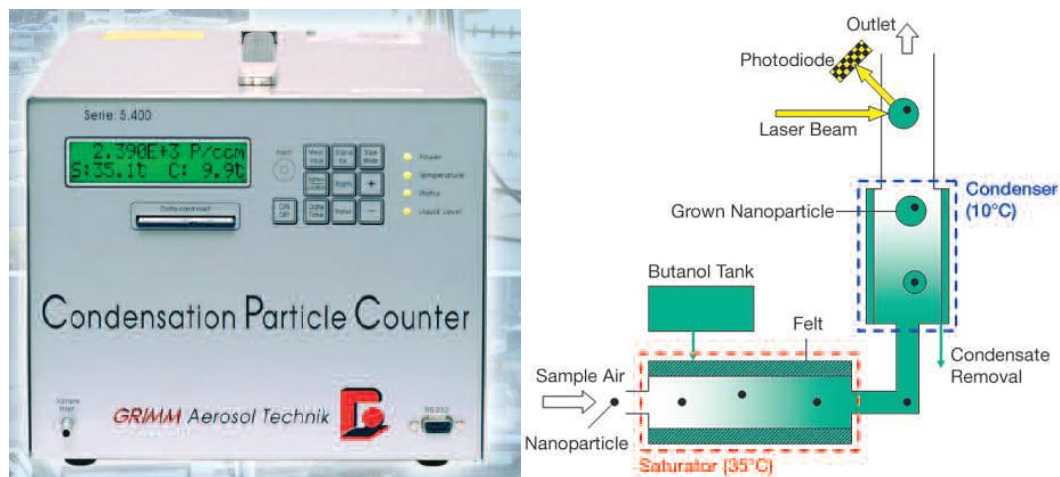
Dimensions

Inner Diameter of Outer Electrode	40 mm
Outer Diameter of Inner Electrode	26 mm

Power

Output of High Voltage Module	5 – 10.000 V, positive inner electrode (negative available on request)
Input of High Voltage Module	0 – 10 V, from CPC or DMA controller
Safety Shutdown of HV	Automatic when opening the DMA
Sensors (internal)	Temperature, absolute pressure, and pressure difference across impactor nozzle

Condensation Particle Counter (SMPS+C, Grimm Aerosol, Germany)



GRIMM Model 5.403 - Mobile Condensation Particle Counter

Particle Detection System

Particle Size Range	4.5 nm (D50, verified with Tungsten oxide) to greater than 3 μm
Particle Concentration Range	0 to 14,000 particles/cm ³ (single particle counting with coincidence correction), to 10 ⁷ particles/cm ³ with photometric mode
Particle Concentration Accuracy	5% (single particle counting), >10% (photometric mode)
Response Time	T90 = 3.9 s
False Counts	$< 2 \times 10^{-4}$ particles/cm ³

Air Flow System

Pumps	Pulse free carbon vane pumps
Flow Rates of Sample Air	Standard flow 0.3 L/min High Flow 1.5 L/min, of which 0.3 L/min sample flow and 1.2 L/min bypass flow ¹⁾
Flow Rate of Sheath Air	3 L/min
Flow Control	Through differential pressure sensors across a heated orifice. Insensitive against variations in ambient temperature and pressure
Aerosol Carrier Gas	Air and inert gases
Liquid System	
Working Fluid	1-Butanol (Reagent-grade p.A.) for activation of hydrophobic and hydrophilic particles
Refill	Automatic refill of internal tank when refill bottle is connected
Condensate Removal	Continuous drain with a micro-pump into drain bottle for highest accuracy

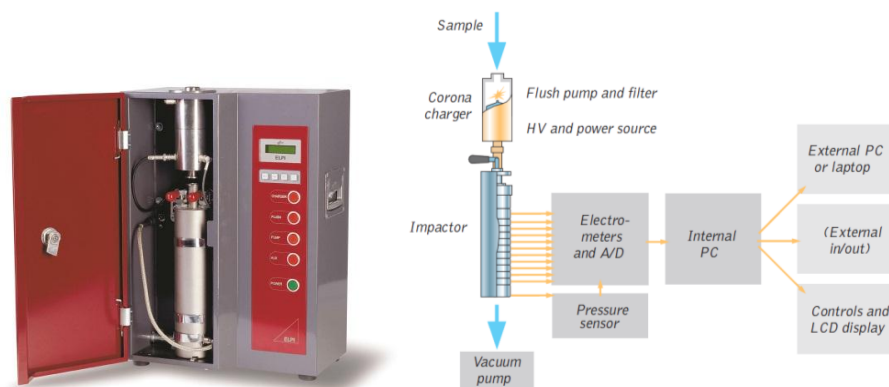
Communications

RS-232	9-pin D connector, ASCII based command set
Memory Card	PCMCIA SRAM 4MB
Status Indication	4 LEDs with 3 colors and messages on the digital display
Analog Inputs	Port for 3 optional analog climatic or gas sensors, plug and play

Operating Conditions

Ambient Temperature	10 to 35°C (50 to 95°F)
Ambient Humidity	0 to 95% RH, noncondensing
Pressure	± 50 mbar to ambient pressure
Power Requirements	85-264 VAC wide range power supply, 47-440 Hz or 120-370 VDC
Dimensions (HxWxD)	22 x 26 x 30 cm (8.7 x 10.2 x 11.8 in)
Weight	13 kg (28.7 lbs)

ELPI™, Dekati Ltd.



DEKATI ELPI™ Electrical Low Pressure Impactor

Specifications

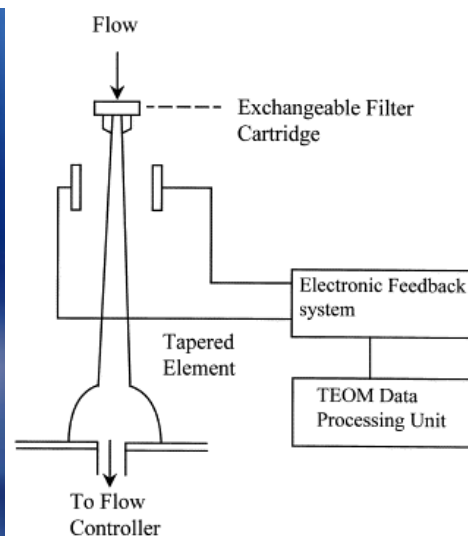
Particle size range	0.007 – 10 µm with filter stage 0.030 – 10 µm standard
Number of size classes	12
Sample flow rate	10 or 30 l/min
Impactor dimensions	Ø 65 x 300 mm
ELPI dimensions	H 570 x W 400 x D 230 mm
Collection plate diameter	25 mm
Unit weight	35 kg
Lowest stage pressure	100 mbar
Pump requirements*	7 m³/h at 100 mbar (10 lpm) 21 m³/h at 100 mbar (30 lpm)
Operating temperature	5 – 40 °C
Operating humidity	0- 90 % RH Non-condensing
Response time	< 5 sec
Computer requirements	Pentium III 500 MHz, 512 MB RAM, MS-Windows NT™, 2000™, XP™ or Vista™

*Suitable pumps available at Dekati Ltd.

Stage	D50% [µm]	D1 [µm]	Number min [1/cm³]	Number max [1/cm³]	Mass min [µg/m³]	Mass max [mg/m³]
13	10					
12	6,8	8,4	0,10	2,0E+04	31	8300
11	4,4	5,3	0,10	2,0E+04	10	2700
10	2,5	3,2	0,17	4,5E+04	3	810
9	1,6	2	0,33	8,8E+04	1,4	370
8	1	1,3	0,6	1,6E+05	0,70	180
7	0,65	0,81	1,1	2,9E+05	0,30	80,0
6	0,4	0,51	2	5,4E+05	0,10	40,0
5	0,26	0,33	3,7	9,8E+05	0,07	18,00
4	0,17	0,21	6	1,7E+06	0,03	8,00
3	0,108	0,14	12	3,1E+06	0,02	4,00
2	0,06	0,081	23	6,1E+06	0,006	1,70
1	0,03	0,042	50	1,4E+07	0,002	0,50
Filter stage	0,007	0,014	250	6,9E+07	0,0004	0,11

Values are for 10lpm ELPI - with 30lpm ELPI the sensitivity is improved by approximately 300%.

TEOM® SERIES 1400A (Thermo Fisher Scientific, USA)



Specifications for Series 1400ab Continuous Ambient Particulate TEOM Monitor	
Measurement Method	Tapered Element Oscillating Microbalance (TEOM) technology
Measurement Ranges	0 to 5,000,000 $\mu\text{g}/\text{m}^3$ (5g/m ³)
Precision	$\pm 1.5\mu\text{g}/\text{m}^3$ (one-hour average), $\pm 0.5\mu\text{g}/\text{m}^3$ (24-hour average)
Accuracy	For Mass Measurement: $\pm 0.75\%$
Resolution	0.1 $\mu\text{g}/\text{m}^3$
Flowrate	Main flowrate: 0.5 to 4.0L/min.; auxiliary flowrate: 2.0 to 18.0L/min.
Data Memory	Internal datalogging of 1 to 8 user-specified variables; capacity of 40 weeks of hourly mass concentration data
Input Output	7 averaged analog inputs ($\pm 2\text{VDC}$ or $\pm 10\text{VDC}$) with user-defined conversion to engineering units, including vector-averaged wind velocity and direction; 3 user-defined analog outputs (0 to 1, 0 to 2, or 0 to 10VDC); 2 User-defined contact closure alarm circuits; two-way RS-232 communication using AK Protocol or German Ambient Network Protocol; and four-line display on TEOM Control Unit
Data Output	Every 2 sec.
Approval[s]	USEPA equivalency designation number EQPM-1090-079 as an equivalent PM-10 monitor, USEPA CACM for PM-2.5 German EPA approval for TSP, PM-10; conforms with European continuous PM-10 monitoring requirements Norms/approvals in Australia, Japan, Korea, and Taiwan CE EN550011 Group 1, Class B (Emissions), EN55082-1 (Immunity), EN61010-1 (Safety) ETL UL- and CSA-equivalent approval
Operating Limits [Temperature Range] [CENTIGRADE]	Temperature of sampled air may vary between -40° and $+60^\circ\text{C}$. TEOM sensor and control units must be weather protected within the range of 2° to 40°C .
Power Requirements	Sensor and Control Units: 120VAC 60Hz 1A; 240V 50 Hz 0.5A Pump: 120V 60Hz 4.25A; 240V 50Hz 2.25A
Dimensions	Base of TEOM sensor unit: 11 x 14 x 13 in. (28 x 36 x 33cm) Heated air inlet: 26 x 3.5 in. dia. (43 x 46cm dia.) TEOM control unit: 18 x 17 x 9 in. (46 x 43 x 22cm)
Weight [ENGLISH]	Base of TEOM Sensor Unit: 40 lb.; TEOM Control Unit: 32 lb.
Weight [METRIC]	Base of TEOM Sensor Unit: 18kg; TEOM Control Unit: 15kg

Appendix B

Extrusion and injection moulding parameters

B.1 Recipes used for compounding of nanogranulates

Table B.1 illustrates the recipes used for compounding of the final granulate for injection moulding.

Table B.1: Recipes used for compounding of the final granulate for injection moulding

Name	Granulate 1	Granulate 2	Macrofiller
PP-GF-nanoSiO ₂	2.2 kg PP+nanosilica	2.2kg PP+glass fibre	1 kg glass fibre
PP-GF-OMMT	2.4 kg PP+nanoclay	2.4 kg PP+glass fibre	1.1 kg glass fibre
PP-GF-microSiO ₂	2.5 kg PP+glass fibre	2.5 kg PP+glass sphere	2 kg glass fibre
PA6-GF-nanoSiO ₂	2.8 kg PA+nanosilica	2.8 kg PA+glass fibre	1.3 kg glass fibre
PA6-GF-OMMT	2.0 kg PA+nanoclay	2.0 kg PA+glass fibre	0.9 kg glass fibre
PA6-GF-microSiO ₂	2.5 kg PA+glass fibre	2.5 kg PP+glass sphere	2 kg glass fibre

Extrusion parameters for nanogranulates

Table B.2 shows the extrusion parameters for the compounding PP and PA6 composites.

Table B.2: Extrusion parameter

	PP Composites	PA6 composites
Screw speed (rpm)	400	400
Pressure (bar)	30 - 35	35 - 40
Temperature (°C)	285 - 290	203 - 205
Extruder efficiency (%)	61 - 65	42 - 43
Vacuum (mbar)	yes	yes
Take-off speed (m/min)	30	45
Side-feeder (rpm)	400	400

Figure B.1 represents the Temperatures in the different barrier zones during compounding of PP and PA6 composites.

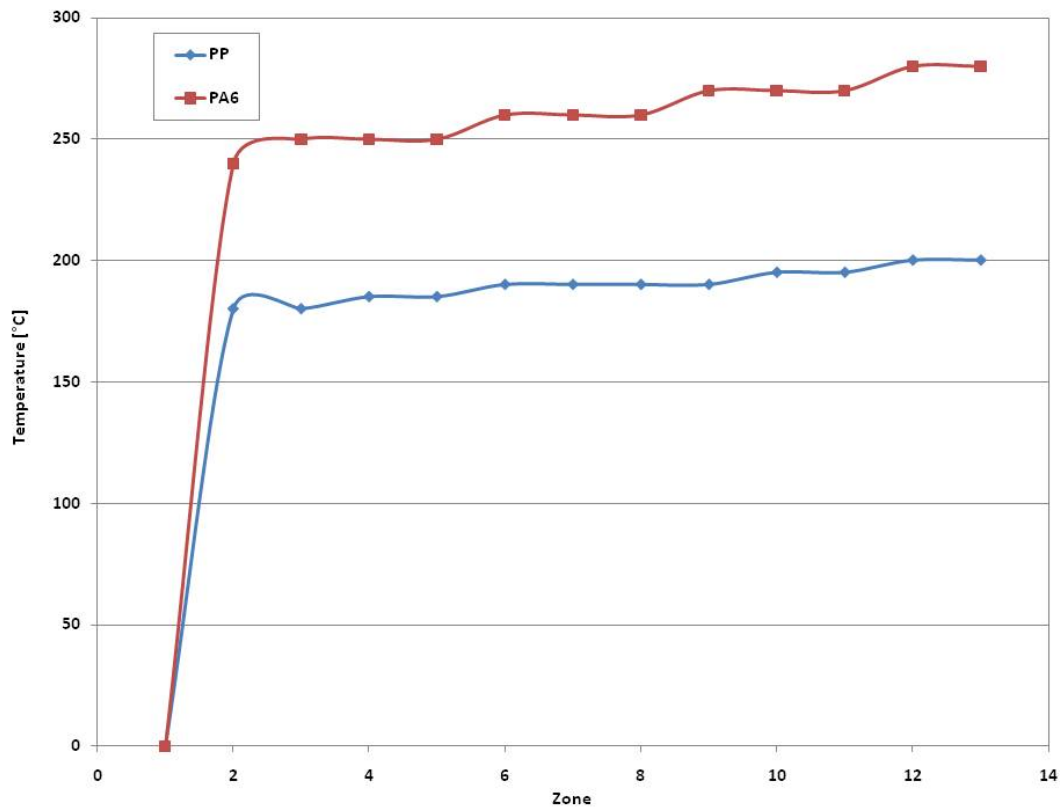


Figure B.1: Extrusion Temperature in different Zones

B.2 Injection moulding parameters

Table B.3 shows the injection moulding parameters of crash cones on a Ferromatik K110 moulding machine with a closing pressure of 1100kN. Injection moulding parameters for the tensile bars can be found in B.4. Tensile bars were injected on a Engel ES200/60 HL ST injection moulding machine, with a closing pressure of 600kN.

Table B.3: Injection moulding parameter for crash cones

Parameter	Unit	PP-GF- nanoSiO ₂	PP-GF- OMMT	PP-GF- microSiO ₂	PP-GF	PA6-GF- nanoSiO ₂	PA6-GF- OMMT	PA6-GF- microSiO ₂	PA6-GF
Pre- Drying		no	no	no	no	yes	yes	yes	yes
Drying temperature	°C	50	50	50	50	80	80	80	80
Drying time	h	6	6	6	6	10	10	10	10
Temperature									
Feed	°C	45	45	45	45	45	45	45	45
Zone4	°C	210	210	210	200	240	240	240	240
Zone3	°C	210	210	210	200	250	250	250	250
Zone2	°C	220	220	220	210	260	260	260	260
Zone1	°C	230	230	230	220	270	270	270	270
Injector	°C	220	220	220	220	270	270	270	270
Tool temperature	°C	45	45	45	40	60	60	60	60
Metered volume	cm ³	220	220	220	250	220	220	220	250
Metering length	mm	157	157	157	157	157	157	157	157
Rotation speed	1/min	100	100	100	100	100	100	100	100
Back pressure	bar	30	30	30	30	30	30	30	30
Cooling time	s	35	35	35	40	40	40	40	40
Metered retirement	s	0,5	0,5	0,5	2	0,5	0,5	0,5	2
Injection pressure	bar	350	a 390	509	500	642	686	686	540
Injection flow rate	cm ³ /s	40	40	40	40	30	30	30	40
Injection time	s	5,49	5,35	5,36		7,03	7,03	7,05	5,33
Switch over point	cm ³	20	20	20	42	20	20	20	25
After-pressure	bar	400	400	400	400	400	400	400	450
After-pressure time	s	4	4	4	4	4	4	4	4
After-pressure velocity	cm ³ /s	50	50	50	50	50	50	50	50
Pad	cm ³	15.4	15.3	18.4	3.5	19.2	20.8	21.1	1.7
Screw diameter	mm	45	45	45	45	45	45	45	45

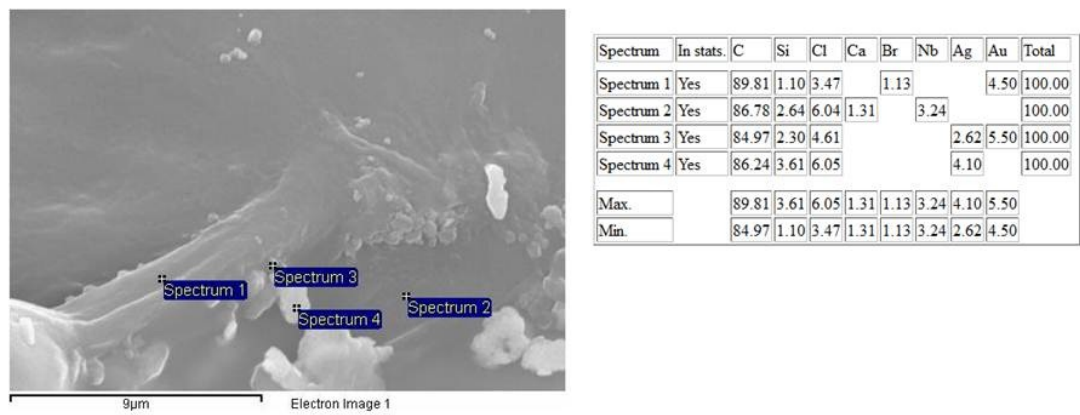
Table B.4: Injection moulding parameter for tensile bars

Parameter		PP-GF- nanoSiO ₂	PP-GF- OMMT	PP-GF- microSiO ₂	PP-GF	PA6-GF- nanoSiO ₂	PA6-GF- OMMT	PA6-GF- microSiO ₂	PA6-GF
Unit									
Pre- Drying		yes	yes	yes	no	yes	yes	yes	yes
Drying temperature	°C	50	50	50		80	80	80	90
Drying time	h	6	6	6		8	8	8	4
Temperature	°C								
Feed	°C	40	40	40	40	60	60	60	60
Zone4	°C								
Zone3	°C	200	200	200	200	250	250	250	250
Zone2	°C	210	210	210	210	260	260	260	260
Zone1	°C	220	220	220	220	270	270	270	270
Injector	°C	220	220	220	220	270	270	270	270
Tool temperature	°C	46	46	46	46	65	65	65	65
Back pressure	bar	6	6	6	6	6	6	6	6
Cooling time	s	30	30	30	20	20	20	20	20
Injection pressure	bar	35	35	35	35	100	100	100	78
Injection flow rate	cm ³ /s	20	20	20	20	15	15	15	15
Injection time	scm ³	1,74	1,76	1,72	1,80	2,36	2,36	2,36	1,58
Switch over point		10	10	10	8.5	9	9	9	9
After-pressure	bar	150	150	150	90	120	120	120	150
After-pressure time	s	8	8	8	10	4	4	4	4
After-pressure velocity	cm ³ /s	10	10	10	10	10	10	10	10
Pad	cm ³	4.6	2.1	4.5	2.7	5.9	5.9	1.5	6.5
Screw diameter	mm	30	30	30	30	30	30	30	30

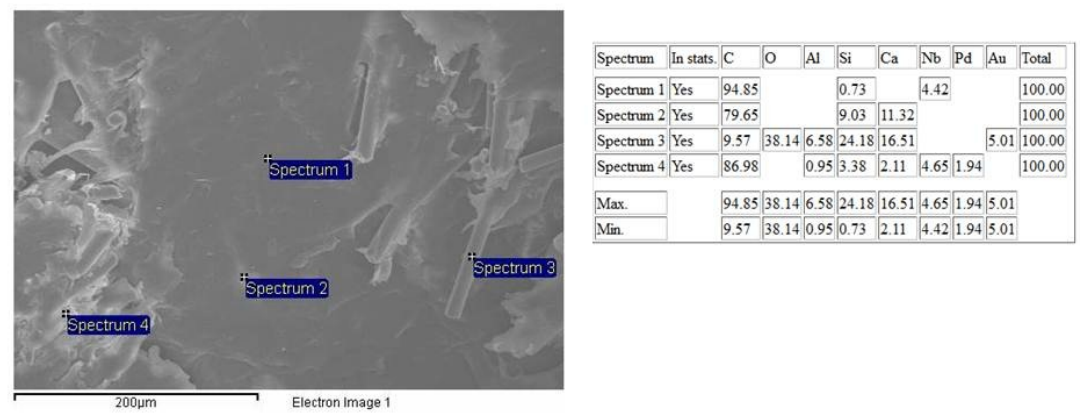
Appendix C

EDX results

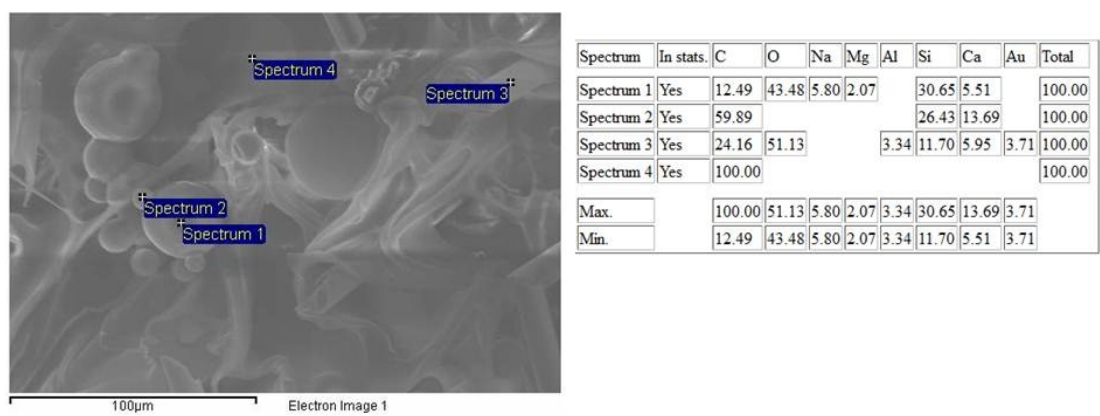
Figure C.1 and C.1 shows the EDX analysis for the injected moulded nanocomposites.



(a) PP-GF-nanoSiO₂

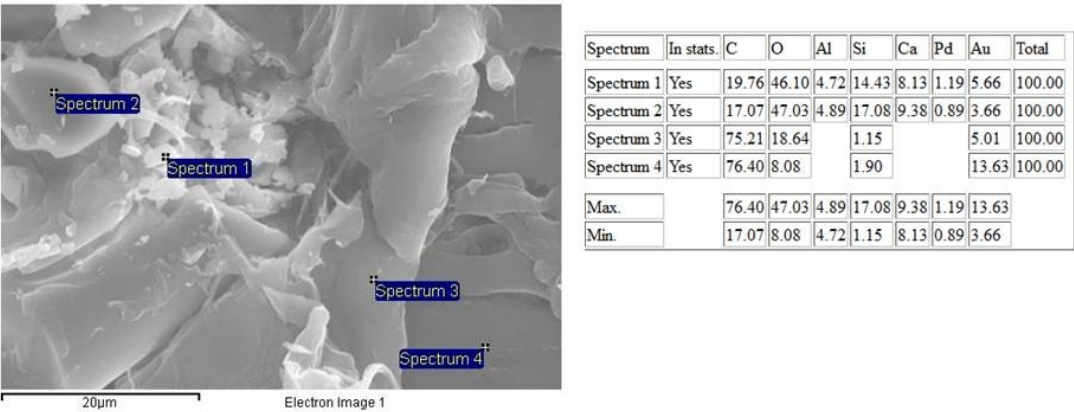


(b) PP-GF-OMMT

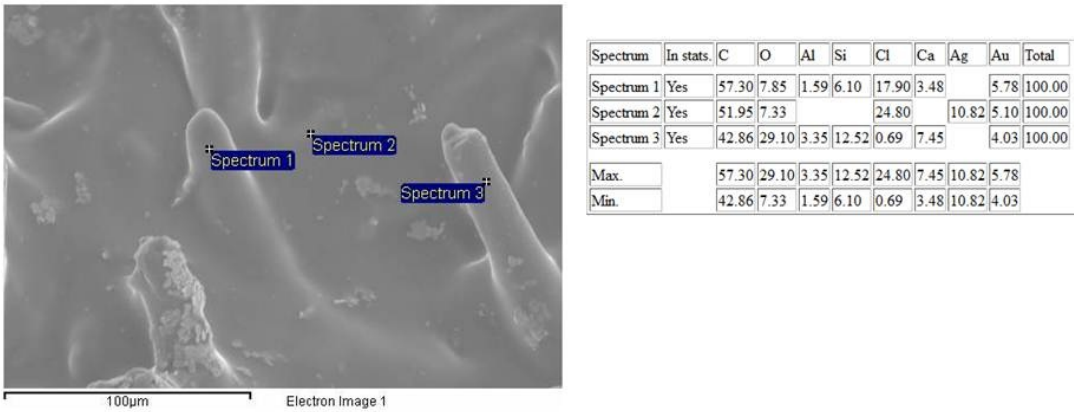


(c) PP-GF-microSiO₂

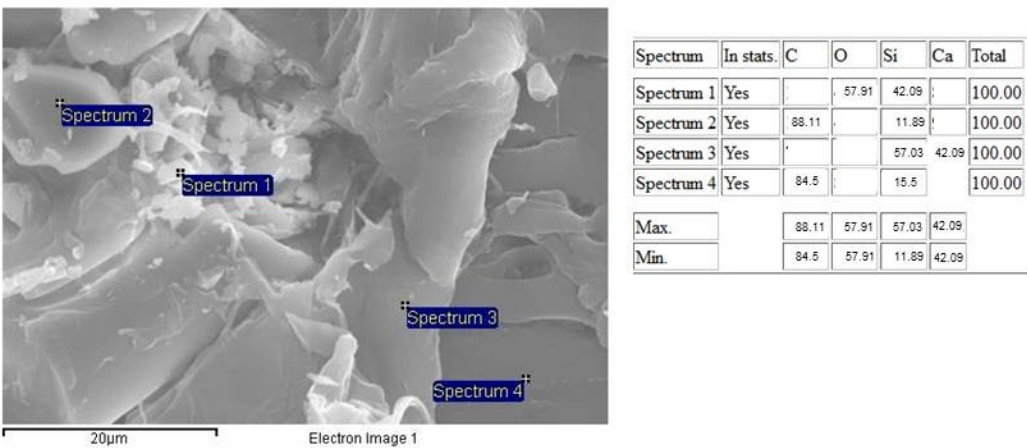
Figure C.1: EDX analysis of PP based nanocomposites



(a) PA6-GF-nanoSiO₂



(b) PA6-GF-OMMT



(c) PA6-GF-microSiO₂

Figure C.2: EDX analysis of PA6based nanocomposites

Appendix D

Injection moulding plates

Table D.1 shows the injection moulding parameters for plates on a Ferromatik K110 moulding machine with a closing pressure of 1100kN.

Table D.1: Injection moulding parameter for tensile bars

		PP-GF	PA6-GF
Parameter	Unit		
Pre- Drying		no	yes
Drying temperature	°C		90
Drying time	h		4
Temperature			
Feed	°C	60	60
Zone4	°C	210	240
Zone3	°C	220	250
Zone2	°C	230	260
Zone1	°C	240	270
Injector	°C	250	270
Tool temperature	°C	40	65
Metered volume	cm ³	110	110
Metering length	mm	100	100
Rotation speed	1/min	236	236
Back pressure	bar	50	35
Cooling time	s	40	30
Injection pressure	bar	221	520
Injection flow rate	cm ³ /s	100	60
Injection time	s	1,62	2,68
Switchover point	cm ³	30	30
After-pressure	bar	280	480
After-pressure time	s	10	4
After-pressure velocity	cm ³ /s	150	50
Pad	cm ³	3	1
Screw diameter	mm	45	45

Appendix E

NEPHH- Deliveable 1.3 Sampling Protocol



D1.3. Sampling Protocol

PROJECT

Project Reference number	CP-FP 228536-2
Project Acronym	NEPHH
Project Full Title	NANOMATERIALS RELATED ENVIRONMENTAL POLLUTION AND HEALTH HAZARDS THROUGHOUT THEIR LIFE CYCLE
Project Web Site	www.nephh-fp7.eu
EC Project Officers	Nicolas Segebarth Fabio Biagioni

DOCUMENT

Deliverable Responsible	CRAN
Document Title	Sampling Protocol
Deliverable Code	D1.3
Corresponding WP	1
Document Type	Report
Dissemination Level	RE
Contractual date of delivery	M12
Status & Version	DRAFT
Approved by	
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Key Words	Sampling methods, Characterisation



CHANGE LOG

Reason for Change	Issue	Revision	Date



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TABLE OF CONTENTS

Executive summary	6
ACRONYMS LIST	7
1. INTRODUCTION	8
2. MATERIALS AND METHODS	9
2.1. Nanocomposites fabrication.....	9
2.2. Characterisation and testing equipment	9
3. DESCRIPTION OF THE ACTIVITIES CARRIED OUT	11
3.1. Development of procedure for samples production	11
3.2. Development of procedure for samples maintenance and storage.....	11
3.3. Development of procedure for samples characterisation	11
3.4. Development of procedure for samples identification - labelling	12
3.5. Development of procedure for samples transferring	12
3.6. Additional relevant remarks	12
4. Sampling procedures	13
4.1. Procedures for samples production	13
4.1.1. Samples from industrial origin	13
4.1.2. Samples generated from macroscale nano-reinforced structures	13
4.1.3. Samples generated from macroscale nano-reinforced structures followed by leaching tests.....	15
4.2. Procedures for samples maintenance and storage	16
4.3. Procedures for samples characterization	16
4.4. Procedures for samples identification - labelling	21
4.5. Procedures for samples transfer	22
4.5.1. Conditions of origin of the samples: particles in suspension	22
4.5.2. Packaging.....	23
4.5.3. Labeling for transporation.....	23
4.5.4. Modes of Transport.....	23
4.6. Additional relevant considerations	24
4.6.1. Samples utilisation waste labelling	24



4.6.2.	Disposal considerations	24
4.6.3.	Methods for cleaning	25
4.6.4.	Personal protective equipment	25
5.	Bibliography	26

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EXECUTIVE SUMMARY

NEPHH (Nanomaterial Related Environmental Pollution and Health Hazard Throughout their Life cycle) Project deals with the toxicological impact of nanoparticles on human health and the Environment at different life stages of nano-enhanced products. This sampling protocol therefore, deals with nanoparticles released from nano-enhanced macro-scale structures from mechanical loading processes (crash, drilling, milling and abrasion) on polypropylenes, polyamides and polyurethane nanocomposites.

Silica based nanofillers have been used to form the nano-reinforced structures covered on this sampling protocol. The pristine polymers and polymer nanocomposites are primarily manufactured in controlled laboratory scale. A set of polypropylene and polyamide nanocomposites are also manufactured from industrial scale dispersions. The various samples are then be used to manufacture nano-reinforced structures through injection moulding process.

The procedure for production, collecting test samples from industrial scale dispersion, samples generated from macroscale nano-reinforced structures and those followed by leaching tests is presented. Given the importance of the samples and unknown risks associated with these, special procedures have been developed covering the samples identification, maintenance and storage, as well as samples transfer to Project partners' laboratories for further toxicity and eco-toxicity investigations.

Series of experiments have been conducted to evaluate and perfect the samples collection and handling procedures. It stems from the fact that generation and handling of nanoparticles released in mechanical loadings is critical to the quality of the toxicity samples. Mechanical performance and morphology investigations have been conducted to allow successful particles generation and collection to happen. The generated particles from mechanical loadings are supplied to Project partners in suspension form. A critical discussion regarding measurement of airborne samples, deficiency in current state-of-the-art equipment and development of the crash chamber for generation of nanoparticles is presented to provide insight on present limitations of the sampling procedures.

It is envisaged the present protocol is enriched in the execution of NEPHH, as ongoing investigations bring new light to the methodologies to be envisaged.



ACRONYMS LIST

APS	Aerodynamic Particle Sizer;
CPC	Condensation Particle Counter;
ELPI	Electrical Low Pressure Impactor;
FMPS	Fast Mobility Particle Sizer;
SMPS	Scanning Mobility Particle Sizer;
TEOM	Tapered Element Oscillating Microbalance

1. INTRODUCTION

The purpose of this protocol is to establish standard procedures for the production, sampling, collection and characterisation of the samples that will be evaluated in the execution of the NEPHH Project.

Such samples include:

- Residues and nanoresidues containing engineered nanoparticles which are released during the physical processing of the engineered nanocomposites (nanomaterials) that will be produced in WP2 (including Drop Weight Impact Testing).
- Residues and nanoresidues containing engineered nanoparticles released during accelerated ageing processes (leaching experiments) conducted on the samples obtained from WP2 and WP3.
- Industrial materials will complete the set of samples to be evaluated from industrial scale dispersion tests.

For the purpose of this protocol some definitions are given [1; 2; 3]:

- “Nanoparticles” are defined as engineered particles materials with one of their dimension as diameter between 1- 100 nanometers.
- “Engineered nanoparticles” are defined as dispersible particles having two or three dimensions greater than 1 nm and less than about 100 nm that make use of properties unique to nanoscale forms of materials. I
- “Nanocomposite” surface modification of engineered nanoparticles to help incorporation of nanocomposite within nanomaterials.
- “Polymer Nanocomposite” (PNC) is a two-phase material where one of the phases has at least one dimension in the nanometre range.
- “Nanomaterials” any material incorporating nanocomposite and/or engineered nanoparticles.
- Aerosol - a material that, while not gaseous itself, remains suspended in air for prolonged periods. Typical examples include dust, and fine-droplet liquid paint or hairspray. Nanoparticulate matter - a collection of particles with at least one dimension smaller than 1 micron yet larger than atoms and molecules.
- Aggregate/aggregation - Material that is composed of a large number of small components which have come together as clusters, usually with branching, porous shares. Aggregation is the process whereby the many small components form clusters, and can be driven by gravity or other forces.

2. MATERIALS AND METHODS

As matrix material, three different kind of thermoplastic will be utilised: polyamide, polypropylene and polyurethane. In various manufacturing processes four different nanoparticle types: nanosilica, layered nanosilicates, glass-nano-fibres and foam-glass-crystal-materials will be integrated into the thermoplastic matrix. Hence, 12 different engineered thermoplastic nanostructures (containing 5 wt.% different nanofiller) will be investigated and also 3 reference samples of virgin thermoplastic polymers (polyamides, polypropylenes and polyurethanes).

2.1. Nanocomposites fabrication

Initial selection among different types of polyamides and polypropylenes was made on the basis of melt flow index value and mechanical properties as required (See NEPHH Project Deliverables 2.1-2.4). Based on those criteria polypropylene (PP) Moplen HP500J from Basell Polyolefins (melt volume flow rate 4.3 g/10 min (230°C/2.16 kg), tensile modulus 1500 MPa, tensile stress at yield 34 MPa and Charpy notched impact strength 4 kJ/m² (23°C)) and Polyamide 6 (PA-6) Tarnamid T-30 (melt volume flow rate 25.0 g/10 min (275°C/5.0 kg), tensile modulus 1100 MPa, tensile stress at yield 28 MPa and Charpy notched impact strength 5 kJ/m² (23°C)) were chosen as appropriate polymeric matrices. Moplen HP500J is a PP homopolymer with good stiffness in addition to good processability, suitable for compounding, whereby Tarnamid T-30 is PA-6 high quality engineering thermoplastic polymer fabricated in the process of ϵ -aminocaprolactam polycondensation. It shows high mechanical strength and high chemical/thermal resistance.

Polyurethane foam (PU) was synthesized (after a set of optimization experiments) in a three-step process – first, to polyol (polyether RF-551) catalyst (N,N-dimethyl cyclohexylamine), water and surfactant (SR-321, Union Carbide, Marietta, GA) were added in order to prepare the polyol premix (component A). In the next step, n-pentane as a physical blowing agent was added to component A. In the third step component B (polymeric 4,4'-diphenylmethane diisocyanate (PM 200)) was added to component A and the mixture was stirred for 10 seconds with an overhead stirrer. Finally, the prepared mixtures were dropped into a mould. All the experiments were performed at ambient temperature of ca. 20°C.

Foam-glass crystal material (FGC) is nanostructured foamglass with improved strength properties. The given effect is provided by formation of crystal particles of no more than 100 nanometers in size. FGC is produced by heat processing of amorphous matrix (~800-850 °C) which includes crystalline phase of SiO₂ numbering from 5 to 15 mass % (maximum) of no more than 1 micron in size. FGC is a light, opaque cellular material. It is an ecologically safe heat-insulation material. It is characterised by low thermal conductivity, high solidity, ecological safety, durability (even in aggressive medium), nonflammability, and convenient use in constructing.

2.2. Characterisation and testing equipment

All the low impact tests will be conducted using a **Rosand instrumented** falling weight impact tester Type 5. The drop weight device was equipped with data acquisition system to acquire force versus time data. Impact energy and velocity can be varied by changing the mass and height of the dropping weight. The velocity of the falling drop mass is measured just before it strikes the specimen. It is also fitted with pneumatic rebound brake which prevents multiple impacts on the specimen. During the testing, the specimen is held in the fixture placed at the bottom of the drop tower which provided a clamped support span. The weight of the cross-head is maintained at a specific value and it is guided through two

frictionless guide columns. The impactor end of the drop mass is fitted with an impact load sensor to record the transient response of the specimens. To carry out the impact tests, test samples are placed in a specially dedicated chamber between the clamps and the height was adjusted depending on the desired energy level. The impactor have 30 mm diameter flat tip. The transient force signal obtained during the test is measured using a piezoelectric load cell located above the impactor tip and was routed through an amplifier and logged against a time-base.

Other mechanical means for particle generation such as milling, sawing and machining will all be conducted using the same specially dedicated chamber.

The particles generated from macroscale structures are classified into two categories:

- The first category deals with the **airborne particles** which will be measured by Scanning Mobility Particle Sizer (SMPS) and will be collected by and Electrostatic Precipitator (ESP). The SMPS measures the particle number size distribution while the ESP collects the airborne particles on a sampling tray. The collected particles will be used for further optical investigations via Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).
- The second category deals with **samples obtained from fracture** and contained in the crash chamber. Those samples will be diluted in dionised water and via several filtration processes separated in size fractions. Characterisation of these samples will occur via optical Microscopy (SEM, TEM), X-Ray Diffraction (XRD), Energy Dispersive X-Ray Spectroscopy (EDX) and Dynamic Light Scattering (DLS).

3. DESCRIPTION OF THE ACTIVITIES CARRIED OUT

In the course of the NEPHH Project a number of partners will deal with a number of samples from different origins; it is therefore relevant to build a up a standard and agreed procedure for the correct management and handling of the samples available.

3.1. Development of procedure for samples production

The selected procedures for samples collected from (i) mechanical fracture tests, (ii) accelerated ageing process and (iii) industrial origin (industrial scale dispersion testing) are presented here in.

3.2. Development of procedure for samples maintenance and storage

Specific procedures for samples maintenance and storage have been defined according to the testing methodologies that will be implemented in the execution of the Project for the evaluation of human health and environmental impacts.

3.3. Development of procedure for samples characterisation

Hazard, the material's inherent potential to cause adverse effects, is based on the chemical and physical properties of the molecule in question, be it conventional or nano-object.

It is established that nanomaterials exhibit properties and behaviour that can be very different compared to the bulk-scale materials of the same chemical identity. Knowledge of size, shape and surface-related properties has been used to account for many of the observed differences. It is widely acknowledged that adequate characterisation of a nanomaterial is necessary to accompany any toxicity study.

For hazard identification, **the material to be tested should be the most relevant form when exposure occurs**. This form may change during the life cycle of the material being tested and it may therefore be necessary to repeat tests on these different forms to characterize risks adequately. When the material is produced by a manufacturer, then sent to another manufacturer to be incorporated into another material and then released to the market (as in Polymer Nanocomposites) hazards arisen from the processing of secondary and tertiary materials should be addressed.

Additionally, it shall be remarked that the physico-chemical characteristics of nanomaterials tend to change in time and depending on the environmental conditions, and therefore the **need of characterisation at different experimental stages**.

For the development of present procedure, the most relevant parameters for the characterisation of the samples have been agreed and selected in order to perform such evaluations at two different stages:

- When samples are obtained and/or produced, so that conditions of origin are determined.
- When samples are received (from those partners producing them): in order to verify and contrast if any potential modification has occurred during transportation.

In present activity relevant international standards have been reviewed, including OECD Standards and ISO TC 229/SC – Nanotechnologies – Guidance on physico-chemical characterization for manufactured nano-objects submitted for toxicological testing. Additionally, reports and main outcomes arisen from other European FP7 Projects

(Engineered Nanoparticles: Review of Health Environmental Safety – ENRHES) have been analyzed.

3.4. Development of procedure for samples identification - labelling

A specific procedure for samples labelling has been designed according to the type and number of samples that will be produced in the execution of the Project. Due to the elevate number of samples that will be evaluated, developed procedure includes a codification system for each type of sample in order to trace back the origin of such specific sample.

3.5. Development of procedure for samples transferring

Procedures for samples transferring from one partner to another have been developed trying to ensure the most effective and safe way also assuring that the properties of the samples are maintained during transportation.

3.6. Additional relevant remarks

In present section some remarks on safety procedures for Partners dealing with NMS have been included. Note that this is just a very preliminary introduction and that Guidance Notes on NMs safe handling will be envisaged in the later execution of the Project.

4. SAMPLING PROCEDURES

4.1. Procedures for samples production

The classification of the different groups of samples to investigate could be made as follows:

- Samples from industrial origin as obtained from industrial scale dispersion tests and providers of bulk materials in their commercial forms.
- Samples generated from macroscale nano-reinforced structures.
- Samples generated from macroscale nano-reinforced structures followed by accelerated ageing processes.

4.1.1. *Samples from industrial origin*

Within the NEPHH Project, VIBA will perform the dispersion tests at industrial scale, by processing the product on extrusion lines made up turbo-mixer, twin screw extruder and pelletizer system.

The preparation of the mixture with turbo-mixer will be performed with the aim to optimize the homogenisation of the components of the recipe. The parameters that will have to be set up include the introduction sequence of the elements in the turbo-mixer, the mixing speed and time. Proper mixing stage, or a perfect homogenisation of the components, will be essential to warrant the effectiveness of the successive extrusion phase, especially concerning the nanoclays dispersion in the polymer matrix.

The previously prepared compound will be fed to the twin screw extruder through a volumetric batcher. To obtain a good dispersion a correct configuration of the screws is essential. For each formulation it will be also necessary to define the correct extruder speed, the temperature profile in different parts of extruder, the optimal production rate.

The extruder's head is equipped with appropriate die plate through which the product will come out in the form of extrudate that, once solidified by cooling in water, will be brought to the third (granulation) stage of the process.

The obtained extrudate, in fact, will be fed to a pelletizer where, through the appropriate blades, will be reduced to the form of cylinders of the desired size.

From a preliminary analysis, each industrial dispersion test will be performed in around one week and the granules used to manufacture macroscale plaque samples for further used for crash studies.

4.1.2. *Samples generated from macroscale nano-reinforced structures*

PA, PP and PU nanocomposites developed in Workpackage 2 will be used in crash tests.

As previously mentioned, particles generated during drop tower impact testing can be classified into two categories:

- The first category deals with the airborne particles which will be measured by Scanning Mobility Particle Sizer (SMPS) and will be collected by an Electrostatic Precipitator (ESP). The SMPS measures the particle number size distribution while the ESP collects the airborne particles on a sampling tray. The collected particles will be only used for microscopy investigations via Scanning Electron

Microscopy (SEM) and Transmission Electron Microscopy (TEM) and used as a reference for the particles in suspension.

- The second category deals with samples obtained from fracture that settle at the bottom of the dust collection chamber. These samples will be diluted in solution dionised water and via several filtration processes separated in size fractions to acquire the particles size to <100 nm. Characterisation of these samples will follow via optical Microscopy (SEM, TEM), X-Ray Diffraction (XRD), Energy Dispersive X-Ray Spectroscopy (EDX) and Dynamic Light Scattering (DLS). **Samples in suspension will be distributed to Project partners for toxicology and ecotoxicologies studies.**

To manage the quality of the samples, a specially designed crash chamber has been developed for this Project to collect the fractures or released nanoparticles during drop weight impact tests. The chamber was build of plexiglass. The lid is made of steel and the top opening is made of flexible PU foam, so that the striker can impact the specimen in free fall. The chamber has two opening, one for the coupling with the measurement instruments (SMP5+C) and the other opening is for designed for easy extraction of the fracture dust particles. The chamber is designed for collection of the generated nanoparticles and moreover to prevent contamination from other sources.

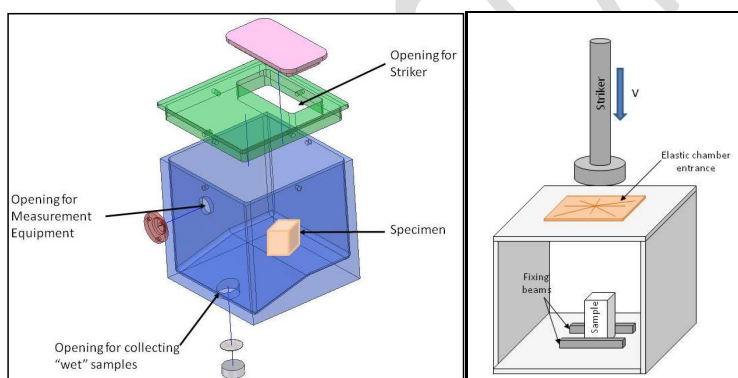


Figure 1 Crash chamber for nanodust collection during low-velocity impact tests

The main outlines of the milling chamber are shown in Figure 2. A closed chamber can be entered by the drilling instrument via an elastically opening. Inside the chamber the sample is fixed by clamps on the ground and the top of the chamber. Additional an inlet for the measurement instrument can be found in the top part of the chamber,

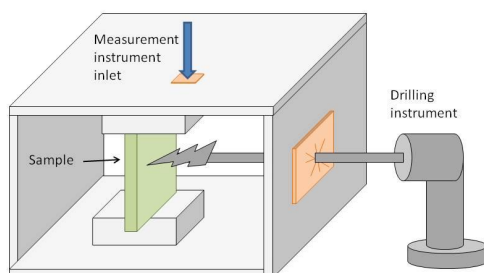


Figure 2 Drilling chamber

4.1.3. Samples generated from macroscale nano-reinforced structures followed by leaching tests

Before and after the collection of residues from crash tests, parts of the samples will be tested under accelerated ageing protocols that reproduce the most realistically the conditions affecting residues while released in the environment. Indeed in addition to atmospheric exposure a significant fraction of potentially toxic small residues produced during crash tests ultimately become aquatic pollutants. More over, the quality of water resources, which may or may not be "contaminated" by nano-objects will be a major issue in the next few years.

For all residues, accelerated weathering simulates damaging effects of long term outdoor exposure by exposing test samples to varying conditions of the most aggressive components of weathering i.e. : ultraviolet radiation, moisture, pH.... But also, the presence of cations like Na⁺, Ca²⁺ and anions SO₄²⁻ and CO₃²⁻ might modify surface properties. For many materials (i.e. glasses and paints) standardized protocols to reproduce weathering exist (ISO 4892 for glasses and ISO 16053/ISO 15181 for Coating materials for exterior wood). But none of them are considering released nano-residues from crash tests. For all residues a first series of aging procedure will consist in batch reactors following the next requirements:

- Samples will be received in dionized water in suspension in DDW with an accurate determined concentration close to 10% in mass (if possible).
- The suspensions will be diluted with Liquid/Solid ratio of 200, 500 and 5000.
- The ionic strength will be varied from 10⁻⁴ to 10⁻¹ and the pH from 3 to 9.
- Duration of experiments will be varying up to 3 weeks.
- For all batch experiments the effect of light will be controlled (Light reproducing the solar spectrum (400 W)).

For the second series of experiments samples are placed in a Climate Chamber (Suntest XLS-Atlas) and subjected to illumination and moistening cycles for 2 months. The leached nano-residues are recovered in the collected water using tangential filtration with 0.01 µm filters.

All residues recovered will be analyzed.

4.2. Procedures for samples maintenance and storage

A number of challenges are associated with the procedure of samples maintenance and storage, especially considering that such conditions will obviously have an influence in the results obtained via characterisation. For instance, nanomaterials' physico-chemical properties in liquid suspensions tend to change with time and surrounding environment. Nanomaterials' tendency to agglomerate and aggregate both in dry and solution media represents a significant challenge too.

The usual considerations for storing chemicals will apply to nanomaterials, including avoiding extremes of temperature, sunlight, and moisture.

Nanomaterials that are supplied as dry powders or dispersions should be stored so that they remain dry or under liquid respectively.

Nanomaterials that are supplied in solutions should be stored taking into account the usual considerations above for any chemical, but also considering the reactivity of the material (if any). Once stock dispersions are prepared, and a full characterisation of the freshly prepared stock has been made including parameters as described in Section 4.3., additional checks should be done to confirm the shelf life of the material. Two key aspects need to be investigated:

- Whether or not the nanomaterial gradually dissolves or transforms such that the solid material disappears.
- Any temporal changes in the particle size distribution and surface charge in the stock dispersion.

Both parameters above will be investigated by NEPHH Project Partner by the use of Techniques as a fast approach for the obtention of the data on shelf stability. A rapid alert system via email will be envisaged to communicate changes undergone.

If changes occur, then protocols should be developed to **restore** the particle size distribution (e.g. re-sonicating the dispersion just before dosing in the case of aggregation). If the stock dispersion cannot be restored, it should be made fresh from the same batch number of the test material and re-characterised. If a different batch number of test material is used, then additional physicochemical characterisation will be required.

As a consequence, the samples will be prepared and delivered immediately after generation to avoid storage problems. All samples for the conduction of the leaching tests, toxicity and testing will be delivered in suspension immediately after sampling.

Stock solutions as delivered by CRAN should be stored at 4°C in order to prevent bacterial growth.

4.3. Procedures for samples characterization

In the execution of the NEPHH Project two main characterisation steps are envisaged:

- Once the procedures for samples production have been completed. That is: samples obtained via physical processing and accelerated ageing processes will be characterised prior transferring them to the rest of the partners.
- Once the samples have reached those partners that will be performing the tests required for the execution of the Project. The intention is to verify if samples have experienced any significant variation during transportation and storage and will also provide a basis for the comparison of the methodologies by both Partners involved (partner producing the sample and partner analyzing the sample).

According to Oberdörster et al [4], there is a strong likelihood that biological activity of nanomaterials will depend on physicochemical parameters not routinely considered in toxicity screening studies.

For the determination of the properties that should be characterised, a literature review has been conducted selecting the main physico-chemical parameters from a hazard assessment perspective.

The list of documents that have been evaluated include:

- Testing Programme of OECD Working Party on Manufactured Nanomaterials (OECD 2008). Note that list by OECD is a non-prioritised list.
- ISO/PDTR 13014 – Note that this document is a working DRAFT.
- Main parameters as described by EHNRES FP7 Project – Final Report
- Oberdörster, G.; Maynard, A.; Donaldson, K.; Castranova, V.; Fitzpatrick, J.; Ausman, K.; Carter, J.; Karn, B.; Kreyling, W.; Lai, D.; Olin, S.; Monteiro-Riviere, N.; Warheit, D.; Yang, H. 2005, "Principles for Characterizing the Potential Human Health Effects from Exposure to Nanomaterials: Elements of a Screening Strategy", *Particle Fibre Toxicology*, Oct 6; 2:8.
- Warheit, D.B., Borm, P.J.A., Hennes, C., Lademann, J. 2007, "Testing Strategies to Establish the Safety of Nanomaterials: Conclusions of an ECETOC Workshop", *Inhalation Toxicology*, vol. 19, pp. 631-643.
- Proposed Minimum Characterization Parameters for Studies on Food and Food-Related Nanomaterials
<http://characterizationmatters.org/2009/12/24/parameters-food/>

Such parameters have been evaluated and prioritised in order to make a selection of the parameters that will be addressed in the execution of the NEPHH Project. Also, the recently published *OECD Preliminary Guidance Notes on Samples Preparation and Dossimetry for the safety testing of Manufactured Nanomaterials (2010)* has been evaluated. Characteristics to be evaluated are listed next.

OCDE – Testing Methods	ISO/PDTR 13014 – Note that this document is a working DRAFT	Main parameters as described by EHNRES FP7 Project – Final Report	Oberdöster et al 2005	Warheit et al. 2007	Minimum information for NMs Characterisation Initiative
## Agglomeration/aggregation	Agglomeration/aggregation state	Aggregation state	Agglomeration state		Agglomeration and/or Aggregation
## Water Solubility	Solubility			Dissolution	
## Crystalline phase		Crystal structure (1)	Crystal structure (1)		Crystal structure / Crystallinity (1)
## Dustiness					
## Crystallite size		Crystal structure (2)	Crystal structure (2)		Crystal structure / Crystallinity (2)
## Representative TEM picture(s)	Shape & Size	Shape & Size	Shape & Size	Shape & Size	Shape & Size
## Particle Size Distribution	Particle Size Distribution	Particle Size Distribution	Particle Size Distribution	Particle Size Distribution	Particle Size Distribution
## Specific surface area	Specific surface area	Surface area	Surface area	Surface area	Surface area
## Zeta potential (Surface charge)	Surface charge	Surface charge	Surface charge		Surface charge
## Surface chemistry (Where appropriate)	Surface chemistry		Surface chemistry		Surface chemistry – Including composition & reactivity
## Photocatalytic activity					

OCDE – Testing Methods	ISO/PDTR 13014 – Note that this document is a working DRAFT	Main parameters as described by EHNRES FP7 Project – Final Report	Oberdöster et al 2005	Warheit et al. 2007	Minimum information for NMs Characterisation Initiative
## Pour density					
## Porosity			Porosity		
## Octanol-water partition coefficient (Where relevant)					
## Redox potential					
## Radical formation potential					
	Composition	Chemical Composition	Chemical Composition	Composition	Chemical Composition / Purity
		Number concentration			

Table 1: Main psicochemical characteristics. Literature review.

Additionally, and considering that samples to be evaluated will be produced and delivered as solutions a number of recommendations have been extracted from the PRELIMINARY GUIDANCE NOTES ON SAMPLE PREPARATION AND DOSSIMETRY FOR THE SAFETY TESTING OF MANUFACTURED NANOMATERIALS – By OECD 2010.

The following would apply to stock dispersions to be evaluated on the course of NEPHH and arguably, this list could be common to human health and ecotoxicology studies:

A) **Physico Chemical Characteristics.** Present set of characteristics is to be provided by NEPHH Partners delivering the Stock Solutions to be evaluated, namely CRAN.

- Measured **mean primary particle size and shape** (for example by electron microscope). The method of particle size determination should be described and the character of the mean (number, volume, z- or intensity) must be given. If a certain given mean/average value is calculated from a primary data (e.g. volume average derived from dynamic light scattering z-average) the calculation procedure should be described.
- **Particle size distribution** and indications of mono or polydispersity (e.g., by dynamic light scattering or similar optical method), or other attempt to describe **aggregates, agglomerates or ranges of particle sizes** in the stock dispersion, including distribution of primary particles. The methodology to derive this size distribution either must be standardised or must be described together with the applied procedures. For DLS the solution was sonicated for 5 min at 35 kW. For nanosight no preliminary work was undertaken. **The method of dispersion (stirring, sonication) should be fully described (duration, stir speed, sonication power etc.)¹.**
- **Mass concentration** (measured) in the stock dispersion (e.g., mg/l).
- For some charged particles, **surface charge** may be critical to the agglomeration process and so the surface charge may be indirectly assessed via measurements of zeta potential. Since the deviation of the zeta-potential is a function of the ionic strength and composition of the dispersing medium, the conditions during determination should be standardised or reported. It would also be important to measure or fix other abiotic factors that might alter this, such as solution pH and ionic strength.
- ***Any other measurement that is particularly relevant for a specific particle type***, for example surface functionality.

B) **Chemical Description.** Information on the test material is to be provided by NEPHH Partners involved in samples production, basically: LAVIOSA and CUT. Impurities, if observed should be reported too.

Other Characteristics including specific surface area, surface chemistry and surface charge, crystal structure and interfacial tension have been disregarded due to the complexity of the samples produced and different types of particles contained on it.

¹ It shall be noticed that the use of solvents or sonication to produce a homogeneous dispersion of nanoparticles at the beginning of toxicity tests may not reflect the behaviour of nanoparticles in the natural conditions in which it is possible that agglomerations predominate. However, the occurrence of agglomeration will inevitably change with dilution, and therefore could also change toxicity.

The Crash Test samples analysis of the SMPS+ is completed by downloading data and review of particle counts at various times and sizes. These samples and the samples obtained from the crash chamber suspension shall be sent to Cranfield University's analytical lab and be prepared for SEM, TEM, XRD, EDX and dynamic light scattering (DLS). Analysis of the samples will yield airborne concentration, as well as morphology and chemical composition. Analysis of passive monitor will also provide information on morphology and chemical composition. The passive sampler can yield particle concentration and size distribution.

In the case of the leaching experiments, all **physical-chemical parameters** of the solutions (pH, eH, salinity) will be registered from T0 to 3 weeks. The evolution of the size and surface properties of the residues will be determined using laser granulometer and FTIR/NMR respectively. As airborne residues, residues after leaching experiments will be prepared for electronic microscopy investigation.

4.4. Procedures for samples identification - labelling

Blind labels will be utilised. Information on bottle label be a "blank" sample coded e.g. as "1", "2", "3" etc. or alternatively as deemed necessary by the participating laboratories. Table 2 shows the selection label codes that must be completed for the identification code established. In order to make the management of the information more feasible, samples description shall be indicated as a code. For instance:

- MMT from Industrial Origin as Bulk Material: NP – IO – MMT
- Polyurethane + Nanosilica Polymeric Samples, Obtained via fracture process: FP – LO – SiO₂+PU

Sample description	☐ Bulk Material – Silicon Based Nanoparticles (NP)	☐ Industrial Origin (IO)	☐ Nanosilica – SiO ₂
			☐ Layered Silicates – MMT-
			☐ Glass NanoFibres – GNF
			☐ Foam-Glass Crystal Material – FGC
	☐ Laboratory Origin (LO)		☐ Nanosilica – SiO ₂
			☐ Layered Silicates – MMT-
			☐ Glass NanoFibres – GNF
			☐ Foam-Glass Crystal Material – FGC
	☐ Sample Obtained via FRACTURE PROCESS (FP)	☐ Industrial Origin (IO)	☐ Nanosilica – SiO ₂ + PP
			☐ Nanosilica – SiO ₂ + PAs
			☐ Glass NanoFibres – GNF + PP
			☐ Glass NanoFibres – GNF + PAs
		☐ Laboratory Origin (LO)	☐ Nanosilica – SiO ₂ + PP
			☐ Nanosilica – SiO ₂ + PAs
			☐ Nanosilica – SiO ₂ + PU
			☐ Layered Silicates –MMT+ PP
			☐ Layered Silicates –MMT + PAs
			☐ Layered Silicates –MMT + PU
			☐ Glass NanoFibres – GNF + PP
			☐ Glass NanoFibres – GNF + PAs
			☐ Glass NanoFibres – GNF + PU
			☐ Foam-Glass Crystal Material –FGC + PP
			☐ Foam-Glass Crystal Material –FGC + PAs
			☐ Foam-Glass Crystal Material –FGC + PU
	☐ Sample Obtained via	☐ Industrial Origin (IO)	☐ Nanosilica – SiO ₂ + PP
			☐ Nanosilica – SiO ₂ + PAs

	ACCELERATED AGEING PROCESS (AP)	☐ Laboratory Origin (LO)	☐ Glass NanoFibres – GNF + PP
			☐ Glass NanoFibres – GNF + PAs
			☐ Nanosilica – SiO ₂ + PP
			☐ Nanosilica – SiO ₂ + PAs
			☐ Nanosilica – SiO ₂ + PU
			☐ Layered Silicates -MMT+ PP
			☐ Layered Silicates -MMT + PAs
			☐ Layered Silicates -MMT + PU
			☐ Glass NanoFibres – GNF + PP
			☐ Glass NanoFibres – GNF + PAs
			☐ Glass NanoFibres – GNF + PU
			☐ Foam-Glass Crystal Material –FGC + PP
			☐ Foam-Glass Crystal Material –FGC + PAs
			☐ Foam-Glass Crystal Material –FGC + PU
			Sample collection DATA
Sample Origin	Indicate the PROJECT PARTNER that has produced / collected /acquired the sample		
Sample Preservative MEDIUM	Indicate the sample preservative that has been used -if any-.		
Sample Reception DATA	<i>Only for those partners receiving samples to be analyzed:</i> Indicate DAY when sample was RECEIVED.		

Table 2 Labels and samples identification codes

4.5. Procedures for samples transfer

In present section procedures for the safe and effective transferring of the samples and materials of study amongst NEPHH Project partners have been established.

Existing protocols such as the Industrial Hygiene Sampling for Nanomaterials – by the Nanoscale Science Research Center-2 have been reviewed and found not applicable for NEPHH Project. Therefore specific a specific procedure has been designed.

A) SENDING THE MATERIALS THAT WILL BE ANNALYZED

4.5.1. Conditions of origin of the samples: particles in suspension

Documents detailing the original status of the particles will accompany the samples.

Since next variables have an influence on the status of the samples, they should be considered for transportation purposes.

Sample Agitation and Correct Orientation of the primary recipient: Samples should not be agitated during transportation. Additionally, in order not to spill contents, recipients should always be in vertical position. Specific supports for primary recipients shall be used with this particular aim.

Exposure to Light: Exposure to light must be avoided since many samples are photo sensible. 100 ml amber glass bottles will be used as primary recipients with this purpose.

Transportation temperature: Carriers should assure that the temperature during transportation will be ambient.

²http://www.science.doe.gov/bes/DOE_NSRC_Approach_to_Nanomaterial_ESH.pdf

Transportation Time: Courier services to be used since transportation time should be as minimum as possible, in order to avoid potential modifications of the samples in the course of the transportation.

4.5.2. Packaging

For samples in suspension amber glass bottles (also named primary containers, since they are in direct contact with the samples) should be tightly sealed to prevent leakage of nanomaterials.

It should have a secondary seal, such as tape seal, or a wire tie to prevent a removable closure from inadvertently opening during transport.

For what refers to powder samples plastic bags will be avoided and substituted by plastic tubes in order to minimize potential safety issues.

Specially for samples in suspension, the outer package should be filled with shock absorbing material that can:

- Protect the inner sample container(s) from damage.
- Absorb liquids that might leak from the inner container(s) during normal events in transport.

4.5.3. Labeling for transportation

The inner package should be labelled with the next data:

- Caution: Nanomaterials sample consisting of (technical description here).
- Contact (name of point of contact) at (contact number) in case of container breakage).

If the nanomaterial is in the form of dry dispersible particles, the following line of text should be included:

Nanoparticulates can exhibit unusual reactivity and toxicity. Avoid breathing dust, ingestion, and skin contact.

Documentation and notifications for nanomaterials transferring should include a description prepared by researchers in the in the forwarding entity describing known properties and other properties that deem reasonably likely to be exhibited by samples transported.

Additionally, a notification to receiving facility of the incoming shipment should be sent by the forwarding entity.

4.5.4. Modes of Transport

All materials should be transported by a qualified carrier. Considering the countries of origin of NEPHH Partners, air transportation is envisaged, disregarding other media such as sea or terrestrial transportation (road / train). Previous experiences with EMS – Express Mail Service have pointed such company as a suitable carrier in terms of times for delivery, amongst other.

As it has been previously mentioned, carrier must assure the maintenance of the temperature of the samples through all the transportation process.

Any incidence arisen during transportation should be documented and reported both to the samples forwarder as well as to the samples receptor.

B) RECEPTION OF THE MATERIALS THAT WILL BE ANNALYZED

The partner that is receiving the samples should proceed according to its internal organization procedures. Nonetheless, in order to assure a standard procedure and samples treatment upon reception by all Project Partners the major lines and actions to be undertaken following the reception of the samples have been listed here:

The quality and stability of the samples should be assured from the moment of reception.

The next data should be registered:

- **Identification of the sample** – According to the procedure 6.4. that has been included in present document. This should be marked in the label of origin.
- **Transportation time.** The exact date when samples have been produced should be registered in the label of origin. (Specific field in the Label – According to the procedure that has been specifically designed). Once samples have been received, the specific reception date should be registered. Time elapsed from sample acquisition / collection / production and reception will influence the acceptance or rejection of the sample. Additional information for acceptance/rejection will be obtained from the initial characterisation procedure as described in section 6.3. of present document (Procedures for samples characterisation).
- **Verification of the integrity of the sample** (register if any accidental release during transportation has occurred, for instance).
- **Name of the Project Partner that has acquired /collected/produced the sample.**
- **Name of the Project Partner that has received the sample** (ideally the name of the person that has collected it should be indicated).

4.6. Additional relevant considerations

Present section consists of a very preliminary introduction to the safety practices that should be implemented at laboratory level for the handling of nanomaterials.

4.6.1. Samples utilisation waste labelling

The product waste should be labelled in accordance with EC directives or respective national laws.

4.6.2. Disposal considerations

Observe all federal, state, and local environmental regulations. Contact a licensed professional waste disposal service to dispose of this material. Dissolve or mix the material with a combustible solvent and burn in a chemical incinerator equipped with an afterburner and scrubber.

4.6.3. Methods for cleaning

Soak up with inert absorbent material and dispose of as hazardous waste. Keep in suitable, closed containers for disposal.

4.6.4. Personal protective equipment

Present section provides just a preliminary overview as investigation will be accomplished in the frame of present task.

- Respiratory protection: Where Respiratory protection is desired, use multi-purpose combination (US) or type ABEK (EN 14387) respirator cartridges. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).
- Hand protection: For prolonged or repeated contact use protective gloves.
- Eye protection: Safety glasses
- Hygiene measures: General industrial hygiene practice.

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