Particle emissions and respiratory exposure to hazardous chemical substances associated with additive manufacturing utilising poly methyl methacrylate

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Mini-dissertation submitted in partial fulfilment of the requirements for the degree *Master of Health Sciences in Occupational Hygiene* at the North West University

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Examination: November 2019

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PREFACE

This mini-dissertation was written in article format in accordance with the specifications for the journal Annals of Work Exposures and Health. This journal requires that references in the text should be in the form Jones (1995), or Jones and Brown (1995), or Jones *et al*. (1995) if there are more than two authors. References must be listed in alphabetical order by name of first author, using the Vancouver style of abbreviation and punctuation. See Chapter 3: Guidelines for authors, for a detailed description on the referencing style.

Chapter 1 consists of a general introduction and problem statement related to additive manufacturing (AM). The research aim, objectives and hypotheses of the study are also included in this section. Chapter 2 comprises of a literature review regarding binder jetting AM, characteristics of the feedstock powder material and the binder liquid as well as particle emissions and emission rates. Chapter 3: Particle emissions and respiratory exposure to hazardous chemical substances, written in a format that meets the journal Annals of Work Exposures and Health specifications. Chapter 4 is a concluding chapter with recommendations, study limitations and future research suggestions.

AUTHORS’ CONTRIBUTIONS

This study was planned and performed by a research team. The contributions of each participating researcher are outlined in Table 1 below.

Table 1: Author contributions

Name	**Contribution**
Ms S van der Walt	• Study design and planning. • Literature research. • Conducting monitoring, data interpretation, writing of the article and formulating of recommendations. • Writing of the mini-dissertation.
Dr S du Preez	• Supervisor. • Assisting with the study planning and design. • Approving the study protocol. • Professional guidance and recommendations. • Assisted with communication with the participating university. • Assisted with interpretation of results. • Review of the mini-dissertation.
Prof JL du Plessis	• Co-supervisor. • Assisting with the study planning and design. • Approving the study protocol. • Professional guidance and recommendations. • Assisted with interpretation of results. • Review of the mini-dissertation.

The following is a statement from the supervisors that confirms each individual’s role in the study:

I declare that I have approved the article and that my role in the study as indicated above is representative of my actual contribution and that I hereby give my consent that it may be published as part of S van der Walt’s MHSc (Occupational Hygiene) mini-dissertation.

Sonette

Dr S du Preez (supervisor)

Prof JL du Plessis (co-supervisor)

ACKNOWLEDGEMENTS

I would like to express my appreciation towards those who contributed and supported me during the completion of this project:

- Dr. S du Preez and Prof. J.L. du Plessis for the opportunity to carry out this project, and for all the help, guidance and feedback they provided me with.
- The Department of Science and Technology for funding this study.
- All the personnel at the Vaal University of Technology who participated in this study, for their assistance, time, patience and positive attitude.
- Nobody has been more important to me in the pursuit of this project than my mother and Alex as their love and guidance is with me in whatever I pursue.

ABSTRACT

Title: Particle emissions and respiratory exposure to hazardous chemical substances associated with additive manufacturing utilising poly methyl methacrylate.

Background: There is limited but growing information available regarding the health hazards associated with additive manufacturing (AM). The study presented in this mini-dissertation is significant considering that no other studies have explored particle emissions or the personal exposure of AM operators to hazardous chemical substances (HCS), such as poly methyl methacrylate (PMMA) powder particles, acetone and methyl methacrylate (MMA), during binder jetting utilising PMMA and acetone.

Aims and objectives: To determine the physical characteristics and chemical composition of PMMA powder. Assess particle emissions associated with binder jetting utilising PMMA powder. Evaluate ambient workplace concentrations as well as personal respiratory exposure concentrations of the AM operator, for particles and volatile organic compounds (VOCs) (such as acetone and MMA) when PMMA powder is utilised during binder jetting AM.

Methods: Physical and chemical characterisation of virgin and used PMMA powder samples included particle size distribution (PSD), particle shape analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD) as well as X-ray fluorescence (XRF). Direct reading particle counting instruments were used to measure particle emissions and emission rates during each phase of the binder jetting process. Internationally recognised methods were used to monitor HCSs in the ambient workplace environment and personal respiratory exposure of the AM operator, during the entire binder jetting process.

Results: There were no noteworthy size differences found between median of the PSD of virgin (58.32 ± 0.52 µm) and used (58.40 ± 0.11 µm) PMMA. From SEM images, the presence of < 10 µm, and a few < 4 µm, sized particles were observed in both the virgin and used powders. PMMA powders comprised mainly of amorphous elements (> 99.23% for virgin powder). In the presence of high background ambient particle number concentrations particle emission rates as high as 3.33×10^{12} particles/min for 0.01 ~ 1.00 µm sized particles were measured during the processing phase. However, no significant differences between the AM phases were observed. Ambient 8-hour Time Weighted Average (TWA) concentrations were measured at 3.83 ± 2.12 mg/m^3 for inhalable particles, 0.77 ± 0.20 mg/m^3 for respirable particles, 15.32 ± 2.62 mg/m^3 for acetone, 0.19 ± 0.08 mg/m^3 for pentane and 0.30 ± 0.03 mg/m^3 for toluene. Personal TWA concentrations were measured at 6.22 ± 4.72 mg/m^3 for inhalable particles, 1.15 ± 0.33 mg/m^3

for respirable particles, 2.02 ± 0.58 mg/m^3 for acetone, 0.16 ± 0.07 mg/m^3 for pentane and 0.16 ± 0.05 mg/m^3 for toluene.

Conclusions: In this study, a comprehensive analysis was performed in order to determine the particle emissions and respiratory hazards, and the extent thereof, to which AM operators of PMMA binder jetting are exposed. Particles sized 0.01 ~ 1.00 µm were the most prevalent sizes emitted. Inhalable, and respirable particles, acetone, pentane and toluene were detected in the workplace atmosphere. All 8-hour TWA personal exposures were below the respective TWA Occupational Exposure Limit Recommended Limit (TWA-OEL-RL), with the exception of exposure to inhalable particles, where exposure exceeded the 10 mg/m^3 TWA-OEL-RL once and averaged above 50% of the OEL. Recommendations for elimination, substitution, engineering, administrative and personal protective equipment control measures were made to reduce exposure to inhalable particles, which could also be applied to other AM facilities making use of the same AM technology and PMMA powders. Study limitations and future studies were also discussed.

Key words:
Particle emission rates; binder jetting; occupational exposure; particle size distribution; 3D printing.

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LIST OF SYMBOLS AND ABBREVIATIONS

±	Approximately
Δt	time difference
3D	Three dimensional
ABS	Acrylonitrile Butadiene Styrene
AER	Air Exchange Rate
AM	Additive manufacturing
ANOVA	Analysis of variance
APC	Airborne Particle Counter
ASTM	American Society for Testing and Materials
ATE	Automatic Test Equipment
BDL	Below detection limit
C	Concentration of the Hazardous Chemical Substances
CAD	Computer-Aided Design
CDPH	California Department of Public Health
C_{in}	Average contaminant concentration during printing
CNC	Computer Numerical Control
C_{out}	Outdoor contaminant concentration during printing
CPC	Condensation Particle Counter
C_{peak}	Peak contaminant concentration during printing
Cu	Copper
DED	Directed Energy Deposition
DNA	Deoxyribonucleic acid
EPA	Environmental Protection Agency
ER	Emission Rates
FFF	Fused Filament Fabrication
FDM^{TM}	Fused Deposition Modelling
GC/FID	Gas Chromatography Flame Ionization Detector
HCS	Hazardous Chemical Substance
HREC	Health Research Ethics Committee
HSE	Health and Safety Executive
IOM	Institute Occupational Medicine
ISO	International Organization for Standardization
k	Contaminant loss rate due to surface deposition
LD_{50}	Lethal Dose
LEV	Local Exhaust Ventilation

LOD	Limit of Detection
MCE	Mixed Cellulose Ester
MDHS	Methods for the Determination of Hazardous Substances
MMA	Methyl methacrylate
NIOSH	National Institute for Occupational Safety and Health
OEL	Occupational Exposure Limit
OHHRI	Occupational Hygiene and Health Research Initiative
OPC	Optical Particle Counter
PBF	Powder Bed Fusion
PPE	Personal protection equipment
PLA	Polylactic acid
PMMA	Poly methyl methacrylate
PSD	Particle Size Distribution
SANAS	South African National Accreditation System
SEM	Scanning Electron Microscopy
SDS	Safety Data Sheet
SLS	Selective Laser Sintering
STEL	Short Term Exposure Limit
STL	Stereo lithography
SVHC	Substances of Very High Concern
T	Duration of exposure
T_8	Total time of exposure (8-hours)
TM	Trademark
TVOC	Total Volatile Organic Compound
TWA	Time Weighted Average
TWA-OEL-RL	Time Weighted Average – Occupational Exposure Limit – Recommended Limit
UFP	Ultrafine particles
VOC	Volatile Organic Compounds
XRD	X-ray Powder Diffraction
XRF	X-ray Fluorescence

Standard units

˚C	degrees Celsius
√	Square root
%	Percentage
<	Less than

>	Greater than
μg/m^3	Microgram per cubic metre
μm	Micrometre
L/min	Litres per minute
m^3	Cubic metre
mm	Millimetre
mm^2	Square millimetre
mg	Milligrams
mg/m^3	Milligram per cubic metre
min	Minutes
nm	Nanometre
particles/min	Particles per minute
particles/m^3	Particles per cubic metre

CHAPTER 1 INTRODUCTION

1.1. Introduction and problem statement

Additive manufacturing (AM) was developed in the late 1980s in order to manufacture models and prototype objects, and is currently regarded as the fastest growing manufacturing method in the health care, electronics and aerospace sectors (Zhou, 2015; Graff *et al*., 2016; Prasad and Devaiah, 2018). Compared to other methods of manufacturing (traditional subtractive or deformation-based manufacturing), AM has fewer geometric limitations which enables the construction of complex structures without the need to assemble various parts (Kellens *et al*., 2017; Mäntyjärvi *et al.,* 2018). The AM process relies on the fusion of raw materials (such as powders, liquid, or filamentous materials), layer upon layer to construct a final three-dimensional (3D) object, without the necessity of moulds, tools, or dyes (Khajavi *et al*., 2014; ISO/ASTM 2015; Kellens *et al*., 2017).

AM comprises of seven different process classifications that differ with regard to the materials, technologies as well as the method of layering used, namely 1) direct energy deposition (DED), 2) vat photo-polymerisation, 3) material jetting, 4) powder bed fusion (PBF), 5) material extrusion, 6) binder jetting and 7) sheet lamination (ISO/ASTM, 2015). The three most widely utilised AM technologies available, are fused deposition modelling (FDM^{TM}) in the material extrusion classification, selective laser sintering (SLS) in the PBF classification, and stereo lithography (STL) in the vat photo-polymerisation classification (Bharti and Singh, 2017). The most common feedstock materials are polymers and metal powders. Ceramics are also used as feedstock material; however, the use thereof is limited to prototypes as a result of the inability of the printed objects to meet performance criteria (Kunchala and Kappagantula, 2018). PMMA may be used as feedstock material for the fabrication of biocompatible structures for medical implants during FDM^{TM} AM (Espalin *et al.,* 2010).

The binder jetting process relies on a powder feedstock material that is fused together with a binder liquid. For the purpose of this study the focus was on poly methyl methacrylate (PMMA) as the feedstock material and acetone as the binder liquid (ISO/ASTM, 2015; Kunchala and Kappagantula, 2018). Industrial scale binder jetting involves three process phases (pre-processing, processing and post-processing) which may present different levels of inhalation and dermal exposure risks to the AM operator (Kwon *et al*., 2017). During the pre-processing phase, the object to be manufactured is designed using computer-aided design (CAD) software, along with the preparation of the AM machine which includes sieving the powder PMMA feedstock material and loading thereof and the acetone binder into the machine (Kwon *et al*., 2017). This may pose a respiratory exposure risk as these hazardous chemical substances (HCSs) may become airborne. The processing phase comprises of the manufacturing of the designed object (Gibson *et al*., 2015). According to Junk and Matt (2015) a roller generates a PMMA powder bed by compressing the powder material on top of the build chamber. A print head sweeps over the surface and selectively deposits the acetone bonding agent on top of the PMMA powder layer to bind loose powder materials, forming an individual 2-dimensional layer (Meteyer *et al.,* 2014). This procedure is repeated until the entire object has been manufactured (Meteyer *et al*., 2014, ISO/ASTM, 2015). This phase is automated and does not carry a high risk of exposure due to the enclosed building chamber preventing the feedstock material of becoming airborne (Gibson *et al*., 2015). The post-processing phase involves the removal and cleaning of the manufactured object (referred to as a green part). It may also involve the infiltration of the manufactured object with epoxy resin to yield a final product with sufficient strength, however this step is optional (Dawes *et al*., 2015; Junk and Matt, 2015). During the post-processing phase there is residual unbound powder surrounding the printed object (referred to as a green part) which may be recycled; however, loose powder may pose an inhalation and dermal exposure risk to the AM operator (Meteyer *et al.,* 2014).

PMMA is a translucent thermoplastic and a synthetic polymer of the monomer methyl methacrylate (MMA) (Odian, 2004). MMA undergoes polymerisation to produce PMMA by means of solution, suspension, and emulsion methods. Respiratory exposure to PMMA powder has been associated with acute adverse health effects such as respiratory tract irritation and coughing (Stanczyk and Van Rietbergen, 2004; American Polymer Standards Corporation, 2017). Acetone is used as a binder liquid for PMMA; thus, the polymer-solvent interaction favours contact between the polymer and solvent over polymer-polymer contact (Zhou *et al*., 2001). Respiratory exposure to acetone vapour may cause coughing, a sore throat, headache, confusion, dizziness and during severe exposure, unconsciousness (NIOSH, 2015).

The physical characteristics of powder particles utilised for AM has an effect on the quality of the final object that is manufactured. The more spherical a particle, the denser the final product. Thus, AM favours the use of spherical particles to irregular morphologies (Dawes *et al*., 2015). According to Tang *et al.* (2015), the remaining powder surrounding the manufactured object may be reused. However; the particles become less spherical with increasing reuse, which may result in a less dense final product. Particle size and shape is relevant from a respiratory health perspective as it has an influence on where the particles may deposit in the respiratory tract when inhaled (Plog and Quinlan, 2001; Hoet *et al*., 2004, Mellin *et al.,* 2016). According to Brown *et al.* (2013), size-selective monitoring is used to sample for particle sizes that are related to specific pathological outcomes. Particles may be categorised according to their location of deposition in the respiratory tract, namely the thoracic fraction, tracheobronchial fraction, respirable fraction and inhalable fraction (ISO 7708:1995). The thoracic fraction is the mass fraction of the inhaled particles which may penetrate beyond the larynx. The tracheobronchial fraction is the mass fraction of inhaled particles which may penetrate beyond the larynx but not the unciliated airway. The respirable fraction is the mass fraction of the inhaled particles which may penetrate the unciliated airway, such as the alveolar region of the lung. The inhalable fraction is the mass fraction of particles that is aspirated into the mouth and nose during normal breathing and may deposit anywhere in the respiratory tract (British Standards Institution, 1993; ISO 7708:1995; Brown *et al.*, 2013). Therefore, it is important to consider the behaviour of different particle sizes and shapes and the respiratory risk they may pose. Smaller particles, such as ultrafine particles (UFPs, < 100 nm) that are inhaled, tend to penetrate deeper into the alveolar region than larger particles, and macrophage-mediated clearance in the alveoli clears such fine particles form the lungs, albeit is slower than mucocilliary clearance in the conducting airways (Mellin *et al*., 2016).

Many AM machines and filament combinations have been shown to emit particles, whereas others have been shown to emit hazardous volatile organic compounds (VOCs) such as styrene and caprolactam (Azimi *et al*., 2016). According to Afshar-Mohajer (2015) and Vaisanen *et al*. (2019), particles and VOCs are emitted during binder jetting. This is a result of the feedstock powder material [zp®150 composite powder (gypsum, calcium sulphate), <10 µm] in the printing chamber moving continuously as well as the injection of the binder liquid (zb®60 binder solution). Particle emission rates refer to the mass of particles that is released by an entire object per unit of time. Particle emission rates from material extrusion AM processes (i.e. FDM™ printers) have been reported extensively (Stephens *et al*. 2013; Zhou *et al*. 2015; Azimi *et al*., 2016; Steinle, 2016; Deng *et al*., 2016; Yi *et al*., 2016; Azimi *et al*., 2017; Zontek *et al*., 2017; Mendes *et al*., 2017). However, for binder jetting this is limited to a single study utilising gypsum powder (Afshar-Mohajer *et al*., 2015). The highest particle emission rate was 4.4×10^4 particles/min for particles 205 to 407 nm in size during the post-processing (ejecting) phase. They did not consider personal exposure of the AM operator to particles or VOCs. However, total volatile organic compound (TVOC) concentrations in the manufacturing area were measured at 1725 µg/m^3. The study presented in this mini-dissertation is significant considering that no other studies have explored particle emissions or the personal exposure of the AM operators to HCS (particles and VOCs) during binder jetting utilising PMMA and acetone.

1.2. Research aim and objectives

1.2.1. The research aim:

To determine the physical characteristics and chemical composition of PMMA powder, assess particle and VOC emissions as well as the workplace respiratory exposure of AM operators to HCS (such as inhalable and respirable particles and VOCs including acetone and MMA) when PMMA powder is utilised during industrial scale binder jetting AM.

1.2.2. The research objectives:

1. To determine the physical characteristics and chemical composition of the PMMA powder utilised during binder jetting AM. The Malvern Morphologi G3 (Malvern Instruments Ltd, UK) was used to quantify particle size distribution (PSD) and shape. Scanning Electron Microscopy (SEM) was used to determine the physical characteristics, external particle morphology, and structure of PMMA samples. X-ray Powder Diffraction (XRD) and X-ray fluorescence (XRF) were used to determine the elemental composition.
2. To determine particle emissions associated with binder jetting utilising PMMA powder by means of direct reading particle counting instruments throughout the three phases of binder jetting AM.
3. To assess ambient concentrations as well as personal respiratory exposure concentrations of the AM operator, for particles and VOCs (such as acetone and MMA) associated with binder jetting by means of area and personal sampling for the duration of the AM process.

1.3. Hypotheses

Hypothesis 1:

Afshar-Mohajer *et al.* (2015) found that particles and VOCs were emitted during binder jetting utilising gypsum powder. They have found that the AM phase with the highest particle emissions is the (removal) post-processing phase. However, powder handling during the pre-processing phase may also cause powder particles to become airborne. It is therefore, hypothesised that inhalable particles are be emitted into the workplace environment during the entire binder jetting AM process utilising PMMA as feedstock material.

Hypothesis 2:

According to Geiss *et al.* (2016), relying only on area sampling may underestimate the concentrations of HCSs to which a person/worker is exposed. Additional personal exposure monitoring must be conducted to quantify exposure to particles and VOC's more accurately (Azimi *et al.,* 2016). It is hypothesised that the AM operators are exposed through inhalation to quantifiable concentrations of HCSs (such as inhalable and respirable particles, MMA and acetone) during binder jetting utilising PMMA and acetone.

1.4. References

Afshar-Mohajer N, Wu C, Ladun T, Rajon DA, Huang Y. (2015) Characterisation of particulate matters and total VOC emissions from a binder jetting 3D printer. Build Environ; 93: 293-301.

American Polymer Standards Corporation. (2017) Polymethyl methacrylate. Available from http://www.ampolymer.com/SDS/PolymethylMethacrylateSDS.html# (accessed 6 May 2018).

Azimi P, Zhao D, Pouzet C, Crain NE, Stephens B. (2016) Emissions of ultrafine particles and volatile organic compounds from commercially available desktop three-dimensional printers with multiple filaments. Environ Sci Technol; 50: 1260-1268.

Azimi P, Fazli T, Stephens B. (2017) Predicting concentrations of ultrafine particles and volatile organic compounds resulting from desktop 3D printer operation and the impact of potential control strategies. J Ind Ecol; 21: 107-119.

Bharti N, Singh S. (2017) Three-dimensional (3D) printers in libraries: perspective and preliminary safety analysis. J Chem Educ; 94: 879-885.

British Standards Institution. (1993) BS EN 481:1993, BS 6069-3.5:1993 Workplace atmospheres – size fraction definitions for measurement of airborne particles. Available from https://www.techstreet.com/standards/bs-en-481-1993?product_id=1115108 (accessed 23 September 2018).

Brown JS, Gordon T, Price O, Asgharian B. (2013) Thoracic and respirable particle definitions for human health risk assessment. Part Fibre Toxicol; 10:1-12.

Dawes J, Bowerman R, Trepleton R. (2015) Introduction to the additive manufacturing powder metallurgy supply chain. Johnson Matthey Tech; 59: 243-256.

Deng Y, Cao S, Chen A, Guo, Y. (2016) The impact of manufacturing parameters on submicron particle emissions from a desktop 3D printer in the perspective of emission reduction. Build Environ; 104: 311-329.

Geiss O, Bianchi I, Barrero-Moreno J. (2016) Lung-deposited surface area concentration measurements in selected occupational and non-occupational environments. J Aerosol Sci; 93: 24-37.

Gibson I, Rosen D, Stucker B. (2015) Additive manufacturing technologies: 3D printing, rapid prototyping, and direct digital manufacturing. Virgin York, NY: Springer. ISBN 1 493 92113 4.

Graff P, Ståhlbom B, Nordenberg E, Graichen A, Johansson P, Karlsson H. (2016) Evaluating measuring techniques for occupational exposure during additive manufacturing of metals: a pilot study. J Ind Ecol; 21: 120-129.

Hoet P, Bruske-Hohlfeld I, Salata O. (2004) Nanoparticles - known and unknown health risk. J Nanobiotechnology; 2: 1-15.

International Organization for Standardization (ISO). (1995). Air quality – particle size fraction definitions for health-related sampling (ISO 7708:1995). Available from https://www.sis.se/api/document/preview/20338/ (accessed 6 May 2018).

ISO/ASTM. (2015) 52900-15 Standard terminology for additive manufacturing – general principles – terminology. ISO/ASTM International, West Conshohocken, PA. Available from www.ISO/ASTM.org (accessed 6 May 2018).

Junk S, Matt R. (2015) Application of polymer plaster composites in additive manufacturing of high-strength components. Mater Sci Forum; 825-826: 763-770.

Kellens K, Mertens R, Paraskevas D, Dewulf W, Duflou J. (2017) Environmental impact of additive manufacturing processes: does am contribute to a more sustainable way of part manufacturing. Procedia CIRP; 61: 582-587.

Khajavi SH, Partanen J, Holmström J. (2014) Additive manufacturing in the spare parts supply chain. Comput Ind; 65: 50-63.

Kunchala P, Kappagantula K. (2018) 3D printing high density ceramics using binder jetting with nanoparticle densifiers. Mater Des; 155: 443-450.

Kwon O, Yoon C, Ham S, Park J, Lee J, Yoo D, Kim Y. (2017) Characterisation and control of nanoparticle emission during 3D printing. Environ Sci Technol; 51: 10357-10368.

Mäntyjärvi K, Junno T, Nemi H, Mäkikangas J. (2018) Design for additive manufacturing in extended dfma process. Key eng; 786: 342-347.

Mellin P, Jönsson C, Åkermo M, Fernberg P, Nordenberg E, Brodin H, Strondl A. (2016) Nano-sized by-products from metal 3D printing, composite manufacturing and fabric production. J Clean Prod; 139: 1224-1233.

Mendes L, Kangas A, Kukko K, Mølgaard B, Säämänen A, Kanerva T, Flores Ituarte I, Huhtiniemi M, Stockmann JH, Partanen J, Hämeri K, Eleftheriadis K, Viitanen A. (2017) Characterisation of emissions from a desktop 3D printer. J Ind Ecol; 21: 94-106.

Meteyer S, Xu X, Perry N, Zhao Y. (2014) Energy and material flow analysis of binder-jetting additive manufacturing processes. Procedia CIRP; 15: 19-25.

National Institute for Occupational Safety and Health (NIOSH). (2015) Acetone icsc: 0087. Available from https://www.cdc.gov/niosh/ipcsneng/neng0087.html (accessed 21 November 2018).

Odian, G. (2004) Principles of polymerization fourth edition. Staten Island, NY: John Wiley and Sons Inc. ISBN 9 780 47147 875 1.

Plog BA, Quinlan PJ. (2001) Fundamentals of industrial hygiene fifth edition. Illinois,USA: National Safety Council Press. ISBN 0 879 12216 1.

Prasad TS, Devaiah M. (2018) Manufacturing of die using rapid prototyping technique. IUP J Mech Eng; 11: 69-79.

Stanczyk M, Van Rietbergen B. (2004) Thermal analysis of bone cement polymerisation at the cement–bone interface. J Biomech; 37: 1803-1810.

Steinle P. (2016) Characterisation of emissions from a desktop 3D printer and indoor air measurements in office settings. J Occup Environ Hyg; 13: 121-132.

Stephens B, Azimi P, El Orch Z, Ramos T. (2013) Ultrafine particle emissions from desktop 3D printers. Atmos Environ; 79: 334-339.

Tang H, Qian M, Liu N, Zhang X, Yang G, Wang J. (2015) Effect of powder reuse times on additive manufacturing of Ti-6Al-4V by selective electron beam melting. J Occup Med; 67: 555 – 563.

Vaisanen AJK, Hyttinen M, Ylonen S, Alonen L. (2019) Occupational exposure to gaseous and particulate contaminants originating from additive manufacturing of liquid, powdered, and filament plastic materials and related post-processes. Occup Environ Hyg; 16:258-271.

Yi J, Nurkiewicz T, LeBouf RF, Duling MG, Chen BT, Schwegler-Berry D, Virji MA, Stefaniak AB. (2016) Emission of particulate matter from a desktop three-dimensional (3D) printer. J Toxicol Environ Health-Part A; 79: 453-465.

Zhou XD, Zhang SC, Huebner W, Ownby PD, Hongchen G. (2001) Effect of the solvent on the particle morphology of spray dried pmma. J Mater Sci; 36: 3759-3768.

Zhou Y, Kong X, Chen A, Cao S. (2015) Investigation of ultrafine particle emissions of desktop 3D printers in the clean room. Procedia Eng; 121: 506-521.

Zontek TL, Ogle BR, Jankovic JT, Hollenbeck SM. (2017) An exposure assessment of desktop 3D printing. Chem Health Saf; 24: 15-25.

CHAPTER 2 LITERATURE REVIEW

2.1. Introduction

In this chapter the use of polymer powders in additive manufacturing (AM) as well as the properties, use and adverse health effects of poly methyl methacrylate (PMMA), methyl methacrylate (MMA) and acetone, the particles (powder) and volatile organic compounds (VOCs) used during binder jetting, will be reviewed. Further, information on the characterisation of particles and the importance thereof from an occupational hygiene perspective will also be provided. The respiratory tract will be discussed for a better understanding of the mechanisms of deposition and clearance of inhaled particles. Previous studies involving emission rates of particles from AM machines/technologies, in particular binder jetting, will be deliberated, whereas VOCs, and the importance thereof will be defined together with the relevant occupational exposure limits (OELs).

2.2. Additive manufacturing

The AM process relies on the design of three-dimensional (3D) models by making use of computer-aided design (CAD) data, and joining raw materials layer upon layer to produce a final 3D product without the requirement of moulds, tools, or dyes (ISO/ASTM, 2015; Kellens *et al.*, 2017; Kwon *et al.*, 2017). Therefore, it is differentiated from traditional subtractive or deformation-based manufacturing methodologies, such as conventional machining or forming processes (Kellens *et al*., 2017). Awareness of AM has grown due to its potential to increase the intricacy of designs and modification of objects, while also decreasing the cost, waste, and shipment that is related with the supply-chain activity (Meteyer *et al.,* 2014; Bours *et al*., 2017).

The health care, electronics and aerospace sectors recognise AM as a powerful source for the manufacturing of intricate structures. However, this fact raises several uncertainties regarding the emission of hazardous chemical substances (HCSs) as well as the possible respiratory health risks to the AM operators (Zhou *et al.*, 2015; Graff *et al.,* 2016). Studies have suggested that exposure to AM emissions could be related to certain health effects such as allergic responses in persons sensitised to chemicals used in the AM industry (such as epoxies and urethanes). Inhalation exposure of particles may cause decreased lung function and respiratory tract inflammation (WHO, 1999). Ultra-fine particles (UFPs) (particles with an aerodynamic diameter of less than 100 nm) to which AM operators are exposed may accumulate in the alveolar and pulmonary regions of the lungs, causing irritation of the airways and mucus membranes (Deak, 1999; Deng *et al.,* 2016; Steinle, 2016).

AM comprises of seven different process classifications with differences regarding the materials, technologies as well as the method of layering used. The process classifications are 1) binder jetting, 2) vat photo-polymerisation, 3) material jetting, 4) powder bed fusion (PBF), 5) material extrusion, 6) direct energy deposition (DED) and 7) sheet lamination (ISO/ASTM, 2015). The three most widely utilised AM technologies available, are fused deposition modelling (FDM^{TM}) in the material extrusion classification, selective laser sintering (SLS) in the PBF classification, and stereo lithography (STL) in the vat photo-polymerisation classification (Bharti and Singh, 2017). The focus of this study is on the binder jetting AM technology utilising the polymer powder PMMA as feedstock material.

2.2.1. Binder jetting technology

Most polymers available for use during binder jetting AM such as PMMA, are based on polyamide 12 and polyamide 11 basic polymers (Schmid and Wegener, 2016). Other potential binder jetting feedstock materials include metal powder, calcium sulphate (gypsum), ceramic powder and virtually any feedstock material in powdered form. Therefore, binder jetting is an appropriate platform to devise material innovations (Afshar-Mohajer *et al.*, 2015; Bai and Williams, 2018; Mirzababaei and Pasebani, 2019; Ziaee and Crane, 2019).

The binder jetting process involves coupling structural powder materials on the powder bed (also referred to as a filler material) with a binder liquid that is selectively deposited by a print head (Figure 1) (ISO/ASTM, 2015; Kunchala and Kappagantula, 2018). The binder liquid utilised during binder jetting determines if the green part (refers to a manufactured object which has limited strength) will have the adequate green strength and density. Therefore, the choice of binder liquid is critical. Potential binding liquids include, polymer-based ink, solvents and colloids (Bai and Williams, 2018). A green part can be strengthened through infiltration of epoxy resin or cyanoacrylate after the object has been manufactured and de-powdered (Junk and Matt, 2015).

The binder jetting process comprises of a powder material and a liquid binder (Figure 1) (ISO/ASTM, 2015). According to Junk and Matt (2015) a roller generates a powder bed by compressing the powder material on top of the build platform. A print head sweeps over the surface and selectively deposits a liquid binder on top of the powder layer (Meteyer *et al.,* 2014). The binder liquid droplets interact with powder particles to bind loose powder materials to form an individual 2-dimensional cross-sectional layer (Figure 1) (Meteyer *et al.,* 2014; Bai and Williams, 2018). After deposition of the liquid binder, the powder bed may be exposed to thermal energy through heating lamps, however, this step is optional depending on the AM machine used. This is done to introduce sufficient mechanical strength into the object being manufactured aiming at enduring gravitational forces involved in the following printing processes (Miyanaji, 2018). Thorough saturation from the binder liquid is limited to the outline of the object being manufactured. The middle area of the object is only saturated approximately 50% to prevent soaking of the powder. However, there is a spatial framework of fully saturated areas applied to the inside of the object to increase the strength of the manufactured object (Junk and Matt, 2015). Once the liquid binder is deposited, movement of these droplets inside the powder pores occurs by means of capillary pressure and the surface tension-induced pressure gradient between the liquid binder and air. An equilibrious state in the process is established when a balance of the capillary pressure across all binder-air interfaces is reached, thus the liquid binder stops migrating within the powder bed. The binder saturation level is defined as the ratio of liquid binder volume to the pore volume of the powder bed. Equilibrious saturation determines the required saturation level for effective formation of green parts (objects) (Miyanaji, 2018). The feed platform is elevated by the thickness of the successive layer while the build platform is depressed by the same measure (Meteyer *et al.,* 2014). An additional powder layer is then spread over the preceding layer (Miyanaji, 2018). The 3D object is formed where the powder is bound to the liquid, with reactive curing (ISO/ASTM, 2015). The procedure is repeated until the entire green part has been manufactured (Meteyer *et al.,* 2014; ISO/ASTM, 2015).

The residual unbound powder in the powder bed remains in position surrounding the manufactured object to support the manufactured object during the building process (Meteyer *et al.,* 2014, Bai and Williams, 2018). According to Junk and Matt (2015) a resting period of approximately 60 to 90 minutes after the printing process is necessary. However, according to Rojas-Nastrucci *et al.* (2017) powdered stainless steel requires curing of the binder liquid in the oven for four hours at a temperature of 185 °C. The excess powder is then removed by vacuum or blown off using compressed air (de-powdering). De-powdering is done in order to remove excessive powder causing inaccuracies in the linear dimension, from the manufactured object (Wang and Zhao, 2017). The surplus powder may be reused immediately without special treatment (Junk and Matt, 2015).

Optionally, following de-powdering, the green part may be put into an incinerator to burn off the binder, to sinter powder particles together and to solidify the object (Figure 1) (Bai and Williams, 2018; Wang and Zhao, 2017). This is done in order to gain ultimate strength and density of the manufactured object (Junk and Matt, 2015; Wang and Zhao, 2017; Bai and Williams, 2018; Kunchala and Kappagantula, 2018). Infiltration involves the submerging of the manufactured object in a solution containing an infiltrant material. The infiltrant will fill the pores between particles (also referred to as the inter-particle pores) of the object by means of capillary action (Kunchala and Kappagantula, 2018). During binder jetting, the manual infiltration of epoxy resin or cyanoacrylate only penetrates the inter-particle pores on the surface area of the manufactured object, while the interior pores of the object is not reached by the infiltrant (Junk and Matt, 2015). Thus, the efficiency of infiltration by the infiltrant is dependent on the inter-particle pore network connectivity that has developed in the manufactured object (Kunchala and Kappagantula, 2018). The manufactured object has areas of inhomogeneity due to the inter-particle pore network not being connected throughout the entire object (Kunchala and Kappagantula, 2018). Therefore, this process is only appropriate for simple tools, and components that are mechanically highly stressed may not be realised (Junk and Matt, 2015).

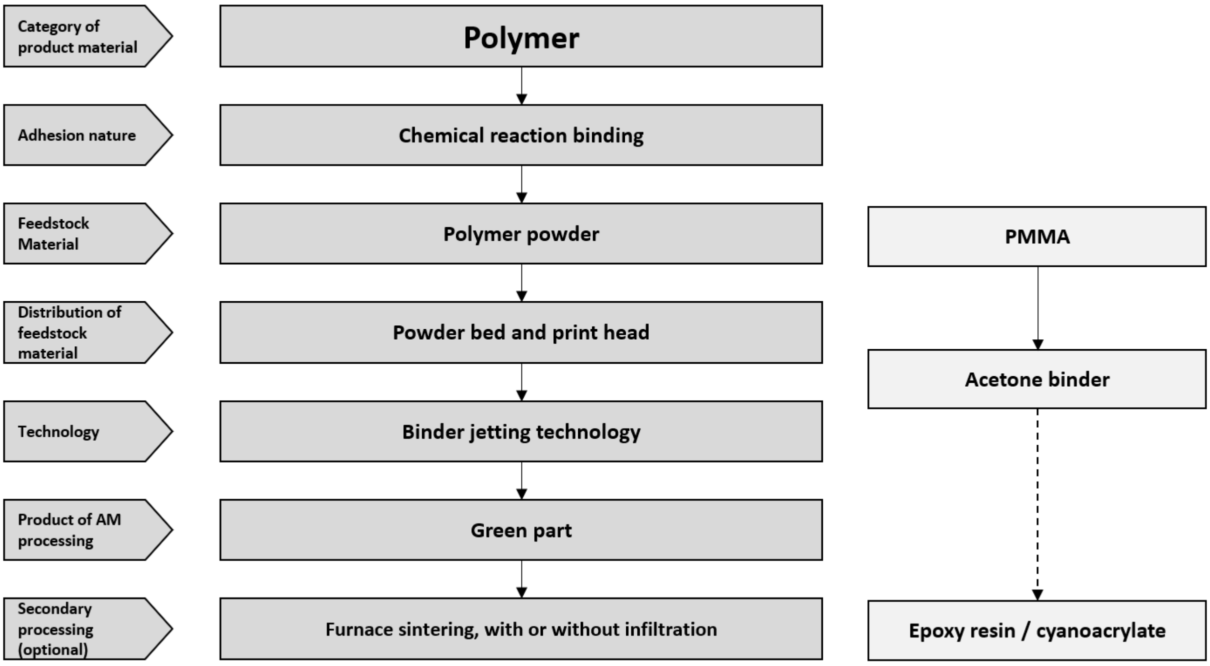

Figure 1: Overview of binder jetting principles for polymer powder, and representation applicable to this study. Optional infiltration is not included in this study (adapted from Voxeljet, 2014; ISO/ASTM, 2015).

2.3. Potential respiratory exposure

AM consists of three production phases namely pre-processing, processing and post-processing (Kwon *et al*., 2017). To date it is not yet known to what extent the AM operator is exposed to particles and VOCs by means of inhalation during industrial scale binder jetting AM utilising PMMA.

2.3.1. Pre-processing phase

During the course of the first phase (pre-processing), the object to be manufactured is designed using CAD software (Shi *et al.,* 2018). This is a computer-based activity and therefore, there is no expected respiratory exposure to HCSs involved during this task. However, there may still be a risk of inhalation of the hazardous substances if the CAD process is being performed in the same room that the manufacturing task takes place. This is followed by the preparation of the AM machine which includes sieving the powder feedstock material (in this study, PMMA); the loading thereof into the machine, as well as weighing and loading of the binder liquid (in this study, acetone) into the feed system (Kwon *et al*., 2017). This part of the pre-processing task may pose a significant respiratory exposure risk when the particles become airborne during handling and loading.

2.3.2. Processing phase

The second phase (processing) comprises of the manufacturing of the 3D object that has been designed. This phase of production is automated and does not carry a high risk of exposure due to the process taking place inside an enclosed build chamber preventing feedstock powder from becoming airborne (Aubin, 1994; Gibson *et al.,* 2015). However, respiratory exposure to airborne contaminants may still occur due to HCSs being accidentally released from openings in the build chamber. Conversely, a study carried out by Bours *et al*. (2017) indicated that the majority of the detectable HCSs were released during the processing phase, and the exposure routes vary subject to the type of AM technology utilised. Consequently, AM operators may be exposed to particles and VOCs during this phase (Azimi *et al*., 2016; Bours *et al*. (2017).

2.3.3. Post-processing phase

The final phase (post-processing) is where the manufactured object is removed from the AM machine, cleaned and refined to produce a product which may be (optionally) strengthened with an infiltrant in order to yield a sufficiently durable final product (Dawes *et al.,* 2015; Junk and Matt, 2015). Techniques used for post-processing may potentially contribute to exposure to hazards (Gibson *et al*., 2015). During the post-processing phase of binder jetting there is residual unbound powder surrounding the manufactured object which may be recycled. However, loose powder may pose an inhalation risk (Meteyer *et al.,* 2014). This is presumably the phase in which there is the highest levels of exposure to HCSs, due to the building platform being opened (Graff *et al.,* 2016). According to a study carried out by Afshar-Mohajer *et al.* (2015), on binder jetting utilising gypsum, powder particles have the highest emission rates during the period where the printer has just been turned off and the top cover removed for the extraction of the manufactured object.

2.4. Poly methyl methacrylate feedstock material

This study focuses on PMMA powder as feedstock material during binder jetting. As stated by Odian (2004), acrylics such as PMMA is a translucent thermoplastic with a high strength-to-weight ratio and is not affected by moisture. It is a synthetic polymer of the monomer methyl methacrylate (MMA). MMA undergoes polymerisation, producing PMMA by using solution, suspension, and emulsion methods.

Neoss Limited (2010) and the American Polymer Standards Corporation (2017), found that PMMA is chemically stable, and no hazardous decomposition products are released under standard conditions of use and storage. However, in environments where PMMA is exposed to fire or ignition sources, carbon oxides such as carbon monoxide and carbon dioxide may be released (Hoehn Plastics Inc, 2011; Neoss Limited, 2010). Decomposition products of PMMA at a temperature of 260 °C include the formation of 2-methyl-oxirane, methyl ester, carbonic acid, dimethyl itaconate and predominantly MMA (95.5%). Decomposition products at a temperature of 300 °C include primarily MMA, and much smaller molecules, such as water, carbon monoxide, carbon dioxide, methane and methanol. However, according to Konda Gokuldoss *et al*. (2017) the binder jetting process does not necessarily involve the use of heat during the building process, unlike some other AM processes.

2.4.1. Uses of poly methyl methacrylate

According to Odian (2004), bulk polymerisation and suspension polymerisation are used to produce polymethacrylate moulding powders. Rigid methacrylate polymer products include applications such as lighting, lenses (such as cell phone lenses, touch screens and automobile light lenses), bathtubs, and shields surrounding hockey rinks (Campbell, 2015; Odian, 2004). PMMA is used as a substitute for inorganic glass and was initially applied in World War II when it was used as aircraft windows and bubble canopies for gun turrets (Ali *et al.,* 2015). It was used for windows due to its 90% transparency and shatter resistant characteristic that can endure weather conditions and ultraviolet radiation (Campbell, 2015).

Solution and emulsion polymerisations are used to produce acrylate and methacrylate polymer products for non-rigid applications such as coatings, textiles and sealants. Trade names for acrylate and methacrylate polymer products include Plexiglass®, Acrylate, Rhoplex, Dicalite, and Lucite (Odian, 2004). PMMA has light transmitting properties that is valuable as optical fibres that are used in telecommunications and endoscopy (Campbell, 2015).

Ligon *et al.* (2017) found that blocks utilised for computer numerical control (CNC) milling of artificial teeth are frequently based on PMMA, this is attributable to its stability and durability. For this reason, it is also used to manufacture furniture and jewellery (Campbell, 2015). In prosthetic and orthopaedic applications, it may also be used as a substitute for screws to adhere an implant to surrounding tissue (Campbell, 2015).

PMMA is used as feedstock material during binder jetting AM (Polzin *et al*., 2013). According to Espalin *et al.* (2010) PMMA may be used as feedstock material for the fabrication of biocompatible structures for medical implants during FDM^{TM} AM.

2.4.2. Adverse health effects of poly methyl methacrylate

Despite the beneficial properties of PMMA, adverse health effects have also been associated with the use of, and exposure to this substance (Stanczyk and Van Rietbergen, 2004). Possible routes of exposure to PMMA include inhalation, skin and eye contact (Neoss Limited, 2010). For the purpose of this study the focus will be on respiratory exposure of AM operators. Acute adverse health effects of PMMA when inhaled include respiratory tract irritation and coughing (American Polymer Standards Corporation, 2017).

PMMA requires more attention regarding its adverse health effects, due to the lack of information available regarding teratogenicity, endocrine disrupter, mutagenic, reproductive and developmental effects (American Polymer Standards Corporation, 2017). PMMA fillers injected into the midface, used to reduce rhytids and treat hollows, is associated with chronic inflammation, eyelid malposition, fibrotic nodules as well as yellowing of the skin (Limongi *et al.,* 2016). Findings from a study carried out by Anancharungsuk *et al.* (2010) showed that the cytotoxicity of sulphur-prevulcanised natural rubber, a material for glove manufacturing, can be considerably reduced by coating the rubber film with PMMA particles. The major shortcomings of PMMA cement that is used in dental and orthopaedic procedures, are the risks of thermal necrosis of surrounding tissue as a result of the generation of high heat in the course of polymerisation and cytotoxicity/chemical necrosis owing to tissue exposure to residual MMA release (Razuin *et al.,* 2013*;* Stanczyk and Van Rietbergen, 2004).

MMA, the main decomposition product of PMMA, is a highly flammable substance. It requires more attention regarding respiratory health effects. Repeated or prolonged exposure may cause skin sensitisation and asthma and may have adverse effects on the nervous system (Dormer *et al.*, 1998). MMA has also been associated with bone cement implantation syndrome. This syndrome is characterized by hypotension, hypoxia, cardiac arrhythmias, as well as cardiac arrest (Razuin *et al.,* 2013*)*.

2.4.3. Particle emissions during AM

According to Azimi *et al*. (2016), the extent and shape of the submicron particles emitted from AM is influenced by the type of printer, feedstock material used, shape of the object being manufactured and the print head. Zhang *et al*. (2017) conducted a study regarding UFP (< 100 nm) emissions from a commercial material extrusion FDM^{TM} AM machine utilising acrylonitrile butadiene styrene (ABS) as feedstock material. It was found that the maximum particle emissions were higher than 10^6 particles/cm^3 (10^{12} particles/m^3) for particles in the size range of 20 nm to 40 nm. This occurred in the period of time that the AM machine was switched on. Binder jetting utilising gypsum powder emitted fine particles due to the continuous movement of powder particles inside of the AM machine chamber. They have found that the highest particle concentration was 0.9-1.16 × 10^4 particles/cm^3 (0.9-1.16 × 10^{10} particles/m^3) for submicron particles with sizes 205 nm to 255 nm during the processing phase (Afshar-Mohajer *et al.*, 2015).

Prolonged or repeated exposure to the PLA utilised in binder jetting may cause adverse health effects such as lung diseases, chest pain, coughing as well as eye irritation and exposure to the resin-like binder solution used may irritate mucous membranes, the upper respiratory tract and cause nausea and headache (Afshar-Mohajer *et al.,* 2015). UFPs may effortlessly cross biological barriers and enter the bloodstream. This may affect several different physiological systems in the body such as the gastrointestinal tract and the liver. However, larger particles (100 – 1000 nm) may also be detrimental to health (Mellin *et al.,* 2016). Particles may coagulate during the first few minutes after emission of high concentrations of UFPs, thus leading to larger particles being formed that would result in deposition of these particles in different areas of the respiratory tract (Stephens *et al.,* 2013).

Bharti and Sing (2017) performed a study to determine the health and safety effects when using FDM^{TM} printers, utilising ABS and polylactic acid (PLA) as feedstock material, in libraries. This study indicated that the concentration of UFPs released during the AM process is 36 to 60 times higher than the background concentration of UFPs. Exposure to UFPs have been linked to adverse health effects as it may enter the pulmonary interstitium and cause pulmonary inflamation (Oberdörster, 2000). Stephens *et al.* (2013) suggests that environments where AM is carried out must be well ventilated due to the possible high concentration of UFP emissions. Different types of materials used in AM each cause UFP emissions with different chemical constituents. The variation may also be caused by the condensation of the synthetic organic vapours from the thermoplastic feedstock. According to a study carried out by Kim *et al.* (2015) the anticipated vast growth of AM requires that more research and preventative control measures must be implemented to protect the health of operators of such printers. Most studies emphasise the process phases of AM in order to obtain information regarding the emissions of each phase. Therefore, there is a need for information regarding the ambient concentration as well as personal exposure to HCSs during the complete AM process. However, it is also necessary to identify the phase or phases of binder jetting utilising PMMA where there will be the highest level of particle emissions as well as emission rates.

2.4.4. Particle emission rates

Emission rate refers to the mass of HCS that are released by an entire object per unit of time, whereas, the specific emission rate refers to the emission rate that is normalised to the area, length or mass of an object (CDPH, 2010). There is insufficient information available regarding emission rates during the binder jetting process (Afshar-Mohajer *et al.,* 2015). Afshar-Mohajer *et al.* (2015) has conducted a study on the characterisation of particle emissions from a binder jetting 3D printer utilising gypsum. An optical particle counter (OPC) (model 1.108, Grimm Technologies Inc., Douglasville, GA) direct reading instrument was used. The findings suggested that powder particles with sizes between 205 and 407 nm had the highest emission rates (4.4×10^4 particles/min) during the period where the printer had just been turned off and the top cover removed for the extraction of the manufactured object. UFP emissions were found to be four to five magnitudes lower for binder jetting with gypsum powder than that of Fused Deposition Modelling (FDM^{TM}) AM processes using PLA. Nevertheless, there was substantially higher emissions of particles larger than 200 nm.

A study carried out by Stabile *et al.* (2017) found that emission rates of particles increased as a function of the increase in extrusion temperature during FDM^{TM} with an inexpensive material extrusion desktop 3D printer. Results from this study indicated that materials emit UFP. However, super-micron particle (particles with an aerodynamic diameter > 1 µm) emissions were not detected. It was predicted that emission rates of 10^{12} particles/min might cause large alveolar surface area dose (up to 200 mm^2 for a 40-minute printing time) in workers during AM activities (Stabile *et al.,* 2017). Stefaniak *et al.* (2018) carried out a study to evaluate the workplace atmospheres in four different facilities that make use of desktop fused filament fabrication (FFF) 3D printers. Direct reading particle counter instruments were used in order to measure the concentration and diameter of airborne particles as well as the total volatile organic compound (TVOC) concentrations. Particle emission rates for FFF 3D printers ranged from 9.4×10^9 to 4.4×10^{11} particles/min. Therefore, Stefaniak *et al.* (2018) found that emission rates from different 3D printers, operating conditions and feedstock materials may reflect variability (Stefaniak *et al.,* 2018).

He *et al.* (2004) performed a study in which the emission characteristics (particle number and mass concentration) of indoor particle sources were measured and quantified in 15 residential houses. It is suggested that the particle number concentration has a greater relation to the probable health effects than the particle mass concentration (He *et al.,* 2004). He *et al. (*2004) found that indoor activities such as cooking, smoking and the use of fan heaters can raise the number concentration of particles by 1.5 to more than 27 times.

Stabile *et al.* (2017) and Stefaniak *et al.* (2018) made use of an equation derived from He *et al.* (2004), to describe the emission source in indoor environments, in order to calculate the particle emission rates (particles/min).

$$\mathrm{ER} = \mathrm{V} \cdot \left[\frac{\mathrm{C_{peak}} - \mathrm{C_{out}}}{\Delta \mathrm{t}} + \overline{\mathrm{AER} + \mathrm{k}} \cdot \bar{\mathrm{C}}_{\mathrm{in}} - \mathrm{AER} \cdot \mathrm{C_{out}}\right] \qquad \text{Equation 1}$$

Where V is the volume of the room (m^3), C_{peak} is the peak contaminant concentration during the AM phase (particle number/m^3), C_{out} represents the outdoor contaminant concentration during the AM phase (it is assumed to be equal to the indoor background particle concentration) (particle number/m^3) (Stefaniak *et al*., 2018). Δt is the time difference between C_{peak} and C_{out} (min), AER represents the air exchange rate in the room (air exchange/h), k is the contaminant loss rate due to surface deposition. $\bar{C}_{in}$ represents the average contaminant concentration during the AM phase (particle number/m^3). AER is taken as 0.22/h if there is no mechanical air movement in the room and k is taken as 1/h in an indoor environment (Stabile *et al*., 2017; Stefaniak *et al*., 2018).

2.5. Acetone binder liquid

According to Zhou *et al*. (2001) acetone and tetrahydrofuran are both solvents for PMMA and may be used as a binder liquid during binder jetting. However, tetrahydrofuran has a much weaker interaction with PMMA compared to acetone. Acetone is a strong solvent for PMMA due to the polymer-solvent interaction that favours contact between polymer and solvent over polymer-polymer contact. Acetone is a VOC and is a Lewis base, giving an electron pair to a receiver compound, and a thermodynamically preferred solvent (Zhou *et al.,* 2001). The acetone diffuses into PMMA to yield a homogenous solution with the solvent. This strong interaction between acetone and PMMA results in the formation of porous particles (Zhou *et al.,* 2001; Ali *et al.,* 2015).

2.5.1. Uses of acetone

Occupational exposure to acetone typically occurs in conjunction with exposure to other solvents. Acetone can be used as a chemical intermediate and solvent (Reisman, 1998). It is used as a solvent in products such as anti-freeze, alkyd paints, varnishes, plastics, modelling clay, adhesives and sealants, acrylic resins, rubber cements, nail polish removers and paint removers (ECHA, 2018; Reisman, 1998). Acetone is used as an intermediate in the production of methacrylate (such as MMA, methacrylic acid and higher methacrylate) via the acetone cyanohydrin process. It is also used as a chemical intermediate in the production of Bisphenol A, and as a solvent in the processing of cellulose acetate (Reisman, 1998).

An acetone vapour polishing system has been developed in order to smooth ABS objects that have been manufactured by means of the material extrusion FDM^{TM} AM technology (Kuo and Mao, 2016). This vapour polishing treatment involves exposing acetone vapour to the ABS object, the vapour absorbs into the object surface layer and reduces the surface viscosity (Neff *et al*., 2018).

2.5.2. Adverse health effects of acetone

Acetone is considered to be a relatively non-toxic and non-explosive solvent, although it may form explosive air/vapour mixtures. Acetone reacts dangerously with alkali hydroxides, strong oxidising agents and strong reducing agents. During prolonged or repeated skin contact with acetone, it can be absorbed by the skin and cause skin drying and defatting that may result in dermatitis. However, the high volatility of acetone renders the dermal absorption thereof insignificant and the main route of exposure is by means of inhalation (Reisman, 1998).

Inhalation exposure to acetone may cause coughing, sore throat, headache, confusion, dizziness and during severe exposure it may cause unconsciousness, because high concentrations of acetone trigger central nervous system disorders (NIOSH, 2015; Institute for Occupational Safety and Health of the German Social Accident Insurance, 2017).

Ingestion of acetone may cause nausea and vomiting. Acetone has been found to have an acute oral LD_{50} of 8400 mg/kg in rats, inhalation LD_{50} of 50 000 mg/m^3 and a dermal LD_{50} >15700 mg/kg in rabbits (Chemical Manufacturer's Association, 1998).

There is no information available regarding reproductive toxicity, teratogenicity, mutagenic and developmental effects related to acetone exposure (Institute for Occupational Safety and Health of the German Social Accident Insurance, 2017).

2.5.3. Volatile organic compounds

According to Afshar-Mohajer *et al.* (2015), the binder jetting process utilising gypsum powder emits VOCs due to the injection of the binder liquid during the processing phase. They have found that the TVOCs reached a maximum value of 1725 µg/m^3. Similar results were attained by Ding *et al.* (2019) for desktop material extrusion FDM^{TM} with PLA as feedstock material. Du Preez *et al*. (2018a) conducted a study on industrial scale material extrusion FDM^{TM} AM machines with ABS, polycarbonate and ultem^{TM} filaments as feedstock materials. They have found that VOC and particle emissions correlate to the scale of the manufacturing (i.e. desktop versus industrial scale AM), as well as the type of feedstock material used.

VOCs (such as acetone) are volatile compounds that contain carbon (this excludes carbon monoxide, carbon dioxide, carbonic acid, metallic carbides and carbonates and ammonium carbonate) that has low vapour pressures at standard conditions (CDPH, 2010). VOCs may be man-made or naturally occurring, for instance when certain liquids or solids are able to emit vapours, in the form of VOCs, at room temperature (EPA, 2015; Costelloe-Kuehn, 2018). VOCs comprise of a variety of chemicals (such as formaldehyde and benzene). Some of these may result in short- and/or long-term adverse health effects (Costelloe-Kuehn, 2018, EPA, 2015; EPA, 2017). Household products containing organic chemicals are widely used and many of these have precautionary labels that stipulate the dangers of the product and procedures that must be followed for safe use (EPA, 2015; EPA, 2017). These items can release VOCs while in use as well as during the time that they are stored (EPA, 2017). Products containing VOCs can have a great impact on the air quality. This may result in adverse effects on human health and the environment (Costelloe-Kuehn, 2018). Sources that emit VOCs and produce indoor air pollution include adhesives, cleaning agents, and pesticides (EPA, 2015). Indoor concentrations of VOCs are steadily higher than the outdoor concentrations (EPA, 2017).

2.5.4. Adverse health effects of volatile organic compounds

Exposure to VOCs may cause acute and chronic health effects at high concentrations, and some are known carcinogens. However, exposure to multiple VOCs at low to moderate levels may also produce acute reactions (EPA, 2015). Some of the common adverse health effects caused by VOC exposure include irritation of the eyes, nose and throat, nausea, headaches, fatigue and loss of coordination and skin hypersensitivity reactions (EPA, 2017).

2.6. Characterisation of particles

The type and size of the powder particles used in AM has an effect on the quality of the final object manufactured as well as on the health of the AM operator (Dawes *et al.,* 2015). Physical characteristics of particles may play a role in the AM process as it has an influence on the density of the final 3D manufactured object. The more spherical a particle, the denser the final product. Thus, AM favours the use of spherical particles to irregular morphologies (Dawes *et al.,* 2015). According to Tang *et al.* (2015), the remaining powder after AM may be reused, however, the particles become less spherical and coarser with the increasing reuse, which may result in a less dense final product. The PMMA powder particle sizes were not mentioned in the safety data sheet (SDS) for Polypor C (PMMA powder) utilised during binder jetting AM (Voxeljet, 2014).

Particle size and shape is relevant from a respiratory health perspective as it has an influence on the location in the respiratory tract where the particles may deposit when inhaled (Hoet *et al*., 2004, Mellin *et al.,* 2016). Therefore, the physical characteristics of the particle have substantial effects on the respiratory hazards posed by powder particles.

Particle size distribution (PSD) has an influence on the thickness of layers manufactured and thus the finer detail of the final product. The use of finer powders with a wide range of PSD is preferred due to the accuracy of the final object rendered. However, this fact increases the respiratory risks associated with AM utilising powders that may become airborne and ultimately inhaled (Dawes *et al.,* 2015). Exposure to materials, normally considered safe, has a greater toxic effect on the human body when in UFP (< 100 nm) form (Mellin *et al.,* 2016). Inhaled UFPs can reach the alveoli of the lungs and may cause respiratory inflammation. These particles may enter the bloodstream and may deposit in organs such as the heart, bone marrow, spleen and lymph nodes. They may also interfere with deoxyribonucleic acid (DNA) and cellular processes leading to disorders of the central nervous system (Mellin *et al.,* 2016; Bharti and Singh, 2017). Therefore, it is clear that the type of feedstock powder selected for the use in AM plays an important role in the quality of the final product as well as the effects that it could have on the health of AM operators involved.

Du Preez *et al*. (2018b) has conducted a study on titanium powder utilised during PBF and its relevance to respiratory health. Characterisation of the AM powder feedstock was done by making use of Scanning Electron Microscopy (SEM), X-ray Powder Diffraction (XRD), particle size distribution and characterisation of the particle shape. The SEM images indicated the presence of particles in the thoracic and respirable size fractions. Particles in the inhalable fraction may deposit anywhere in the upper respiratory tract when inhaled, whereas the particles in the respirable fraction may penetrate to the alveolar region of the lung (ISO 7708:1995; Brown *et al.*, 2013). XRD analysis results differed from the chemical composition stated in the safety data sheet (SDS) and the static image analysis indicated that the titanium powder particles had a smooth surface and a spherical shape (du Preez *et al*., 2018b). Particle shape also has an influence on where the particles may deposit in the respiratory tract when inhaled (Hoet *et al*., 2004, Mellin *et al.,* 2016).

2.7. Respiratory exposure to particles emitted from AM

In the following sections different particle sizes and deposition thereof in the respiratory tract and defence mechanisms of the respiratory tract will be explored.

2.7.1. Particle size and deposition in the respiratory tract

Particle size and shape are the determining factors of where the particles may deposit in the respiratory tract when inhaled (Hoet *et al*., 2004, Mellin *et al.,* 2016). Particles may be categorised according to their location of penetration in the respiratory system, namely the thoracic fraction, the tracheobronchial fraction, the respirable fraction and the inhalable fraction (ISO 7708:1995; Brown *et al.*, 2013). The thoracic fraction is the mass fraction of the particles inhaled, which may penetrate beyond the larynx. The tracheobronchial fraction is the mass fraction of particle inhaled which may penetrate beyond the larynx but not the unciliated airway. The respirable fraction is the mass fraction of the particles inhaled which may penetrate the unciliated airway, the alveolar region of the lung. The inhalable fraction is the mass fraction of particles aspirated into the mouth and nose during normal breathing and may deposit anywhere in the respiratory tract (ISO 7708:1995; Brown *et al.*, 2013).

Particles that are smaller in size, such as UFPs (< 100 nm), tend to penetrate deeper into the alveolar region than larger particles and there is no natural mechanism that easily clears such fine particles form the lungs. It is alleged that larger particles will remain in the lungs for a longer period of time before it is released back through the airway (Mellin *et al.,* 2016).

According to Fröhlich and Salar-Behzadi (2014), there are for mechanisms by which inhaled aerosol particles can be deposited in the respiratory tract, this includes: (1) inertial impaction; (2) interception; (3) gravitational sedimentation; and (4) diffusion.

Inertial impaction is a mechanism of deposition for particles with an aerodynamic diameter greater than 2 μm (Fröhlich and Salar-Behzadi, 2014). When airflow deviates from its original direction, a particle (within the airflow) adjacent to the airway wall follows the initial direction and does not adjust within the moving airstream (Plog and Quinlan, 2001). Large particles are inclined to inertially impact on the extra thoracic and upper tracheobronchial airways (Fröhlich and Salar-Behzadi, 2014). Inertial impaction is relative to the particle density, square of its diameter, and the airflow velocity and is therefore most efficient for particles which are larger, denser, and in a high velocity airflow (Plog and Quinlan, 2001).

During deposition by means of interception, the particle is able to follow the air stream due to the particles' smaller size, low density, or low velocity of the air stream. However, it still comes in contact with the surface of the airway wall. The particle intercepts with the airway wall, and no longer follows the air stream (Plog and Quinlan, 2001). This deposition is also dependent on the particle shape and therefore, interception is capable of trapping intermediate-sized particles (Plog and Quinlan, 2001; Fröhlich and Salar-Behzadi, 2014).

Gravitational sedimentation is the mechanism of deposition for particles with an aerodynamic diameter larger than 1 μm (Fröhlich and Salar-Behzadi, 2014). All particles are attracted towards the centre of the earth due to gravity. This causes the particles to settle in the airway (Plog and Quinlan, 2001). Deposition usually occurs in the tracheobronchial tracts' smaller conduction airways (Fröhlich and Salar-Behzadi, 2014). Particle sedimentation is relative to its mass, therefore larger particles will settle faster than smaller particles (Plog and Quinlan, 2001).

Brownian diffusion is the mechanism of deposition for particles with an aerodynamic diameter of 0.5 up to 1 μm (Fröhlich and Salar-Behzadi, 2014). This refers to the irregular movement of very small particles that react to individual air molecules. The particles tend to collide with an airway wall (Plog and Quinlan, 2001). Collision may cause the particle to deposit on the surface of the airway (Plog and Quinlan, 2001; Fröhlich and Salar-Behzadi, 2014). Diffusion is indirectly correlated to the particles' square diameter, and the airstream velocity and therefore, small particles that have a low velocity tend to diffuse (Plog and Quinlan, 2001).

2.7.2. Respiratory defence mechanisms (clearance)

The inspired air is contaminated with toxic gases, particles and microbes (Lambrecht *et al.*, 2011). Respiratory clearance refers to the physical removal of these materials that deposit on airway surfaces (Schlesinger, 1985). The respiratory system has a number of ways of filtering incoming air to protect the delicate gas exchange surfaces in the lung (Richardson, 2006). Clearance mechanisms involved are regionally distinct (Schlesinger, 1985).

Large particles (>10 µm) that pass through the nose get trapped in the nasal hairs that extend across the nares. Therefore, only a few percent of these particles will pass through to the respiratory tract (Richardson, 2006; Wilkinson *et al*., 2012). Slightly smaller particles get trapped in the bronchial tree and small particles (1-5 µm) get trapped in bronchiole mucus or in the alveolar fluid (Richardson, 2006).

Clearance in the conducting airways occurs by way of the mucociliary system (Schlesinger, 1985). The nasal passages and tracheobronchial airways to the terminal bronchioles are lined with ciliated epithelium which secretes a thick mucus layer (Schlesinger, 1985; Richardson, 2006). Particles that come into contact with the mucus get trapped and swept by the cilia in the direction of the naso- and oro-pharynx. From there the particles are removed from the respiratory tract by sneezing and coughing, or swallowed and destroyed by gastrointestinal fluid (Richardson, 2006; Lambrecht *et al*., 2011; Wilkinson *et al*., 2012). This is to prevent the particles from reaching deeper levels of the respiratory tract (Richardson, 2006).

Clearance in the respiratory region (alveolar clearance) of the lung may occur via a number of mechanisms (Schlesinger, 1985). Alveoli do not contain cilia and mucus, because this will slow down the gas exchange rate of oxygen and carbon dioxide (Lechtzin, 2016). Alveolar macrophages, residing on the alveolar surface, is part of the first line of defence mechanisms to protect the lungs from carbon particles, bacteria and other debris (Richardson, 2006; Lechtzin, 2016). These macrophages isolate, transport and detoxify the deposited particles. They are part of the mononuclear phagocytic system in the body that moves by means of ameboid motion (Schlesinger, 1985). Macrophages can assist in the interference of infiltration of deposited particles through the alveolar epithelium and the consequent translocation to other sites, by means of phagocytic ingestion (Schlesinger, 1985; Richardson, 2006). Proteolytic enzymes allow the macrophages to digest organic materials, however, additional white blood cells (particularly neutrophils) can be recruited to help bind, ingest and digest pathogens (Lechtzin, 2016). Afterwards macrophages are cleared from the respiratory region by way of the mucociliary system. The efficiency of clearance is determined by the integrated operation of the macrophages and mucociliary apparatus (Schlesinger, 1985).

2.8. Respiratory exposure monitoring

Short *et al.* (2015) found that AM manufacturer manuals have deficiencies in their guidelines to protect the health and safety of their operators. It is necessary to conduct respiratory exposure monitoring to assess the extent of occupational exposure during binder jetting and compare it to the OEL, as required by the Occupational Health and Safety Act 85 of 1993 Regulations for HCS, 1995 of South Africa (Department of Employment and Labour, 1995; Bours *et al*., 2017).

Methods used for personal respiratory exposure monitoring must represent the concentration of the particles and VOCs present in the breathing zone of the AM operator. Results acquired from these methodologies must be compared to the OELs for the different HCSs found. This is to determine the extent of the AM operators' exposure to different airborne HCS, with the aim of recommending appropriate control measures for improved respiratory protection (HSE, 2006).

Area sampling may also be used for the monitoring of particles and VOCs concentrations in the workplace atmosphere in order to evaluate the effectiveness of the controls and protect the individuals that may be affected (HSE, 2006). Direct reading particle counter instruments may be used to monitor the ambient particle emissions (Afshar-Mohajer *et al.,* 2015). Personal- and area monitoring can be used in conjunction with each other in order to achieve a more comprehensive representation of the HCS in the environment to which the AM operators may be exposed (HSE, 2006).

2.9. Occupational exposure limits for acetone and particles

The South African Department of Employment and Labour is the custodian of the Occupational Health and Safety Act and the Regulations for HCS of 1995. With the intention of protecting the health and safety of persons at work against excessive HCSs exposure, these regulations state the HCSs airborne concentrations that may not be exceeded (OELs) (Department of Employment and Labour, 1995). According to the Regulations for Hazardous Chemical Substances (1995), the employer is obligated to implement and uphold a measurement programme that consists of monitoring the HCSs the workers are exposed to in order to ensure that the workplace is safe and free from risks to the health of workers. The 8-hour Time Weighted Average-Occupational Exposure Limit – Recommended Limit (TWA-OEL–RL) refers to the concentration of an airborne substance that is averaged over the reference period of 8-hours not likely to cause adverse health effects if persons are exposed to day-to-day inhalation at that concentration. PMMA has no available international 8-hour TWA-OEL–RL, however, it is used during binder jetting in powder form. Therefore, the 8-hour TWA-OEL-RL concentration for respirable dust (5 mg/m^3) and inhalable dust (10 mg/m^3) is applicable (Department of Employment and Labour, 1995). MMA is recognised as a skin sensitiser and the main decomposition product of PMMA. It has an 8-hour TWA-OEL–RL of 410 mg/m^3 (Borak *et al.,* 2011; Department of Employment and Labour, 1995). Acetone has a TWA-OEL-RL of 1780 mg/m^3 and a short-term exposure limit (STEL) OEL-RL of 3560 mg/m^3 (Department of Employment and Labour, 1995).

2.10. Conclusion

As application of AM is growing, it is important to emphasize the hazards that go hand in hand with the process in order to protect the health of the AM operators that are exposed to this environment. According to Zhang *et al.* (2017), the 3D printing materials most frequently used appear to be ABS and PLA in material extrusion FDM^{TM} AM. There is a necessity for information concerning the emissions and respiratory exposure regarding binder jetting AM utilising PMMA, as this is a powder material not often researched for this purpose. It is necessary to determine the physical and chemical characteristics of the particles the AM operators are exposed to. This is to determine where in the respiratory tract the particles can penetrate and may deposit so that the correct control measures can be selected and implemented in order to protect the AM operators from exposure to these substances. It is important to understand the reaction between the feedstock material (PMMA) and the binder liquid (acetone) in order to choose the correct monitoring method to determine which HCSs the operators are exposed to as well as to select the correct methods of control to protect the operators. It was found that SDSs for specific chemicals, utilised during AM, have insufficient information available regarding potential hazards and safe operating practises. This may place the health of the AM operators at risk as it may create a false sense of security regarding the safety of the work environment is (du Preez *et al.,* 2018b; Short *et al.,* 2015). It is essential to identify the particle and VOC emissions associated with binder jetting utilising PMMA as feedstock material, to determine the magnitude of exposure of the AM operators and compare it to the relevant OELs.

2.11. References

Afshar-Mohajer N, Wu C, Ladun T, Rajon DA, Huang Y. (2015) Characterisation of particulate matters and total VOC emissions from a binder jetting 3D printer. J Build Environ; 93: 293-301.

Ali U, Karim K, Buang N. (2015) A review of the properties and applications of poly (methyl methacrylate) (pmma). Polymer Reviews; 55: 678-705.

American Polymer Standards Corporation. (2017) Polymethyl methacrylate. Available from http://www.ampolymer.com/SDS/Polymethyl methacrylateSDS.html# (accesse: 6 May 2018).

Anancharungsuk W, Polpanich D, Jangpatarapongsa K, Tangboriboonrat P. (2010) In vitro cytotoxicity evaluation of natural rubber latex film surface coated with PMMA nanoparticles. Colloids and Surfaces B: Biointerfaces; 78: 328-333.

ISO/ASTM. (2015) 52900-15 Standard terminology for additive manufacturing – general principles – terminology. ISO/ASTM International, West Conshohocken, PA.

Aubin RF. (1994) A world wide assessment of rapid prototyping technologies Report No. 94/13. East Hartford, CT: United Technologies Research Centre.

Azimi P, Zhao D, Pouzet C, Crain NE, Stephens B. (2016) Emissions of ultrafine particles and volatile organic compounds from commercially available desktop three-dimensional printers with multiple filaments. Environ Sci Tech; 50: 1260-1268.

Bai Y, Williams CB. (2018) Binder jetting additive manufacturing with a particle-free metal ink as a binder precursor. Mater Des; 147: 146-156.

Bharti N, Singh S. (2017) Three-dimensional (3D) printers in libraries: perspective and preliminary safety analysis. J Chem Educ; 94: 879-885.

Borak J, Fields C, Andrews LS, Pemberton, MA. (2011) Methyl methacrylate and respiratory sensitization: a critical review. Crit Rev Toxicol; 41: 230-268.

Bours J, Adzima B, Gladwin S, Cabral J, Mau S. (2017) Addressing hazardous implications of additive manufacturing: complementing life cycle assessment with a framework for valuating direct human health and environmental impacts. J Ind Ecol; 21: 25-36.

Brown JS, Gordon T, Price O, Asgharian B. (2013) Thoracic and respirable particle definitions for human health risk assessment. Part Fibre Toxicol; 10:1-12.

Campbell J. (2017) Poly (methyl methacrylate). Available from https://nwulib.nwu.ac.za/login?url=https://search.ebscohost.com/login.aspx?direct=true&db=ers&AN=89144949&site=eds-live (accessed 30 November 2018).

California Department of Public Health (CDPH). (2010) Standard method for the testing and evaluation of volatile organic chemical emissions from indoor sources using environmental platforms. Available from https://standards.nsf.org/apps/group_public/download.php/11782/CDPH-IAQ (accessed 20 November 2018).

Chemical Manufacturer's Association. (1998) Acetone cas n°: 67-64-1. Available from http://www.inchem.org/documents/sids/sids/67641.pdf (accessed 20 November 2018).

Costelloe-Kuehn B. (2018) Volatile organic compounds. Available from https://nwulib.nwu.ac.za/login?url=https://search.ebscohost.com/login.aspx?direct=true&db=ers&AN=89475441&site=eds-live (accessed 21 November 2018).

Dawes J, Bowerman R, Trepleton R. (2015) Introduction to the additive manufacturing powder metallurgy supply chain. Johnson Matthey Tech Rev; 59: 243-256.

Deak SM. (1999) Safe work practices for rapid prototyping. Rapid Prototyp J; 5: 161-163.

Deng Y, Cao S, Chen A, Guo, Y. (2016) The impact of manufacturing parameters on submicron particle emissions from a desktop 3D printer in the perspective of emission reduction. Build Environ; 104: 311-329.

Department of Employment and Labour. South Africa. Hazardous Chemical Substances Regulations, 1995. Available from http://www.acts.co.za/occupational-health-and-safety-act-1993/ index.html (accessed 20 November 2018).

Ding S, Ng BF, Shang X, Liu H, Lu X, Wan MP. (2019) The characteristics and formation mechanisms of emissions from thermal decomposition of 3D printer polymer filaments. Sci Total Environ; 692: 984-994.

Dormer W, Gomes R, Meek ME. (1998) Methyl methacrylate. Available from http://www.who.int/ipcs/publications/cicad/en/cicad04.pdf (accessed 21 November 2018).

du Preez S, LeBouf RF, Stefaniak AB, du Plessis J. (2018a) Exposures during industrial 3D printing and post-processing tasks. Rapid Prototyp J; 24: 865-871.

du Preez S, de Beer DJ, du Plessis LJ. (2018b) Titanium powders used in powder bed fusion: their relevance to respiratory health. SAJIE; 29: 94-102.

Espalin D, Arcaute K, Rodriguez D, Medina F, Posner M, Wicker R. (2010) Fused deposition modeling of patient-specific polymethylmethacrylate implants. Rapid Prototyp Jo; 16: 164-173.

European chemicals agency (ECHA). (2018) Acetone. Available from https://echa.europa.eu/substance-information/-/substanceinfo/100.000.602 (accessed 20 November 2018).

Environmental Protection Agency (EPA). (2015) Indoor air pollution an introduction for health professionals. Available from https://www.epa.gov/sites/production/files/2015-01/documents/indoor_air_pollution.pdf (accessed 5 November 2019).

Environmental Protection Agency (EPA). (2017) Volatile organic compounds' impact on indoor air quality. Available from https://www.epa.gov/indoor-air-quality-iaq/volatile-organic-compounds-impact-indoor-air-quality#main-content (accessed 20 November 2018).

Fröhlich E, Salar-Behzadi S. (2014) Toxicological assessment of inhaled nanoparticles: role of in vivo, ex vivo, in vitro, and I silico studies. J Mol Sci; 15: 4795-4822.

Gibson I, Rosen D, Stucker B. (2015) Additive manufacturing technologies: 3D printing, rapid prototyping, and direct digital manufacturing. Virgin York, NY: Springer. ISBN 1 493 92113 4.

Graff P, Ståhlbom B, Nordenberg E, Graichen A, Johansson P, Karlsson H. (2016) Evaluating measuring techniques for occupational exposure during additive manufacturing of metals: a pilot study. J Ind Ecol; 21: 120-129.

He C, Morawska L, Hitchins J, Gilbert D. (2004) Contribution from indoor sources to particle number and mass concentrations in residential houses. Atmos Environ, 38: 3405-3415.

Health and Safety Executive (HSE). (2006) Monitoring strategies for toxic substances. Available from http://www.hse.gov.uk/pUbns/priced/hsg173.pdf (accessed 29 August 2018).

Hoehn Plastics Inc. 2011. Polymethyl methacrylate. Available from http://www.hoehnplastics.com/pdf/SDS-110-Polymethyl-Methacrylate.pdf (accessed 21 November 2018).

Hoet P, Bruske-Hohlfeld I, Salata O. (2004) Nanoparticles - known and unknown health risk. J Nanobiotechnology; 2: 1-15.

Institute for Occupational Safety and Health of the German Social Accident Insurance substance database. (2017) Acetone. Available from http://gestisen.itrust.de/nxt/gateway.dll/gestis_en/000000.xml?f=templates$fn=default.htm$vid=gestiseng:sdbeng$3.0 (accessed 7 July 2018).

International Organization for Standardization (ISO). (1995). Air quality – particle size fraction definitions for health-related sampling (ISO 7708:1995). Available from https://www.sis.se/api/document/preview/20338/ (accessed 6 May 2018).

Junk S, Matt R. (2015) Application of polymer plaster composites in additive manufacturing of high-strength components. Mater Sci Forum; 825-826: 763-770.

Kellens K, Mertens R, Paraskevas D, Dewulf W, Duflou J. (2017) Environmental impact of additive manufacturing processes: does am contribute to a more sustainable way of part manufacturing. Procedia CIRP; 61: 582-587.

Kim Y, Yoon C, Ham S, Park J, Kim S, Kwon O, Tsai J. (2015) Emissions of nanoparticles and gaseous material from 3D printer operation. Environ Sci Tech; 49: 12044-12053.

Konda GP, Kolla S, Eckert J. (2017) Additive manufacturing processes: selective laser melting, electron beam melting and binder jetting—selection guidelines. Mater; 10: 672.

Kunchala P, Kappagantula K. (2018) 3D printing high density ceramics using binder jetting with nanoparticle densifiers. Mater Des; 155: 443-450.

Kuo CC, Mao RC. (2016) Development of a precision surface polishing system for parts fabricated by fused deposition modeling. Mater Manuf Process; 31: 1113-1118.

Kwon O, Yoon C, Ham S, Park J, Lee J, Yoo D, Kim Y. (2017) Characterisation and control of nanoparticle emission during 3D printing. Environ Sci Tech; 51: 10357-10368.

Lambrecht BN, Neyt K, GeurtsvanKessel CH. (2011) Pulmonary defence mechanisms and inflammatory pathways in bronchiectasis. Eur Respir Rev; 52: 11-21.

Lechtzin N. (2016) Defence mechanisms of the respiratory system. Available from https://www.msdmanuals.com/home/lung-and-airway-disorders/biology-of-the-lungs-and-airways/defense-mechanisms-of-the-respiratory-system (accessed 20 November 2018).

Ligon S, Liska R, Stampfl J, Gurr M, Mülhaupt R. (2017) Polymers for 3D printing and customized additive manufacturing. Chem Rev; 117: 10212-10290.

Limongi RM, Tao J, Borba A, Pereira F, Pimentel AR, Akaishi P, Velasco AA. (2016) Complications and management of polymethyl methacrylate (pmma) injections to the midface. Aesthet Surg J; 36: 132-135.

Malvern Panalytical. (2015) Morphologi g3 user manual. Available from https://www.malvernpanalytical.com/en/learn/knowledge-center/user-manuals/MAN0410EN (accessed 6 May 2018).

Mellin P, Jönsson C, Åkermo M, Fernberg P, Nordenberg E, Brodin H, Strondl A. (2016) Nano-sized by-products from metal 3D printing, composite manufacturing and fabric production. J Clean Prod; 139: 1224-1233.

Meteyer S, Xu X, Perry N, Zhao Y. (2014) Energy and material flow analysis of binder-jetting additive manufacturing processes. Procedia CIRP; 15: 19-25.

Mirzababaei S, Pasebani S. (2019) A review on binder jet additive manufacturing of 316l stainless steel. J Manuf Mater Process; 82: 1-36.

Miyanaji H, Zhang S, Yang L. (2018) A new physics-based model for equilibrium saturation determination in binder jetting additive manufacturing process. Int J Mach Tool Manu; 124: 1-11.

National Institute for Occupational Safety and Health (NIOSH). (2015) Acetone icsc: 0087. Available from https://www.cdc.gov/niosh/ipcsneng/neng0087.html (accessed 21 November 2018).

Neoss Limited. (2010) Pmma SDS. Available from https://wcam.engr.wisc.edu/Public/Safety/SDS/PMMA%20(solid).pdf (accessed 21 November 2018).

Neff C, Trapuzzano M, Crane NB. (2018) Impact of vapor polishing on surface quality and mechanical properties of extruded abs. Rapid Prototyp J; 2: 501.

Oberdörster G. (2000) Pulmonary effects of inhaled ultrafine particles. Int Arch Occup Environ Health; 74: 1–8.

Odian, G. (2004) Principles of polymerization fourth edition. Staten Island, NY: John Wiley and Sons Inc. ISBN 9 780 47147 875 1.

Plog BA, Quinlan PJ. (2001) Fundamentals of industrial hygiene fifth edition. Illinois, USA: National Safety Council Press. ISBN 0 879 12216 1.

Polzin C, Spath S, Seitz H. (2013) Characterization and evaluation of a PMMA-based 3D printing process. Rapid Prototyp J; 19: 37-43.

Razuin R, Effat O, Shahidan MN, Shama DV, Miswan MFM. (2013) Bone cement implantation syndrome. Malays J Pathol; 35: 87-90.

Reisman DJ. (1998) Environmental health criteria 207, acetone. Available from http://www.inchem.org/documents/ehc/ehc/ehc207.htm (accessed 20 November 2018).

Richardson M. (2006) The respiratory system - part 3: lungs, pleura and respiratory defence mechanisms. Nurs Times; 102: 22-23.

Schlesinger RB. (1985) Effects of inhaled acids on respiratory tract defence mechanisms. Environ Health Perspect; 63: 25-38.

Rojas-Nastrucci EA, Nussbaum JT, Crane NB, Weller TM. (2017) Ka-Band Characterization of Binder Jetting for 3-D Printing of Metallic Rectangular Waveguide Circuits and Antennas. IEEE T Microw Theory; 65: 3099-3108.

Schmid M, Wegener K. (2016) Additive manufacturing: polymers applicable for laser sintering (ls). Procedia Eng; 149: 457-464.

Shi Y, Zhang Y, Baek S, De Backer W, Harik R. (2018) Manufacturability analysis for additive manufacturing using a novel feature recognition technique. Comput Aided Des Appl; 15: 941-952.

Short DB, Sirinterlikci A, Badger P, Artieri B. (2015) Environmental, health, and safety issues in rapid prototyping. Rapid Prototyp J; 21: 105-110.

Stabile L, Scungio M, Buonanno G, Arpino F, Ficco G. (2017) Airborne particle emission of a commercial 3D printer: the effect of filament material and printing temperature. Indoor Air; 27: 398-408.

Stanczyk M, Van Rietbergen B. (2004) Thermal analysis of bone cement polymerisation at the cement–bone interface. J Biomech; 37: 1803-1810.

Steinle P. (2016) Characterisation of emissions from a desktop 3D printer and indoor air measurements in office settings. J Occup Environ Hyg; 13: 121-132.

Stefaniak AB, Johnson AR, du Preez S, Hammond DR, Wells JR, Ham JE, LeBouf RF, Menchaca KW, Martin SB, Duling MG, Bowers LN, Knepp AK, Su FC, de Beer DJ, du

Plessis JL. (2018) Evaluation of emissions and exposures at workplaces using desktop 3-dimensional printers. J Chem Health Saf; 26: 19-30.

Stephens B, Azimi P, El Orch Z, Ramos T. (2013) Ultrafine particle emissions from desktop 3D printers. Atmos Environ; 79: 334-339.

Tang H, Qian M, Liu N, Zhang X, Yang G, Wang J. (2015) Effect of powder reuse times on additive manufacturing of Ti-6Al-4V by selective electron beam melting. J Occup Med; 67: 555-563.

Thermo Fisher Scientific. 2018. Safety data sheet. Available from https://www.fishersci.com/shop/SDSproxy?storeId=10652&productName=AC418060010&productDescription=POLY (accessed: 25 May 2018).

Voxeljet. (2014) Safety data sheet 1907/2006/EC – reach (GB) Voxeljet – Polypor- pulver typ C. Voxeljet AG 86316 Friedberg.

Wang Y, Zhao ZF. (2017) Investigation of sintering shrinkage in binder jetting additive manufacturing process. Procedia Manuf; 10: 779-790.

World Health Organization (WHO). (1999) Hazard Prevention and Control in the Work Environment: Airborne Dust. Occupational and Environmental Health Department of Protection of the Human Environment. Available from https://apps.who.int/iris/handle/10665/66147 (accessed: 23 January 2020).

Wilkinson TS, Sallenave J, Simpson J. (2012) Pulmonary Defence Mechanisms. Curr Respir Med Rev; 8: 149-162.

Zhang Q, Wong JPS, Davis AY, Black MS, Weber RJ. (2017) Characterisation of particle emissions from consumer fused deposition modeling 3D printers. Aerosol Sci Tech; 51: 1275-1286.

Zhou XD, Zhang SC, Huebner W, Ownby PD, Hongchen G. (2001) Effect of the solvent on the particle morphology of spray dried pmma. J Mater Sci; 36: 3759-3768.

Zhou Y, Kong X, Chen A, Cao S. (2015) Investigation of ultrafine particle emissions of desktop 3D printers in the clean room. Procedia Eng; 121: 506-521.

Ziaee M, Crane NB. (2019) Binder jetting: a review of process, materials, and method. Addit Manuf; 28: 781–801.

CHAPTER 3 MANUSCRIPT ON PARTICLE EMISSIONS AND RESPIRATORY EXPOSURE TO HAZARDOUS CHEMICAL SUBSTANCES

Annals of Work Exposures and Health

Annals of Work Exposures and Health publishes original research and development material that helps reduce risk of ill-health resulting from work, and welcomes submissions in these areas.

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Title, abstract and keywords: Titles should be constructed to succinctly describe the major issue or question examined by the paper and should not assert the research findings as a truth. Recognisable, searchable terms and keywords must be included to enable readers to more effectively find your paper. To optimise the visibility of your paper we advise you to make a list of the 10 most likely search terms that your intended readers will use to find your work, and to ensure that these appear in your title, the abstract and the keywords. The 'number one' search term from your list should appear somewhere in the paper's title. The 'top 5' search terms (including 'number one') should each appear at least once in the abstract, with the 'top 3' appearing more than once if possible. It is important that your abstract is written in a naturalistic and engaging style that will encourage readers to follow up by reading the full paper. The 'bottom 5' search terms can then be added as keywords.

Authorship: Persons should only be named as authors if they have made substantial contributions to the conception or design of the work, or the acquisition, analysis or interpretation of data for the work AND have assisted with the drafting or revising of the paper for important intellectual content AND have final approval of the version to be published AND can take responsibility for the accuracy of the work. Other contributions may be recognised by acknowledgement at the end of submission.

Structure of paper: Papers should generally conform to the pattern: Introduction, Methods, Results, Discussion, and Conclusions, unless these are clearly inappropriate. A paper must be prefaced by an abstract of the argument and findings, which may also be arranged under the same headings.

Design and analysis: The quality of the data and analysis must always be good enough to justify the inferences and conclusions drawn. Particular attention should be given to design of sampling surveys, which should be planned using modern statistical principles, and to the treatment of results below the limit of detection.

Units and symbols: SI units must be used, though their equivalent in other systems may be given as well.

Figures: These include photographs, diagrams and charts. The first submission should include good quality low resolution copies of Figures, and may be incorporated into the text or at the end of the manuscript.

Tables: Tables should be numbered consecutively and given a suitable caption. As with Figures, it is helpful to incorporate them into the text of the first submission, but in the revised version each table should be presented on a separate page. Footnotes to tables should be provided below the table and should be referred to by superscript lowercase letters.

References: References should only be included which are essential to the development of an argument or hypothesis, or which describe methods for which the original account is too long to be reproduced. References in the text should be in the form Jones (1995), or Jones and Brown (1995), or Jones *et al*. (1995) if there are more than two authors, and they should be incorporated naturally into the text.

Examples:
Jones and Brown (1995) and Hospath *et al* (2006) observed total breakdown of control..., or Total breakdown of control has sometimes been observed (Jones and Brown, 1995; Hospath *et al*., 2006).

At the end of the paper, references should be listed in alphabetical order by name of first author, using the Vancouver Style of abbreviation and punctuation. ISBNs should be given for books and other publications where appropriate. Material unobtainable by readers should not be cited. Personal Communications, if essential, should be cited in the text (e.g., Professor O.H. Poobah, Institute for Dusty Sciences). Internet material can be referred to if it is likely to be permanently available; the date on which it was last accessed should be given. References will not be checked editorially, and their accuracy is the responsibility of authors.

Examples:
Simpson AT, Groves JA, Unwin J, Piney M. (2000) Mineral oil metal working fluids (MWFs)—Development of practical criteria for mist sampling. Ann Occup Hyg; 44: 165–72.
Vincent JH. (1989) Aerosol sampling: science and practice. Chichester, UK: John Wiley. ISBN 0 471 92175 0.
Swift DL, Cheng Y-S, Su Y-F, Yeh H-C. (1994) Ultrafine aerosol deposition in the human nasal and oral passages. In Dodgson J, McCallum RI, editors. Inhaled Particles VII. Oxford: Elsevier Science. p. 77–81. ISBN 0 08 040841 9 H.
British Standards Institution. (1986). BS 6691: 1986. Fume from welding and allied processes. Part 1. Guide to methods for the sampling and analysis of particulate matter. London: British Standards Institution.
Morse SS. (1995) Factors in the emergence of infectious diseases. Emerg Infect Dis [serial online] 1995 Jan–Mar;1(1). Available from: URL: http://www.cdc.gov/ncidod/ EID/eid.htm (accessed 25 Oct 2010).

Particle emissions and respiratory exposure to hazardous chemical substances associated with additive manufacturing utilising poly methyl methacrylate

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Word count:
5629 (excluding the abstract, tables, figures, and references).

Key words:
Particle emission rates; binder jetting; occupational exposure; particle size distribution; 3D printing.

Abstract

Title: Particle emissions and respiratory exposure to hazardous chemical substances associated with additive manufacturing utilising poly methyl methacrylate.

Background: There is limited but growing information available regarding the health hazards associated with additive manufacturing (AM). During industrial scale binder jetting, utilising poly methyl methacrylate (PMMA), there is potential for the emission of hazardous chemical substances (HCSs) such as PMMA powder particles, methyl methacrylate (MMA) and acetone. This may cause inhalation exposure that may bring about potential health effects.

Aims and objectives: To determine the chemical composition and physical characteristics of PMMA powder, to assess particle and volatile organic compound (VOC) emissions as well as the respiratory exposure to HCSs (inhalable and respirable particles and VOCs including acetone and MMA) of AM operators when PMMA powder is utilised during industrial scale binder jetting.

Methods: Physical and chemical characterisation of virgin and used PMMA powder samples included particle size distribution (PSD), particle shape analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD) as well as X-ray fluorescence (XRF). Direct reading particle counting instruments were used to measure particle emissions and emission rates. Internationally recognised methods were used to monitor HCSs in the ambient workplace environment and personal respiratory exposure of the AM operator, during binder jetting.

Results: There is no PMMA powder particle size or composition declaration in the manufacturer’s safety data sheet (SDS). Therefore, PSD, SEM, XRD and XRF results could not be compared to the SDS. There were no noteworthy size differences found between the median PSD of virgin (58.32 ± 0.52 µm) and used (58.40 ± 0.11 µm) PMMA. SEM images indicated the presence < 10 µm and < 4 µm sized particles in both virgin and used powders. In the presence of high background ambient particle number concentrations particle emission rates as high as 3.33×10^{12} particles/min for 0.01 ~ 1.00 µm sized particles were measured during the processing phase. However, no significant differences between the AM phases were observed. Ambient 8-hour Time Weighted Average (TWA) concentrations were measured at 3.83 ± 2.12 mg/m^3 for inhalable particles, 0.77 ± 0.20 mg/m^3 for respirable particles, 15.32 ± 2.62 mg/m^3 for acetone, 0.19 ± 0.08 mg/m^3 for pentane and 0.30 ± 0.03 mg/m^3 for toluene. Personal exposure concentrations were measured at 6.22 ± 4.72 mg/m^3 for inhalable particles, 1.15 ± 0.33 mg/m^3 for respirable particles, 2.02 ± 0.58 mg/m^3 for acetone, 0.16 ± 0.07 mg/m^3 for pentane and 0.16 ± 0.05 mg/m^3 for toluene.

Conclusions: Particles sized 0.01 ~ 1.00 µm were the most prevalent sizes emitted. Inhalable, and respirable particles, acetone, pentane and toluene were detected in the workplace atmosphere. All 8-hour TWA personal exposures were below the respective Time Weighted Average – Occupational Exposure Limit – Recommended Limit (TWA-OEL-RL), with the exception of exposure to inhalable particles, where exposure exceeded the 10 mg/m^3 TWA-OEL-RL once and averaged above 50% of the OEL. Recommendations were made to reduce exposure to inhalable particles, which could also be applied to other AM facilities making use of the same AM technology and PMMA powders.

Introduction

Additive manufacturing (AM) is considered to be one of the fastest growing methods of manufacturing (Prasad and Devaiah, 2018). This statement is particularly accurate in the case of health care, electronics and aerospace sectors that recognise AM as a powerful source for the manufacturing of intricate structures (Zhou, 2015; Graff *et al*., 2016). The AM process relies on the design of three-dimensional (3D) models by making use of computer-aided design (CAD) data, and joining raw materials layer upon layer to produce a final 3D product (ISO/ASTM, 2015; Kellens *et al*., 2017; Kwon *et al*., 2017). The growth of the AM industry has brought the emission of hazardous chemical substances (HCSs) and the potential respiratory health risks to the AM operators involved under scrutiny (Zhou, 2015; Graff *et al*., 2016).

The binder jetting process, one of the seven AM processes, involves the structural polymer powder poly methyl methacrylate (PMMA) feedstock material being bonded with acetone as the binder liquid (ISO/ASTM, 2015; Kunchala and Kappagantula, 2018). The three phases (pre-processing, processing and post-processing) of the binder jetting AM process involve different levels of inhalation risks to the AM operator (Kwon *et al*., 2017). The pre-processing phase involves designing the 3D object by making use of CAD software and preparation of the AM machine (i.e. sieving the powder PMMA feedstock material and loading the feedstock material and the acetone binder into the machine) (Kwon *et al*., 2017). This may pose a risk for respiratory exposure as the PMMA powder feedstock material and acetone vapour may become airborne during the preparation of the machine. The processing phase comprises of the manufacturing (printing) of the object that was designed (Gibson *et al*., 2015). A print head sweeps over the powder bed and selectively deposits the acetone binder liquid on top of the powder layer to bind loose PMMA powder materials (Meteyer *et al*., 2014). This procedure is repeated until the entire object (also referred to as a green part) has been manufactured (Meteyer *et al*., 2014, ISO/ASTM, 2015). According to Gibson *et al.* (2015), this phase of AM is automated and does not carry a high risk of exposure due to the enclosed building chamber preventing the feedstock material from becoming airborne. Post-processing involves the removal and cleaning of the manufactured object (green part). It may also involve the infiltration of the manufactured object with epoxy resin to yield a final product with increased strength, however, this step is optional (Dawes *et al*., 2015; Junk and Matt, 2015). During this phase there is residual unbound PMMA powder surrounding the manufactured object, as well as epoxy resin vapour, which may become airborne and pose an inhalation risk to the AM operator (Meteyer *et al*., 2014).

The translucent thermoplastic PMMA is a synthetic polymer of the monomer methyl methacrylate (MMA) (Odian, 2004). MMA undergoes polymerisation to produce PMMA by means of solution, suspension, and emulsion methods. Respiratory exposure to PMMA has been linked to acute adverse health effects such as respiratory tract irritation and coughing (Stanczyk and Van Rietbergen, 2004; American Polymer Standards Corporation, 2017). Acetone is used as a binder liquid for PMMA. Thus, the polymer-solvent interaction favours contact between the polymer and solvent over polymer-polymer contact (Zhou *et al*., 2001). Inhalation exposure to acetone vapour may cause coughing, a sore throat, headache, confusion, dizziness and during severe exposure, unconsciousness (NIOSH, 2015).

The type and size of powder particles utilised for AM has an effect on the quality of the final object that is manufactured (Dawes *et al*., 2015). The physical characteristics of particles have an influence on the density of the final 3D manufactured object. Particle size and shape is relevant from a respiratory health perspective as it has an influence on where the particles may deposit in the respiratory tract when inhaled (Plog and Quinlan, 2001; Hoet *et al*., 2004; Mellin *et al*., 2016). Therefore, it is important to consider the behaviour of different particle sizes and shapes and the respiratory risk they may pose. Smaller particles, such as ultrafine particles (UFPs, < 100 nm) that are inhaled, tend to penetrate deeper into the alveolar region than larger particles, and there is no natural mechanism that easily clears such fine particles from the lungs. It is alleged that larger particles will remain in the lungs for a longer period of time before it is cleared by way of respiratory clearance mechanisms (Mellin *et al*., 2016).

Particle emission rates refer to the mass of particles that are released by an entire object per unit of time. Particle emission rates and volatile organic compound (VOC) emissions from material extrusion AM processes [i.e. desktop Fused Deposition Modeling (FDM^{TM}) printers] have been reported extensively (Stephens *et al*., 2013; Zhou *et al*., 2015; Azimi *et al*., 2016; Steinle, 2016; Deng *et al*., 2016; Yi *et al*., 2016; Azimi *et al*., 2017; Zontek *et al*., 2017; Mendes *et al*., 2017). However, for binder jetting reporting is limited to a single study utilising gypsum powder (Afshar-Mohajer *et al*., 2015). They have found that the highest particle concentration was 0.9-1.16 × 10^4 particles/cm^3 (0.9-1.16 × 10^{10} particles/m^3) for particles with sizes 205 nm to 255 nm during the processing phase, whereas, the highest particle emission rates (4.4 × 10^4 particles/min) were during the (removal) post-processing phase. Afshar-Mohajer *et al*. 2015 also found that the total volatile organic compound (TVOC) emissions reached a maximum value of 1725 µg/m^3. The aims of this study are to determine the physical characteristics and chemical composition of PMMA powder, assess particle and VOC emissions as well as the respiratory exposure to HCS (inhalable and respirable particles and VOCs including acetone and MMA) of AM operators when PMMA powder is utilised during industrial scale binder jetting AM.

Materials and methods

This quantitative study was performed at an AM facility located at a tertiary institution in SA. This study involved the manufacturing of three identical objects (an impeller PMMA investment casting pattern) with dimensions of; x-323.607 mm, y-323.610 mm and z-88.161 mm; and had a surface area of 1 688 402.5 mm^2. The binder jetting utilising PMMA printing room contains a single AM machine that was used to build three prototype objects under the same printing conditions over three days. Processing time for each build was approximately four and a half hours, excluding pre-processing and post-processing.

Workplace description

The room in which binder jetting AM was conducted at this facility is an enclosed area (113.73 m^3) with closed windows and a ventilation system as well as a local exhaust ventilation (LEV) system, leading directly to the outside environment (both not in working order). This facility makes use of the binder jetting process for the manufacturing of 3D objects with an industrial scale AM machine (Voxeljet VX500) (Voxeljet, Germany) 3D printer utilising PMMA powders and acetone as the binder liquid at a temperature of 30 ºC. There was only one AM operator performing work in this area at the time of the study. The AM operator initiated the pre-processing phase by opening the build chamber, cleaning the AM machine using a vacuum, loading Polypor C (PMMA feedstock powder used during binder jetting), weighing and loading the acetone binder into the AM machine. Then, the build chamber was closed and work was performed at the computer workstation next to the AM machine with the intention of commencing the processing (building) phase. During the processing phase, the operator left the printing room, returning hourly to confirm the state of the AM machine. In-between, the operator was involved with other tasks (i.e. office work and operating other types of AM machines) that may have caused exposure to HCS not related to binder jetting. Once the processing phase was completed, the manufactured object was kept inside of the AM machine for 24 hours before post-processing took place. Therefore, post-processing of the manufactured object was only done the day after the object was manufactured. Post-processing entailed the removal of excess powder surrounding the object utilising a vacuum and compressed air within an enclosed de-powdering station in the same room. No epoxy resin was used to infiltrate the manufactured object. The AM operator did not make use of any personal protective equipment during the entire AM process.

Powder particle physical and chemical characterisation

Bulk samples of virgin and used PMMA feedstock powders (Polypor C, Voxeljet) were collected in separate storage vials for analyses. Detailed investigations of PMMA powder particle size distribution (PSD) and particle shape were performed using the automated Malvern Morphologi G3 microscope (Malvern Instruments Ltd, UK). Each PMMA powder sample (approximately 5 mm^3) was placed in the dispersion unit of the instrument, and then dispersed. Images of individual particles were taken and automatic scanning then analysed the images. Analysis was repeated three times for both virgin and used PMMA powders (du Preez *et al*., 2018).

PMMA powders' physical characterisation was further investigated using the Phenom pro-desktop Scanning Electron Microscopy (SEM) (Phenom PRO Desktop SEM, Phenom-World B., Netherland) at a 5 kV magnification power level in order to visualise particles with a size smaller than 10 µm. Approximately 5 mm^3 of virgin and used PMMA powders each were separately dispensed on top of adhesive carbon strips. Samples were covered by a gold palladium source with a SPI module sputter coater (SPI-Module^{TM}, Sputter Coater, SPI Supplies, USA) (du Preez *et al*., 2018).

The chemical composition of virgin and used PMMA powders was analysed by means of X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) analysis. XRD analyses involved pulverising powder samples to a finer powder and then placing these samples onto a spinner stage inside the XRD. A powder diffractometer was utilised to conduct the XRD analyses and a Cu X-ray tube was used to scan the samples (X'Pert Pro XRD, PANalytical, the Netherlands., PW3376/00 Co LFF tube, PANalytical, the Netherlands) (du Preez *et al*., 2018). XRF analyses involved the moulding of pressed pellets by adding a binding material to the powder samples and pressing the moulded pellets under a weight of 20 tons. X-ray tubes were used to scan the samples in order to yield information on the chemical composition of the powder sample (Axios^{Max}, PANalytical, the Netherlands).

Particle emission monitoring

In order to monitor and assess powder particle emissions in real-time during the different phases of binder jetting AM, particles were counted using the airborne particle counter (APC) (AeroTrak™ Portable Particle Counter 9310, TSI Inc., MN, USA) and the condensation particle counter (CPC) (CPC Model 3007, TSI Inc., MN, USA). The CPC was used to determine the particle number concentration in the size range of 0.01 ~ 1.00 µm. The CPC has a maximum detectable size range between 1 up to 3 µm, however, it is important to take into account that inert impaction may in all likelihood cause the loss of particles larger than 1 µm in size in the inlet (ISO 7708:1995). The APC was used to determine the number concentration of particles in the size range of 0.30 to 10 µm. Each day before sampling took place ambient outdoor (background) particle number concentrations were recorded prior to any activity in the AM room for approximately 10 minutes, as this was a requirement in order to perform the particle emission rate (ER) calculations. The instruments were used to record particle number concentrations during each separate phase of the AM process. Data was collected (every 1 minute for the APC and 10 seconds for the CPC) for the duration of each phase of the manufacturing process of each object. All direct reading instrument measurements were taken at a distance of one meter from the AM machine at a height of 1.50 meters.

The emission rates (particles/min) of particles were calculated by making use of the method described in He *et al.* (2004) and Stabile *et al.* (2017) (Equation 1).

$$\mathrm{ER} = \mathrm{V} \cdot \left[\frac{\mathrm{C_{peak}} - \mathrm{C_{out}}}{\Delta \mathrm{t}} + \overline{\mathrm{AER} + \mathrm{k}} \cdot \bar{\mathrm{C}}_{\mathrm{in}} - \mathrm{AER} \cdot \mathrm{C_{out}}\right] \qquad \text{Equation 1}$$

Where V was the volume of the room (m^3), C_{peak} was the peak contaminant concentration during the AM phase (particle number/m^3), C_{out} represented the outdoor contaminant concentration during the AM phase (it was assumed to be equal to the indoor background particle concentration) (particle number/m^3) (Stefaniak *et al*., 2018). Δt was the time difference between C_{peak} and C_{out} (min), AER represented the air exchange rate in the room (air exchange/h), k was the contaminant loss rate due to surface deposition. $\bar{\mathrm{C}}_{\mathrm{in}}$ represented the average contaminant concentration during the AM phase (particle number/m^3). AER was taken as 0.22/h as there was no mechanical air movement in the room and k was taken as 1/h in an indoor environment (Stabile *et al*., 2017; Stefaniak *et al*., 2018).

Area and personal HCS exposure monitoring

Respiratory exposure of the AM operator to HCS (particles and VOCs) was assessed by means of personal sampling. Area (static) sampling was also conducted to investigate the HCS in the ambient workplace environment. Methods for the Determination of Hazardous Substances (MDHS) 14/4 was used to determine emissions of inhalable and respirable particles by utilising an Institute of Occupational Medicine (IOM) ‘multidust’ dual-fraction respirable sampling device (International Occupational Medicine, SKC Inc., PA, USA) (HSE, 2014). The IOM sampler utilises a polyurethane foam insert to collect the larger particles, and the smaller particles will pass through the foam insert and eventually deposit on a 25 mm diameter mixed cellulose ester (MCE) membrane filter (HSE, 2014). NIOSH method 2537 for methyl and ethyl methacrylate was used to determine the concentration of MMA to which the operator was exposed, by making use of XAD$^{®}$-2, 400/200 mg solid sorbent tubes (226-153 SKC) (NIOSH, 2003). NIOSH method 2027 for ketones was used to determine exposure to acetone during the AM process, by making use of silica gel, 500/1000 mg solid sorbent tubes (NIOSH, 2016). Method MDHS 88 was used to monitor for other VOCs which may have been present using 350 mg passive charcoal samplers (575-001 SKC) (HSE, 1997). The area samplers were placed at a distance of approximately 1.00 meter from the AM machine, the de-powdering station and the post-processing station, at a height of 1.50 meter. Personal samplers were placed in the breathing zone of the AM operator. Due to limited space in the printing room and only one AM operator performing the AM tasks, two sets of area samples and one set of personal samples were taken. A set of samples was collected for each entire object built (this included the pre-processing, processing and post-processing phases). Each set of samples consisted of an IOM ‘multidust’ dual-fraction respirable sample, XAD$^{®}$-2 400/200 mg solid sorbent tube, silica gel 500 mg/1000 mg solid sorbent tube and a 575-001 SKC 350 mg passive charcoal sample. Area monitoring consisted of the use of 12 sets of samples, whereas 6 sets of personal samples were taken and 4 sets of field blank samples. Therefore, a total of 88 samples were taken consisting of 22 IOM ‘multidust’ dual-fraction respirable samples, 22 XAD$^{®}$-2 400/200 mg solid sorbent tubes, 22 silica gel 500 mg/1000 mg solid sorbent tubes and 22 SKC 575-001 350 mg passive charcoal samples, including field blanks. The VOC samples were refrigerated after use until analysis could be performed.

GILAir Plus (Sensidyne, FL, USA) exposure monitoring pumps were calibrated at 0.05 L/min for acetone and MMA sampling and at 2 L/min for particle sampling, as required by the respective methodologies. The calibration was performed prior to exposure monitoring, and the flow rate was confirmed after monitoring, by making use of the Gillian Gilibrator-2 (Gillian

Gilibrator-2, Sensidyne Inc., FL, USA). If the flow rate after monitoring deviated 5% from the flow rate taken prior to monitoring, the sample would have been discarded. This information, together with the blank samples and samples used for measurement analyses results, were used to calculate the 8-hour Time Weighted Average (TWA) exposure concentration for particle and VOCs using this formula.

$$\mathrm{TWA} = \frac{C_1T_1 + C_2T_1 + C_nT_n}{T_8} \quad \text{Equation 2}$$

Where C refers to the concentration of the HCS measured during the AM phase (mg/m^3), T is the duration of exposure at the concentration of C (hours) and T_8 is the total time of the shift period, for the remaining time the concentration was assumed to be zero to make up 8-hours (Schoeman and van den Heever, 2015).

Laboratory analyses

Analyses of all area and personal samples collected were carried out by a South African National Accreditation System (SANAS) accredited laboratory. Gravimetric analysis for inhalable and respirable particles was performed for the IOM ‘multidust’ dual-fraction respirable sampler (MDHS 14/4). Gas Chromatography Flame Ionization Detector (GC/FID) analysis was performed for methyl methacrylate (MMA) in the XAD$^{®}$-2 samples (NIOSH 2537) and acetone in the silica gel samples (NIOSH 2027) and sorbent desorption and GC/FID were performed to analyse for VOCs (MDHS 88). The limit of detection (LOD) for gravimetric weighing was < 0.30 mg for inhalable particles and < 0.03 mg for respirable particles. Both acetone and MMA had a LOD of 0.0001 mg. The VOC results were converted to air concentration; therefore, each sample presented a different limit of quantitation as the exposure of each sample varied (Huber, 2010).

Statistical data analyses

Statistical analyses were performed using GraphPad Prism 8.2.1 (GraphPad Software, La Jolla, USA). Basic descriptive statistics were used to determine the mean, minimum and maximum range and standard deviation of the variables. Throughout a p-value of ≤ 0.05 was considered statistically significant. The particle size of virgin PMMA powders was compared to used PMMA powders by making use of an independent t-test. The analysis of variance (ANOVA) test, followed by the Dunn’s multiple comparisons test were used to determine if there were significant differences in particle emission rates between the three AM phases and particle sizes in each phase. Personal and area sampling results that were found to be below the LOD were replaced with values that were calculated by the LOD divided by the square root of two substitution method (Ganser and Hewett, 2010). 8-Hour TWAs were calculated from the concentration results (for each HCS measured in mg/m^3) and the time duration of exposure (hours) for the entire AM process (Equation 2). The AM operators' personal 8-hour TWA exposures were compared to the Time Weighted Average – Occupational Exposure Limit – Recommended Limit (TWA-OEL-RL) to determine whether exposures were compliant with the South African Regulations for Hazardous Chemical Substances (Department of Employment and Labour, 1995).

Ethics approval

This study was approved by the Health Research Ethics Committee (HREC) of the North-West University (ethics number NWU-00123-18-A1). All AM operators involved with binder jetting AM utilising PMMA were invited to take part in this study voluntarily as stated in the informed consent.

Results

To begin with, PMMA powder particle characterisation (physical and chemical) is described, followed by explanation of particle emissions and emission rates, area and personal exposure monitoring of the AM operator to HCS.

Physical and chemical characterisation of powder particles

Powders used for AM are often recycled without treatment thereof before re-using it. The median particle size for virgin and used powders was 58.32 ± 0.52 μm and 58.40 ± 0.11 μm respectively. Ten percent of particles were smaller than 46.91 μm for virgin PMMA powder and 46.84 μm for used PMMA powder. PSD indicated no particles larger than 202.31 μm for virgin PMMA powder and 342.06 μm for used powder. At d(0.1) and d(0.5) there was no significant difference in the size distribution for virgin and used PMMA powder (Table 1). At d(0.9), a statistical significant difference was observed between virgin and used PMMA powder particle size. The PMMA powder particle sizes measured could not be compared to the safety data sheet (SDS) for Polypor C (PMMA powder) as it was not stated in the SDS (Voxeljet, 2014).

From SEM images, the presence of < 10 μm, and a few < 4 μm, sized particles were observed in both the virgin and used powders (Figure 1A and B). PMMA powder particles appeared smooth with a spherical shape, with no observed differences between the virgin and used powders (Table 1 and Figure 1).

Table 1: PSD and particle shape analysis of PMMA powders. Data reported as mean ± standard deviation.

Powder	**n**	**Particle size distribution (µm)**			**Shape**	
		d(0.1)	**d(0.5)**	**d(0.9)**	**Circularity**	**Convexity**
Virgin	3	46.91 ± 0.17	58.32 ± 0.52	85.59 ± 3.72*	0.94 ± 0.004	0.99 ± 0.001
Used	3	46.84 ± 0.24	58.40 ± 0.11	90.73 ± 4.48*	0.93 ± 0.006	0.99 ± 0.001

- d(0.1) 10%; d(0.5) 50%; d(0.9) 90% of the particles are smaller than the stated diameter.
- n represents the number of repeat analyses.
- * Statistically significant differences ($p \le 0.05$).
- Circularity: Ratio of the perimeter of a circle with an area that is equivalent to the particle, divided by the actual particle perimeter. Circularity of 1 represents a perfect circle.
- Convexity: Particle edge roughness measurement. A convexity of 1 represents a smooth surface.

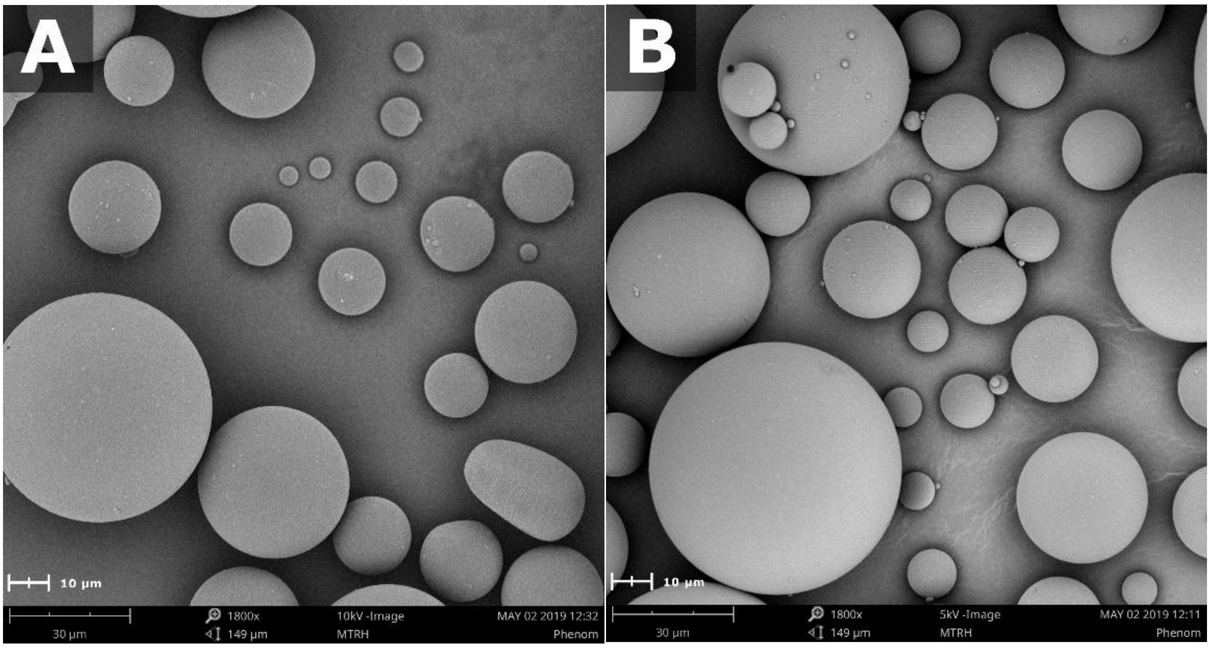


Figure 1: SEM images from virgin (A) and used (B) PMMA powders visualised on a 30 µm scale.

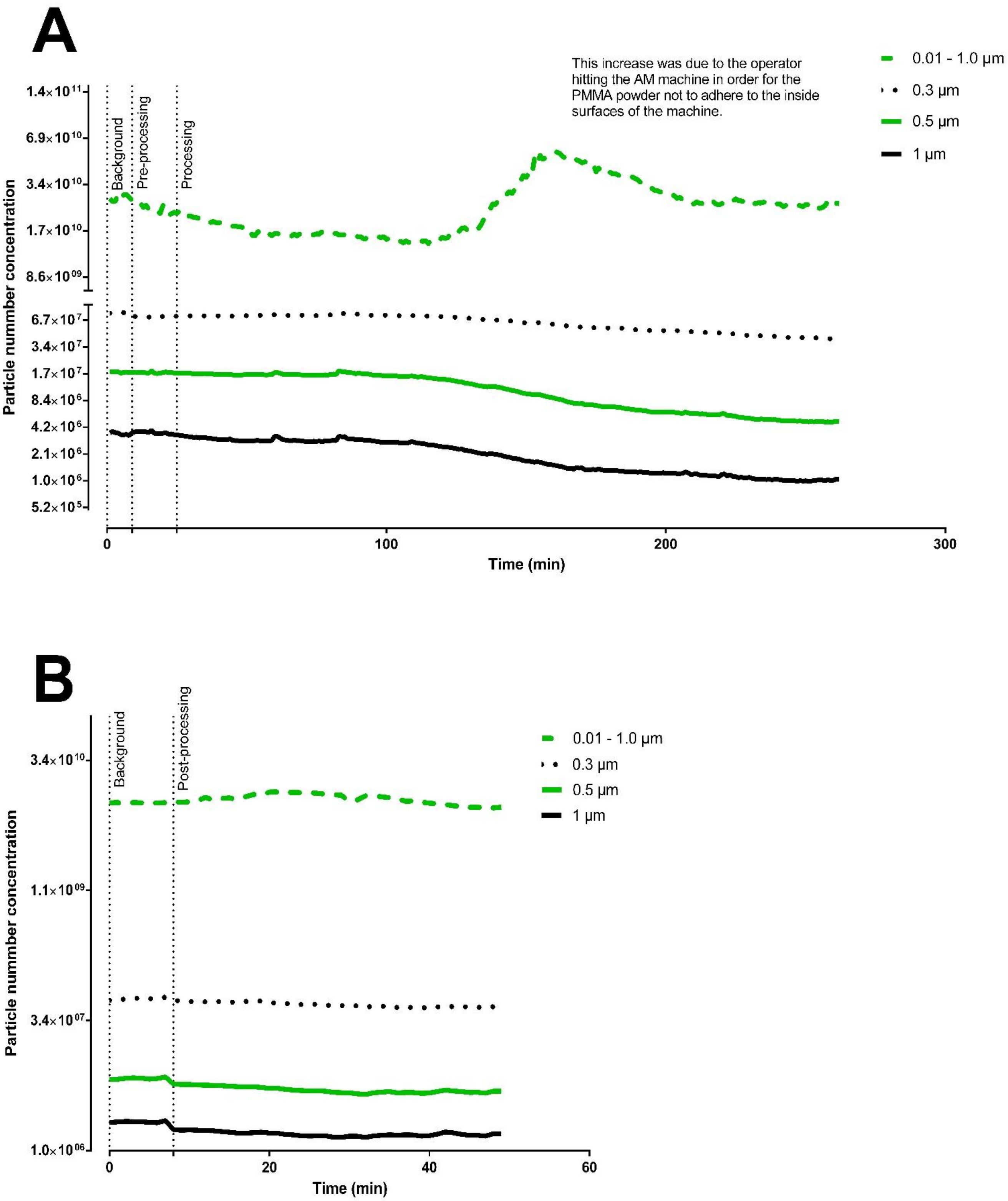
According to the PMMA feedstock SDS, the powder consists only of a dibenzoyl peroxide mixture. XRD and XRF chemical composition analyses revealed that both virgin and used PMMA powders comprised of respectively 99.23% and 99.12% amorphous elements with < 0.1% fluorine and 0.56% silicon dioxide in virgin PMMA powder and 0.68% silicon dioxide in the used PMMA powder.

Particle emissions and emission rates

The duration of pre-processing, processing, and post-processing phases was approximately 37 ± 22.61 minutes, 270 minutes and 28 ± 13.87 minutes respectively. Background particle number concentrations before pre-processing and processing for particles in the 0.01 ~ 1.00

µm, 0.3 µm, 0.5 µm and 1 µm size fractions measured at 1.88 × 10^{10}, 5.83 × 10^7, 1.54 × 10^7 and 5.51 × 10^6 particles/m^3 respectively (Figure 2A). The particle number concentration decreased throughout the pre-processing phase for particles in the 0.01 ~ 1.00 µm size fraction, whereas the particle number concentration for 0.3 µm, 0.5 µm and 1 µm sized particles remained relatively unchanged during this phase. During the processing phase the particle number concentration for 0.01 ~ 1.00 µm, 0.3 µm, 0.5 µm and 1 µm sized particles decreased as the phase continued, and measured as low as 1.03 × 10^6 particles/m^3. It was found that the particle number concentration increased during the processing phase for the 0.01 ~ 1.00 µm particle size fraction. The AM operator struck the AM machine, with a rubber hammer, to prevent the PMMA powder from adhering to the inside surfaces of the AM machine. This may have caused particles adhering to the outside of the machine to become airborne. The background particle number concentrations before the post-processing phase commenced were at 1.11 × 10^{10} (0.01 ~ 1.00 µm), 5.96 × 10^7 (0.3 µm), 7.15 × 10^6 (0.5 µm) and 2.25 × 10^6 (1 µm) particles/m^3 (Figure 2B). The particle number concentration for particles in the 0.01 ~ 1.00 µm size fraction gradually increased to 1.48 × 10^{10} particles/m^3 and decreased to 9.71 × 10^9 particles/m^3 at the end of the phase. Whereas particles in the 0.3 µm to 1 µm size fractions decreased before the post-processing phase commenced, reaching a low of 1.84 × 10^6 particles/m^3. This may be due to the use of the de-powdering station as control measure to prevent particles from becoming airborne and being inhaled.

Figures 3 and 4 illustrate the particle emission rates during binder jetting AM utilising PMMA in particle size ranges of 0.01 ~ 1.00 µm and 0.3 µm – 10 µm respectively. High ambient background particle number concentrations prevented the calculation of particle emission rates during the post-processing phase (0.3 – 1 µm). The maximum particle emission rate for the 0.01 ~ 1.00 µm sized particles was 3.33 × 10^{12} particles/min (n=3), no significant differences between AM phases were observed. Particle emission rates for 0.3 µm sized particles were 1.15 × 10^{10} particles/min during pre-processing (n=1) and 8.88 × 10^9 particles/min during processing (n=1). Particle emission rates for 0.5 µm sized particles were 2.69 × 10^9 particles/min during pre-processing (n=1) and 1.58 × 10^9 particles/min during processing (n=1). Particle emission rates for 1 µm sized particles were 6.86 × 10^8 particles/min during pre-processing (n=2). The particle emission rates for 3 µm to 5 µm sized particles ranged between 1.67 × 10^7 particles/min during post-processing and 5.34 × 10^7 particles/min during post-processing. The highest particle emission rate for 10 µm sized particles was 1.93 × 10^7 particles/min during post-processing. The particle emission rates during the post-processing phase were significantly higher than that of pre-processing and processing phase for 10 µm sized particles (n=3).



This increase was due to the operator hitting the AM machine in order for the PMMA powder not to adhere to the inside surfaces of the machine.

Figure 2: Illustration of particle number concentrations during the pre-processing, processing phases (A) and post-processing phase (B) for one binder jetting process.

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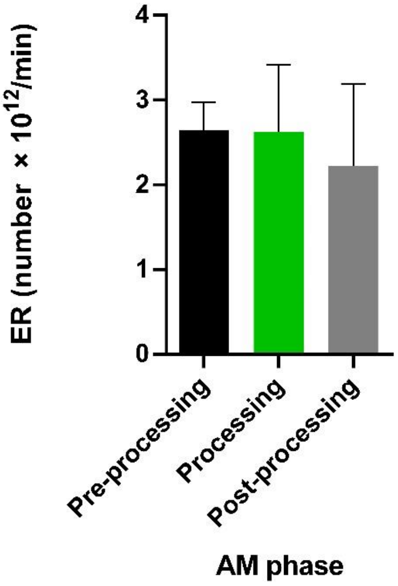


Figure 3: 0.01 ~ 1.00 µm particle emission rates during the binder jetting process phases (n=3).

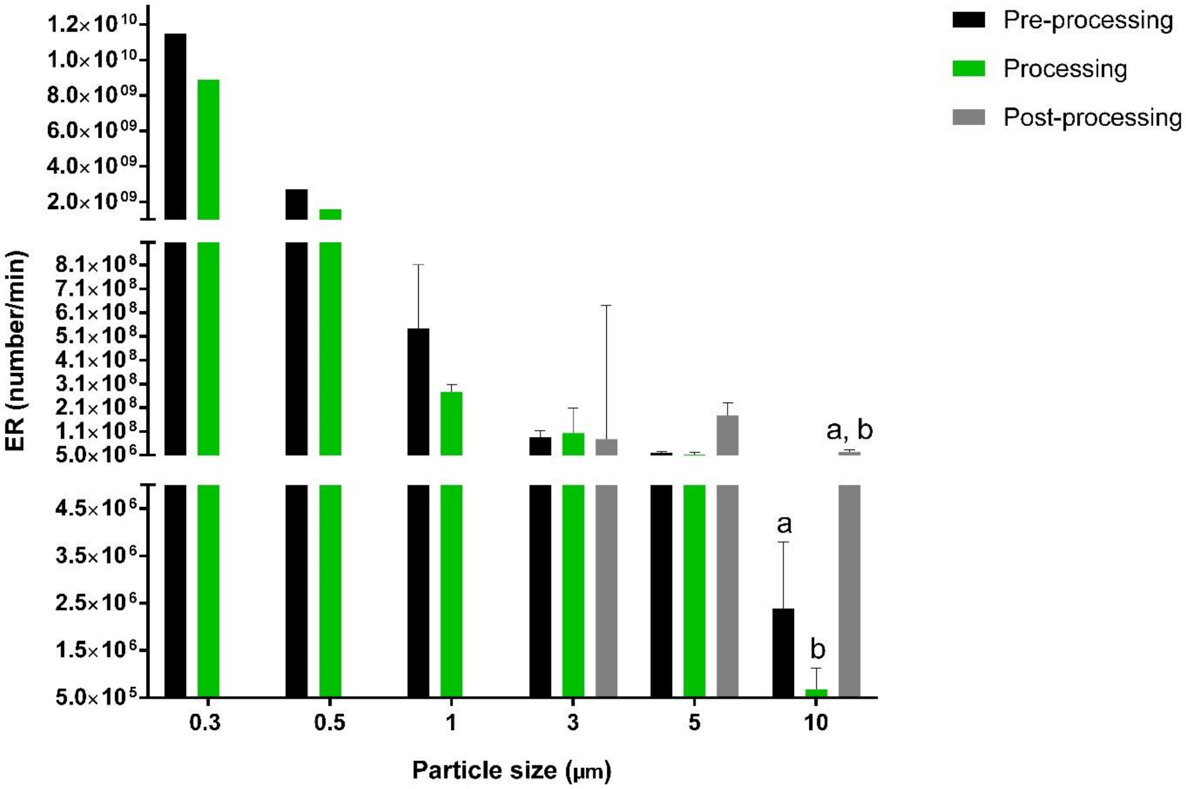


Figure 4: Particle size channels emission rates during the binder jetting process (a – b represents AM phases with significant differences).

Area and personal HCS exposure monitoring

The ambient and personal HCSs exposure concentrations are presented in Table 2. The ambient inhalable particle concentration ranged between below detection level (BDL) mg/m^3 and 6.25 mg/m^3, and the respirable particle concentration between BDL mg/m^3 and 2.36 mg/m^3. The AM operator was exposed to inhalable particles at concentrations ranging from BDL mg/m^3 to 11.31 mg/m^3 and for respirable particles from BDL mg/m^3 to 2.78 mg/m^3. The personal 8-hour TWA exposure of the AM operator to inhalable particles was higher than the ambient concentration in the printing area. One of the personal exposure measurements exceeded the TWA-OEL-RL of 10 mg/m^3 and another exceeded the action level (50% of OEL) of 5 mg/m^3.

The ambient acetone concentrations ranged between BDL mg/m^3 and 4.08 mg/m^3, whereas the AM operator was exposed to acetone concentrations ranging from BDL mg/m^3 to 3.02 mg/m^3. The ambient 8-hour TWA concentration (15.32 ± 2.62 mg/m^3) in the printing room was considerably higher than the personal exposure (2.02 ± 0.58 mg/m^3) of the AM operator.

No MMA was detected in the workplace atmosphere and the AM operator was not likely exposed to MMA (all personal exposure samples were BDL mg/m^3).

VOCs detected with passive samplers were pentane and toluene, however, most of the ambient concentrations and personal exposure concentrations were BDL mg/m^3. Ambient concentrations ranged between BDL mg/m^3 and 1.60 mg/m^3 for pentane, and BDL mg/m^3 and 1.76 mg/m^3 for toluene. Personal exposure of the AM operator during the entire AM process ranged between BDL mg/m^3 and 1.51 mg/m^3 for pentane, and BDL mg/m^3 and 1.25 mg/m^3 for toluene.

Discussion

The aim of this study was to determine the physical and chemical characteristics of the PMMA powder utilised during binder jetting AM, to assess particle emissions and emission rates, as well as to measure respiratory exposure of the AM operator to HCSs associated with this process.

Particle size is relevant from a respiratory health perspective as it has an influence on where the particles may deposit in the respiratory tract when inhaled (Hoet *et al*., 2004, Mellin *et al*., 2016). The use of finer powders with a wide range of PSD is preferred in AM due to its accurate rendering of the final object. However, this preference increases the respiratory

Table 2: Summary of HCS concentrations during the entire binder jetting process utilising PMMA powder feedstock material and acetone.

	Area					Personal				
HCS	**Sampling time hours**	**n**	**Concentration mg/m^3**	**Concentration range mg/m^3**	**8-hour TWA mg/m^3**	**n**	**Concentration mg/m^3**	**Concentration range mg/m^3**	**8-hour TWA mg/m^3**	**TWA-OEL-RL mg/m^3**
Inhalable particles	5.12 ± 0.54	12^+	2.07 ± 2.39*	BDL – 6.25	3.83 ± 2.12	6^+	3.90 ± 5.01*	BDL – 11.31	6.22 ± 4.72	10
Respirable particles			0.58 ± 1.00*	BDL – 2.36	0.77 ± 0.20		1.03 ± 1.24*	BDL – 2.78	1.15 ± 0.33	5
Acetone	5.12 ± 0.55	12^+	2.73 ± 0.84*	BDL – 4.08	15.32 ± 2.62	6^+	1.17 ± 1.20*	BDL – 3.02	2.02 ± 0.58	1780
MMA	5.12 ± 0.55	12^+	BDL	BDL	BDL	6^+	BDL	BDL	BDL	410
Pentane	5.15 ± 0.50	12^+	0.64 ± 0.53*	BDL – 1.60	0.19 ± 0.08	6^+	0.61 ± 0.58*	BDL – 1.51	0.16 ± 0.7	1800
Toluene			0.79 ± 0.51*	BDL – 1.76	0.30 ± 0.03		0.66 ± 0.65*	BDL – 1.25	0.16 ± 0.05	188

- n represents the number of samples taken.
- $^+$ area samples < LOD: Inhalable particles and Respirable particles 7 samples, Acetone 1 sample, MMA 12 samples, Pentane 9 samples, Toluene 6 samples.
- $^+$ personal samples < LOD: Inhalable particles and Respirable particles 2 samples, Acetone 4 samples, MMA 6 samples, Pentane 5 samples, Toluene 5 samples.
- * BDL concentration calculated from LOD$\sqrt{2}/volume\ (m^3)$.
- Inhalable particle LOD – 0.3 mg, respirable particle LOD – 0.03 mg, MMA and acetone LOD – 0.0001 mg.
- South African TWA-OEL-RL (Department of Employment and Labour, 1995).

risks associated with AM utilising powders that may become airborne and are ultimately inhaled (Dawes et al., 2015). AM feedstock powders are often recycled without treatment thereof before re-using it (Junk and Matt, 2015).

The PSD analysis results indicated similarities between the size ranges of the virgin and used PMMA powder particles. It was found that ten percent of the virgin and used powder particles were smaller than 46.91 µm and 46.84 µm respectively. SEM images together with particle shape analyses indicated that the virgin and used powder particles were smooth and spherically shaped. Both virgin and used particle size ranges were < 100 nm. Therefore, all particles can be categorised in the inhalable fraction of particles suspended in air that are able to be aspirated into the mouth and nose during normal breathing and may deposit anywhere in the respiratory tract (British Standards Institution, 1993; ISO 7708:1995). SEM imaging indicated the presence of particles that are < 10 µm and < 4 µm in size (Figure 1 A and B).

Particles suspended in the air that are in the < 10 µm size fraction (thoracic fraction) may be inhaled and reach beyond the larynx, whereas < 4 µm sized particles (respirable fraction) may penetrate the unciliated airways (ISO 7708:1995; Brown *et al*., 2013).

The SDS indicated that the powder consists of a mixture of dibenzoyl peroxide as well as substances of very high concern (SVHC), however the specific SVHC are not mentioned and are presumed to be below 0.1% (Voxeljet, 2014). Our analysis found that PMMA powders comprised mainly of amorphous elements (> 99.23% for virgin powder). The SDS has no mention of the PMMA particle size or a comprehensive chemical composition for this specific powder. This may cause a false sense of security for the AM operators as they are not aware of the health risk involved with their operation. However, according to the PSD, all particles (virgin and used) when suspended in air were in the inhalable fraction. To conclude, the type of feedstock powder selected for the use in AM plays an important role in the quality of the final product, but may also negatively affect the health of AM operators involved.

In the presence of high background ambient particle number concentrations (Figure 2 A and B) particle emission rates as high as 3.33×10^{12} particles/min for 0.01 ~ 1.00 µm sized particles were measured during the processing phase (Figure 3). This facility makes use of other AM processes. However, the binder jetting utilising PMMA printing room contains a single AM machine that was used to build three prototype objects under the same printing conditions over three days. There was no ventilation system or LEV system in working order to control particle emissions in this room. It is suspected that the use of other AM processes, deficiency of housekeeping in the binder jetting utilising PMMA printing room and the defective ventilation and LEV systems may be the reason for the high ambient background particle number concentrations (Figure 2 A and B).

Over-all, the foremost particle emissions and particle emission rates measured were for particle sizes in the range of 0.01 ~ 1.00 µm at 3.3×10^{12} particles/min during the processing phase (Figure 3). Emission rates were calculated on the basis of the trends in particle number concentration for each AM phase, specifically the average-, peak- and outside-concentration. The post-processing phase occurred to some extent inside a de-powdering station for 24 hours after the processing phases were completed. This may have caused lower particle emissions and emission rates during this phase. No significant differences were found in the emission rates during the different AM phases for particles in the size range of 0.01 ~ 1.00 µm and 5 µm. However, a significant difference was found between the AM phases with post-processing being the phase with the highest particle emission rates ($1.93 \pm 1.00 \times 10^7$ particles/min) for particles in the 10 µm size range. Afshar-Mohajer *et al*. (2015) has found that powder particles with sizes between 205 and 407 nm had the highest emission rates (4.4×10^4 particles/min) during the post-processing phase of binder jetting using gypsum. Emission rates calculated in this study (0.01 ~ 1.00 µm) were comparable to those found in Stabile *et al*. (2017) during FDM^{TM} utilising polylactic acid (PLA) (9.98×10^{10} particles/min).

According to Afshar-Mohajer (2015), particles and VOCs are emitted during binder jetting. This is a result of the constant movement of the feedstock powder material in the printing chamber as well as the injection of the binder liquid. Findings from area monitoring confirmed the presence of inhalable and respirable particles, acetone, pentane and toluene in the workplace atmosphere (Table 2). The ambient 8-hour TWA for inhalable particles was 3.83 ± 2.12 mg/m^3. The VOC with the highest concentration in the ambient environment was acetone (BDL mg/m^3 – 4.08 mg/m^3), the binder liquid used.

Personal exposure monitoring indicated that inhalable particles were the predominant particles measured, reaching an average 8-hour TWA of 6.22 ± 4.72 mg/m^3. One of the measurements exceeded the TWA-OEL-RL of 10 mg/m^3 and another the action level of 5 mg/m^3. The personal exposure concentrations of the AM operator to acetone, pentane and toluene were far below the TWA-OEL-RL, whereas MMA concentrations were all BDL mg/m^3. According to a study carried out by Steinle *et al*. (2016) on material extrusion FDM^{TM} utilising acrylonitrile butadiene styrene (ABS) and PLA, inhalable and respirable particle emissions were below the LOD when measured gravimetrically. They have found that styrene was the predominant VOC emitted when utilising ABS, whereas MMA was the foremost VOC emitted when utilising PLA. Due to the TWA-OEL-RL and action level of inhalable particles that were exceeded, action should be taken and control measures implemented in order to decrease AM operator exposure (Department of Employment and Labour, 1995). The AM operator at this facility had additional responsibilities involving various different AM technologies utilising other forms of feedstock materials such as nylon powders and silica sand. Co-exposure, to non-binder jetting feedstock materials, may have caused personal exposure to inhalable and respirable particles that were not only due to work with binder jetting AM. The personal exposure data collected from this study represents the exposure of an AM operator when performing work as in a “real-world” AM workplace, where more than one AM process may be ongoing simultaneously, but the longest period of time is spent in the binder jetting room. However, it is presumed that the exposure to acetone, pentane and toluene was mainly due to the binder jetting process as the ambient workplace concentrations of these substances were higher than the personal exposure concentrations.

According to the South African Occupational Health and Safety Act (Act 85 of 1993) Regulations for Hazardous Chemical Substances, the employer is obligated to implement and uphold a measurement programme that consists of monitoring the HCSs to which the workers are exposed in order to ensure that the workplace is safe and free from risks to the health of workers (Department of Employment and Labour, 1995). As indicated by this study, the manufacturer’s SDS has shortcomings on information that is significant from a health perspective. Therefore, it is recommended that all AM facilities conduct physical and chemical characterisation analyses for the feedstock powder utilised and compare the results with the SDS provided by the manufacturer. Recommended control measures include; repairing the ventilation system and maintain the LEV system in good working order, making use of LEV and providing AM operators with information and training regarding the source of potential exposure to HCS as well as the health risks that are related to exposure to these HCS. This facility provided new appropriate respiratory protective equipment [Phuza Moya filtering facepiece (FFP2)] each day. However, the AM operator did not make use of this. The employer is therefore obligated to provide the AM operator with training on the use and importance of respiratory protective equipment, a respirator fit test, enforcement of the wearing of the provided respiratory protective equipment and medical surveillance (Department of Employment and Labour, 1995).

A limitation to this study was that the facility, at which the monitoring took place, did not make use of the infiltration procedure to strengthen the green part. This is therefore recommended as a future study. Future studies should aim to investigate the relationship between personal exposure of the AM operator to inhalable and respirable particles strictly during binder jetting AM with no co-exposures of other non-binder jetting feedstock materials. Further investigation of emissions during binder jetting utilising other available feedstock materials (such as stainless steel) is also recommended.

Conclusion

In this study, a comprehensive analysis was performed in order to determine the particle emissions and respiratory hazards, and the extent thereof, to which AM operators of PMMA binder jetting are exposed. In the presence of high background ambient particle number concentrations particles sized 0.01 ~ 1.00 µm were the most prevalent sizes emitted and particle emission rates were comparable to that of other AM process types such as material extrusion FDM™. Inhalable, and respirable particles, acetone, pentane and toluene were detected in the workplace atmosphere. All 8-hour TWA personal exposures were below the respective TWA-OEL-RL, with the exception of exposure to inhalable particles, where exposure exceeded the 10 mg/m^3 TWA-OEL-RL once and averaged above 50% of the OEL.

References

Afshar-Mohajer N, Wu C, Ladun T, Rajon DA, Huang Y. (2015) Characterisation of particulate matters and total VOC emissions from a binder jetting 3D printer. J Build Environ; 93: 293-301.

American Polymer Standards Corporation. (2017) Polymethyl methacrylate. Available from http://www.ampolymer.com/SDS/PolymethylMethacrylateSDS.html# (accessed 6 May 2018).

Azimi P, Zhao D, Pouzet C, Crain NE, Stephens B. (2016) Emissions of ultrafine particles and volatile organic compounds from commercially available desktop three-dimensional printers with multiple filaments. Environ Sci Tech; 50: 1260-1268.

Azimi P, Fazli T, Stephens B. (2017) Predicting concentrations of ultrafine particles and volatile organic compounds resulting from desktop 3D printer operation and the impact of potential control strategies. J Ind Ecol; 21: 107-119.

British Standards Institution. (1993) BS EN 481:1993, BS 6069-3.5:1993 Workplace atmospheres – Size fraction definitions for measurement of airborne particles. Available from https://www.techstreet.com/standards/bs-en-481-1993?product_id=1115108 (accessed 23 September 2018).

Brown JS, Gordon T, Price O, Asgharian B. (2013) Thoracic and respirable particle definitions for human health risk assessment. Part Fibre Toxicol; 10:1-12.

Dawes J, Bowerman R, Trepleton R. (2015) Introduction to the additive manufacturing powder metallurgy supply chain. Johnson Matthey Tech Rev; 59: 243-256.

Deng Y, Cao S, Chen A, Guo, Y. (2016) The impact of manufacturing parameters on submicron particle emissions from a desktop 3D printer in the perspective of emission reduction. Build Environ; 104: 311-329.

Department of Employment and Labour. South Africa. Hazardous Chemical Substances Regulations, 1995. Available from http://www.acts.co.za/occupational-health-and-safety-act-1993/ index.html (accessed 20 November 2018).

du Preez S, de Beer DJ, du Plessis LJ. (2018) Titanium powders used in powder bed fusion: their relevance to respiratory health. SAJIE; 29: 94-102.

Ganser GH, Hewett P. (2010) An Accurate Substitution Method for Analyzing Censored Data. J Occup Environ Hyg; 99: 233-244.

Gibson I, Rosen D, Stucker B. (2015) Additive manufacturing technologies: 3D printing, rapid prototyping, and direct digital manufacturing. Virgin York, NY: Springer. ISBN 1 493 92113 4.

Graff P, Ståhlbom B, Nordenberg E, Graichen A, Johansson P, Karlsson H. (2016) Evaluating measuring techniques for occupational exposure during additive manufacturing of metals: a pilot study. J Ind Ecol; 21: 120-129.

He C, Morawska L, Hitchins J, Gilbert D. (2004) Contribution from indoor sources to particle number and mass concentrations in residential houses. Atmos Environ, 38: 3405-3415.

Health and Safety Executive (HSE). (1997) Volatile organic compounds in air. Available from http://www.hse.gov.uk/pubns/mdhs/pdfs/mdhs88.pdf (accessed 29 August 2018).

Health and Safety Executive (HSE). (2014) General methods for sampling and gravimetric analysis of respirable, thoracic and inhalable aerosols. Available from http://www.hse.gov.uk/pubns/mdhs/pdfs/mdhs14-4.pdf (accessed 6 May 2018).

Hoet P, Bruske-Hohlfeld I, Salata O. (2004) Nanoparticles - known and unknown health risk. J Nanobiotechnology; 2: 1-15.

Huber L. (2010) Validation of analytical methods. Germany: Agilent Technologies. Publication number 5990-5140EN.

International Organization for Standardization (ISO). (1995). Air quality – particle size fraction definitions for health-related sampling (ISO 7708:1995). Available from https://www.sis.se/api/document/preview/20338/ (accessed 6 May 2018).

ISO/ASTM. (2015) 52900-15 Standard terminology for additive manufacturing – general principles – terminology. ASTM International, West Conshohocken, PA. Available from www.astm.org (accessed 6 May 2018).

Junk S, Matt R. (2015) Application of polymer plaster composites in additive manufacturing of high-strength components. Mater Sci Forum; 825-826: 763-770.

Kellens K, Mertens R, Paraskevas D, Dewulf W, Duflou J. (2017) Environmental impact of additive manufacturing processes: does am contribute to a more sustainable way of part manufacturing. Procedia CIRP; 61: 582-587.

Kunchala P, Kappagantula K. (2018) 3D printing high density ceramics using binder jetting with nanoparticle densifiers. Mater Des; 155: 443-450.

Kwon O, Yoon C, Ham S, Park J, Lee J, Yoo D, Kim Y. (2017) Characterisation and control of nanoparticle emission during 3D printing. Environ Sci Tech; 51: 10357-10368.

Mellin P, Jönsson C, Åkermo M, Fernberg P, Nordenberg E, Brodin H, Strondl A. (2016) Nano-sized by-products from metal 3D printing, composite manufacturing and fabric production. J Clean Prod; 139: 1224-1233.

Mendes L, Kangas A, Kukko K, Mølgaard B, Säämänen A, Kanerva T, Flores Ituarte I, Huhtiniemi M, Stockmann JH, Partanen J, Hämeri K, Eleftheriadis K, Viitanen A. (2017) Characterisation of emissions from a desktop 3D printer. J Ind Ecol; 21: 94-106.

Meteyer S, Xu X, Perry N, Zhao Y. (2014) Energy and material flow analysis of binder-jetting additive manufacturing processes. Procedia CIRP; 15: 19-25.

National Institute for Occupational Safety and Health (NIOSH). (2003) Methyl and ethyl methacrylate: method 2537, issue 3. Available from https://www.cdc.gov/NIOSH/docs/2003-154/pdfs/2537.pdf (accessed: 6 May 2018).

National Institute for Occupational Safety and Health (NIOSH). (2015) Acetone icsc: 0087. Available from https://www.cdc.gov/niosh/ipcsneng/neng0087.html (accessed 21 November 2018).

National Institute for Occupational Safety and Health (NIOSH). (2016) Ketones: method 2027, issue 1. Available from https://www.cdc.gov/niosh/docs/2014-151/pdfs/methods/2027.pdf (accessed 6 June 2018).

Odian, G. (2004) Principles of polymerization fourth edition. Staten Island, NY: John Wiley and Sons Inc. ISBN 9 780 47147 875 1.

Plog BA, Quinlan PJ. (2001) Fundamentals of industrial hygiene fifth edition. Illinois, USA: National Safety Council Press. ISBN 0 879 12216 1.

Prasad TS, Devaiah M. (2018) Manufacturing of die using rapid prototyping technique. IUP J Mech Eng; 11: 69-79.

Schoeman JJ, van den Heever DJ. (2015) Occupational hygiene: the science-volume 1. Bloemfontein, FS: VDH Industrial Hygiene CC. ISBN 9 780 62063 414 4.

Stabile L, Scungio M, Buonanno G, Arpino F, Ficco G. (2017) Airborne particle emission of a commercial 3D printer: the effect of filament material and printing temperature. Indoor Air; 27: 398-408.

Stanczyk M, Van Rietbergen B. (2004) Thermal analysis of bone cement polymerisation at the cement–bone interface. J Biomechanics; 37: 1803-1810.

Steinle P. (2016) Characterisation of emissions from a desktop 3D printer and indoor air measurements in office settings. J Occup Environ Hyg; 13: 121-132.

Stefaniak AB, Johnson AR, du Preez S, Hammond DR, Wells JR, Ham JE, LeBouf RF, Menchaca KW, Martin SB, Duling MG, Bowers LN, Knepp AK, Su FC, de Beer DJ, du Plessis JL. (2018) Evaluation of emissions and exposures at workplaces using desktop 3-dimensional printers. J Chem Health Saf; 26: 19-30.

Stephens B, Azimi P, El Orch Z, Ramos T. (2013) Ultrafine particle emissions from desktop 3D printers. Atmos Environ; 79: 334-339.

Voxeljet. (2014) Safety data sheet 1907/2006/EC – reach (GB) Voxeljet – Polypor- pulver typ C. Voxeljet AG 86316 Friedberg.

Yi J, Nurkiewicz T, LeBouf RF, Duling MG, Chen BT, Schwegler-Berry D, Virji MA, Stefaniak AB. (2016) Emission of particulate matter from a desktop three-dimensional (3D) printer. J Toxicol Environ Health-Part A; 79: 453-465.

Zhou XD, Zhang SC, Huebner W, Ownby PD, Hongchen G. (2001) Effect of the solvent on the particle morphology of spray dried pmma. J Mater Sci; 36: 3759-3768.

Zhou Y, Kong X, Chen A, Cao S. (2015) Investigation of ultrafine particle emissions of desktop 3D printers in the clean room. Procedia Eng; 121: 506-521.

Zontek TL, Ogle BR, Jankovic JT, Hollenbeck SM. (2017) An exposure assessment of desktop 3D printing. J Chem Health Saf; 24: 15-25.

CHAPTER 4 CONCLUDING CHAPTER

4.1. Background

Additive manufacturing (AM) was developed to manufacture models and prototype objects. It is experienced as one of the fastest growing manufacturing methods (Prasad and Devaiah, 2018). AM has been applied in the aerospace, automobile and medicinal industries due to its ability to reduce object production time, cost and material consumption, as well as a higher-level of geometrical complexity (Khorram Niaki and Nonino, 2017; González-Henríquez *et al.,* 2019). According to González-Henríquez *et al*. (2019) polymers have been rendered the most widely utilised feedstock material due to its adaptability.

From an occupational hygiene viewpoint, it is necessary to assess the health risks involved/present in the workplace as well as to determine the potential exposure of the workers to hazardous chemical substances (HCSs) (Department of Employment and Labour, 1995). According to Chase (2019), particles with sizes ≤ 10 µm are able to become airborne effortlessly, and cause a potential inhalation risk to the AM operator. Furthermore, particles with sizes ≤ 4 µm have the capacity to penetrate deep into the gas exchange areas of the lungs when inhaled. This study is the first to establish the particle emissions and emission rates, as well as respiratory exposure to HCSs that is released during binder jetting AM that makes use of poly methyl methacrylate (PMMA) as feedstock material.

4.2. Main findings

The general aim of this study is to assess the physical and chemical characteristics of the PMMA powder feedstock, assess particle emissions as well as the workplace respiratory exposure of AM operators to HCS [such as inhalable and respirable particles and volatile organic compounds (VOCs) including acetone and methyl methacrylate (MMA)] when PMMA powder is utilised during industrial scale binder jetting AM. The aim has been achieved based on the realisation of the following objectives.

In the first place the objectives for this study have been to determine the physical characteristics and chemical composition of the PMMA powder utilised during binder jetting AM. This was assessed by means of Particle Size Distribution (PSD), Scanning Electron Microscopy (SEM), X-ray Powder Diffraction (XRD) and X-ray fluorescence (XRF) analyses of bulk virgin and used PMMA samples. PSD analysis results indicated that the median particle size for virgin and used powder was 58.32 ± 0.52 µm and 58.40 ± 0.11 µm respectively. However, 90% of the virgin PMMA powder particles were smaller than 85.59 ± 3.72 µm, whilst for the used power it was 90.73 ± 4.48 µm. This indicated a statistically significant difference between virgin and used PMMA powder. SEM imaging illustrated the presence of small number of particles < 10 µm and < 4 µm sized particles. XRD analysis indicated that both virgin and used PMMA powder comprises mainly (99.23% and 99.12% respectively) of amorphous elements. Consequently, the first objective of this study has been met.

The second objective has been to determine particle emissions associated with binder jetting utilising PMMA powder by means of direct reading particle counting instruments throughout the three phases of binder jetting AM. This study has confirmed the emission of particles in the 0.01 to 10 µm size fractions as well as inhalable and respirable particles in the workplace environment (refer also to Objective 3). Some of the ambient inhalable and respirable particle samples were found to be BDL (n=7). High ambient background particle number concentrations and the effectiveness of the de-powdering station led to lower particle emissions preventing the calculation of particle emission rates during the post-processing phase (0.3 – 1 µm). Particle emission rates as high as 3.33×10^{12} particles/min for 0.01 ~ 1.00 µm sized particles was measured during the processing phase. No evidence was found that there are statistically significant differences amongst the particle emission rates during the various AM phases. However, a significant difference was found between the size fractions during the AM phases with post-processing being the phase with the highest particle emission rates ($1.93 \pm 1.00 \times 10^{7}$ particles/min) for particles in the 10 µm size range. Therefore, the second objective of this study has been met.

The third objective has been to assess ambient concentrations as well as personal respiratory exposure concentrations of the AM operator, for particles and VOCs (such as acetone and MMA) associated with binder jetting by means of area and personal sampling for the duration of the AM process. Ambient concentrations were assessed by collecting area (static) samples and task-based direct reading instrument monitoring. Ambient inhalable and respirable concentrations of particles ranged between Below Detection Limit (BDL) to 6.25 and BDL to 2.36 mg/m^3 respectively (n=7 was BDL), acetone concentrations ranged between BDL to 4.08 mg/m^3 (n=1 was BDL), all MMA concentrations were BDL, pentane concentrations ranged between BDL to 1.60 mg/m^3 (n=9 was BDL) and BDL to 1.76 mg/m^3 for toluene (n=6 was BDL). Personal respiratory exposure concentrations of the AM operator were assessed by means of personal sampling during the entire task-based AM process. This was done by collecting personal exposure samples within the breathing zone of the AM operator spending the majority of the time in the binder jetting room. Findings from the sample analyses indicated that the AM operator was exposed to inhalable particles in the range of BDL to 11.31 mg/m^3, respirable particles in the range of BDL to 2.78 mg/m^3 (n=2 was BDL), acetone concentrations in the range of BDL to 3.02 mg/m^3 (n=4 was BDL) and MMA were all BDL. The 8-hour TWA personal exposure results for VOCs (pentane and toluene), monitored with passive samplers, were below their respective occupational exposure limits (OELs). The AM operator's exposure was therefore lower than the time weighted average – occupational exposure limit – recommended limit (TWA-OEL-RL) for all HCSs that were monitored except for inhalable particles. One of the measurements taken was found to be above the TWA-OEL-RL of 10 mg/m^3, and the average was found to be above the action level. Consequently, the third objective of this study has been met.

Two hypotheses have been formulated for this study. The first hypothesis is that inhalable particles are emitted into the workplace environment during the entire binder jetting AM process utilising PMMA as feedstock material. This study has verified that ambient inhalable and respirable particles were emitted into the workplace environment, however some samples were BDL (n=7). Particles in the 0.01 ~ 1.00 µm size fractions were also emitted during the entire binder jetting process. No significant differences were found between the particle emission rates for the different binder jetting AM phases based on the 0.01 ~ 1.00 µm particle size fraction. This hypothesis is therefore partially accepted.

The second hypothesis is that the AM operators are exposed through inhalation to quantifiable concentrations of HCSs (such as inhalable and respirable particles, acetone and MMA) during binder jetting utilising PMMA and acetone. Inhalable and respirable particles (4 samples), acetone (2 samples), all MMA samples were BDL, pentane (1 sample) and toluene (1 sample) were detected in some of the personal exposures. All 8-hour TWA personal exposures were below the respective TWA-OEL-RL, with the exception of exposure to inhalable particles, where the 10 mg/m^3 TWA-OEL-RL exposure was exceeded once and averaged above 50% of the OEL. This hypothesis is therefore partially accepted.

4.3. Limitations of the study

This study was limited by the number of samples collected, as there is only one AM operator performing the AM operations. This prevented the determination of personal exposure of different AM operators performing different actions for the AM process. There is limited information available regarding AM utilising PMMA as a feedstock material. Therefore, there is limited information available regarding the occupational health of the AM operators. There is a limitation on comparative studies for AM making use of binder jetting and PMMA. This is due to only one facility in South Africa making use of this process and, therefore, there are very few AM operators to assess. The AM operators are not in the AM room for the entire duration of the AM process as they are also conducting work in other AM rooms making use of other AM technologies and feedstock materials. Therefore, the personal monitoring results cannot be detected as only originating from exposure to the HCSs investigated for the purpose of this study, and may not be representative of personal exposure of AM operators only working with binder jetting utilising PMMA. However, the personal exposure data collected for this study represents the exposure of an AM operator when performing work as in a "real-world" AM workplace where more than one AM process may be in progress simultaneously.

4.4. Recommendations

Observations made at the AM facility during exposure monitoring include the lack of adequate ventilation and insufficient personal protective equipment (PPE) for the all persons entering the room at some point during the AM process. It was also observed that AM operators involved with other AM technologies entered the manufacturing room to make use of the scale used for weighing manufactured objects as well as binder liquid. The PPE required to enter the AM room is indicated on the door before entering, but not all of these recommendations are followed by the AM operator or others visiting in this area. Therefore, stricter rules should be implemented at this workplace by the employer. The dust respirator [Phuza Moya filtering facepiece (FFP2)], provided is sufficient to protect against the other HCSs (VOCs), such as acetone, pentane and toluene to which the operators are exposed, as personal exposure to these VOCs were considerably lower than the OEL. There are windows in this PMMA AM room which open directly into a corridor and others into a nylon AM room, probably causing exposure to other HCSs not associated with AM utilising PMMA. Control measures should be implemented in accordance to the sequence of the hierarchy of control, consisting of elimination, followed by substitution, engineering control, administrative control and lastly PPE (HSE, 2013).

4.4.1 Elimination and substitution

Eliminating the HCSs (PMMA feedstock powder and acetone) used during the binder jetting process will not be possible. However, it is recommended that the use of other types of AM process feedstock materials is prohibited in this PMMA AM room, and should be removed during the manufacturing process. It is not possible to substitute any of the HCS materials used in order to decrease the exposure of the AM operators. However, the cleaning method can be substituted, as the facility makes use of industrial vacuum cleaners only once a week. This is not effective and cause particles to build up on surfaces. Therefore, it is recommended that this printing room should be cleaned daily with wet-methods such as wiping surfaces with a damp cloth or making use of a vacuum cleaner utilising a water filtration system to prevent resuspension of powder particles and causing unnecessary exposure to the AM operators (Department of Employment and Labour, 1995).

4.4.2 Engineering controls

The release of HCSs in the AM room may be controlled by making use of ventilation systems, enclosure methods and separation of workspaces in order to prevent AM operator inhalation of HCSs. This may sequentially lower the concentration of HCS in the environment and, therefore, inhalation exposure (Department of Employment and Labour, 1995; HSE, 2017). Specific engineering controls are described in the paragraphs below.

It was observed that the ventilation and local exhaust ventilation (LEV) systems in the AM room in which binder jetting utilising PMMA powder took place, were not in working order. LEV may be used to reduce airborne HCSs in the form of particles and vapours by removing it from the AM environment directly to the outside environment, also decreasing the AM operator’s inhalation exposure. It is recommended that a movable receiving hood LEV system is used in order to capture the airborne contaminants in the area where it is generated, such as above the de-powdering station during post-processing phase, above the AM machine and during the processing phase (HSE, 2017).

The door to the AM room opens many times during printing as the operator enters to ensure that the printing process is stable as well as operators involved with other AM technologies enter this room to use equipment stored in this area. This causes the excess loose powder particles remaining around the manufactured object to become airborne as the door is right next to the station where the finished part is kept before post-processing takes place. The manufactured object remains in this area for approximately 24 hours. Therefore, the AM operator may be exposed to airborne powder particles which can easily be avoided. It is recommended that the manufactured object (green part) is moved to another area of the room where there is less air movement, or to enclose this bin to prevent the powder particles from becoming airborne (Department of Employment and Labour, 1995).

Equipment used in this working environment should be stored in an enclosed cabinet in order to prevent the build-up of powder on these items of equipment, sequentially avoiding these powder particles of becoming airborne when disturbed and protecting the AM operator from the respiratory hazard.

It is recommended that separate scales are provided for each AM technology and feedstock material used. Currently only one scale is used for various AM technologies and this may cause exposure of the AM operators to HCSs not related to AM utilising PMMA.

4.4.3 Administrative control

According to the South African Regulations for HCS (1995), the AM operators should receive information and training regarding the source of potential exposure to HCS as well as the health risks that are related to exposure to these HCSs. The AM operators should also be informed about the precautionary measures that have been taken by their employer to protect against the risks that are associated with exposure to the HCS present. They should be informed and trained on the necessity, correct use and maintenance of the engineering control methods, personal protective equipment (PPE) and respiratory protective equipment (RPE). It is important to provide information and training on the significance of personal hygiene, good housekeeping in the workplace as well as the necessary procedures that should be followed in case of accidents or emergency situations to avoid excessive exposure to the HCS in the working environment. Not all surfaces in the AM room were cleaned regularly, therefore, build-up of powder particles occurred. Cleaning protocols should be improved to eliminate the chances of powder build-up and consequently avoid inhalation risks to the AM operator if the powder particles would become airborne when disturbed. It is recommended that the AM room is thoroughly cleaned after each AM process (Department of Employment and Labour, 1995; HSE, 2013).

As there is currently no working ventilation or LEV system in place in this printing room, it is recommended that the exposure control measures already in place are repaired and maintained in a good working order. After reparations it is required that the effectiveness is inspected and thorough examinations are done every two years to ensure the control method is maintained and in good working order. It is allowed that AM utilising PMMA feedstock material and acetone as a binder liquid may be performed by one person. It is recommended that the other personnel that come and go in this area refrain from doing so and stay out of the AM room during the AM process to limit the number of employees that are exposed, by way of inhalation, to airborne HCS. The period of time that the AM operator is exposed to the airborne HCS by way of inhalation may be decreased, so that they are only exposed during the times that they have to prepare for pre-processing, checking in on the print hourly and during post processing.

4.4.4 Personal protective equipment

It was observed that the AM operators for binder jetting utilising PMMA have signage on the door clearly indicating which PPE they are required to wear when entering the AM room. This includes a respirator, safety eyewear, protective gloves and steel toe capped safety footwear. The AM operator on duty only wore steel toe capped safety footwear. However, a box of active carbon valved nuisance dust respirators [Phuza Moya filtering facepiece (FFP2)] was readily available at the entrance of the AM room.

The employer should provide the AM operator with training on the use and importance of respiratory protective equipment (RPE), and a respirator fit test and medical surveillance should be carried out (Department of Employment and Labour, 1995). As this facility already provides the appropriate RPE, it is recommended that the employer ensures that the supplied protective equipment is used and regularly replaced, punitive measures should be in place if the precautionary procedures are not followed.

4.5. Future studies

The intention of this study was to determine the chemical composition and physical characteristics of PMMA powder utilised during binder jetting AM. To assess HCSs (such as PMMA particles, MMA and acetone) emissions, and determine emission rates of HCSs associated with binder jetting utilising PMMA powder. This was done by means of direct reading instruments throughout the three different phases of AM. To assess personal respiratory exposure of AM operators to VOCs (specifically MMA and acetone) and PMMA particle emissions associated with binder jetting by means of personal sampling during the entire task-based AM process.

- Future studies should aim to investigate the relationship between personal exposure of the AM operator to inhalable and respirable particles strictly during binder jetting AM with no co-exposures to other non-binder jetting feedstock materials.
- It was indicated by the findings of this study that toluene was present in the personal and area samples taken. It is recommended that biological monitoring and medical surveillance

are done as this is compulsory if an assessment indicated that the AM operator may be exposed to HCSs listed, such as toluene, in Table 3 of the Regulations for Hazardous Chemical Substances (Department of Employment and Labour, 1995).

- It is recommended that this study is repeated with the post-processing using epoxy resin or cyanoacrylate. This could not be done in this study due to the AM facility not making use of this process for the specific objects manufactured.
- Further investigation of emissions during binder jetting utilising other available feedstock materials (such as stainless steel) is also recommended.

4.6. References

Chase K. (2019) Confined Spaces: airborne dust & particulates accumulate quickly. ISHN; 53: 22–23.

Department of Labour. South Africa. (1995) Hazardous Chemical Substances Regulations, 1995. Available from http://www.acts.co.za/occupational-health-and-safety-act-1993/index.html (accessed 20 November 2018).

González-Henríquez CM, Sarabia-Vallejos MA, Rodriguez-Hernandeze J. (2019) Polymers for additive manufacturing and 4D-printing: Materials, methodologies, and biomedical applications. Prog Polym Sci; 94: 57-116.

Health and Safety Executive (HSE). (2013) Control of substances hazardous to health. The control of substances hazardous to health regulations 2002 (as amended). Approved code of practice and guidance. Available from: http://www.hse.gov.uk/pubns/priced/l5.pdf (accessed 28 September 2019).

Health and Safety Executive (HSE). (2017) Controlling airborne contaminants at work: a guide to local exhaust ventilation (LEV). Norwich, UK: The Stationery Office. ISBN 978 0 7176 6613 3.

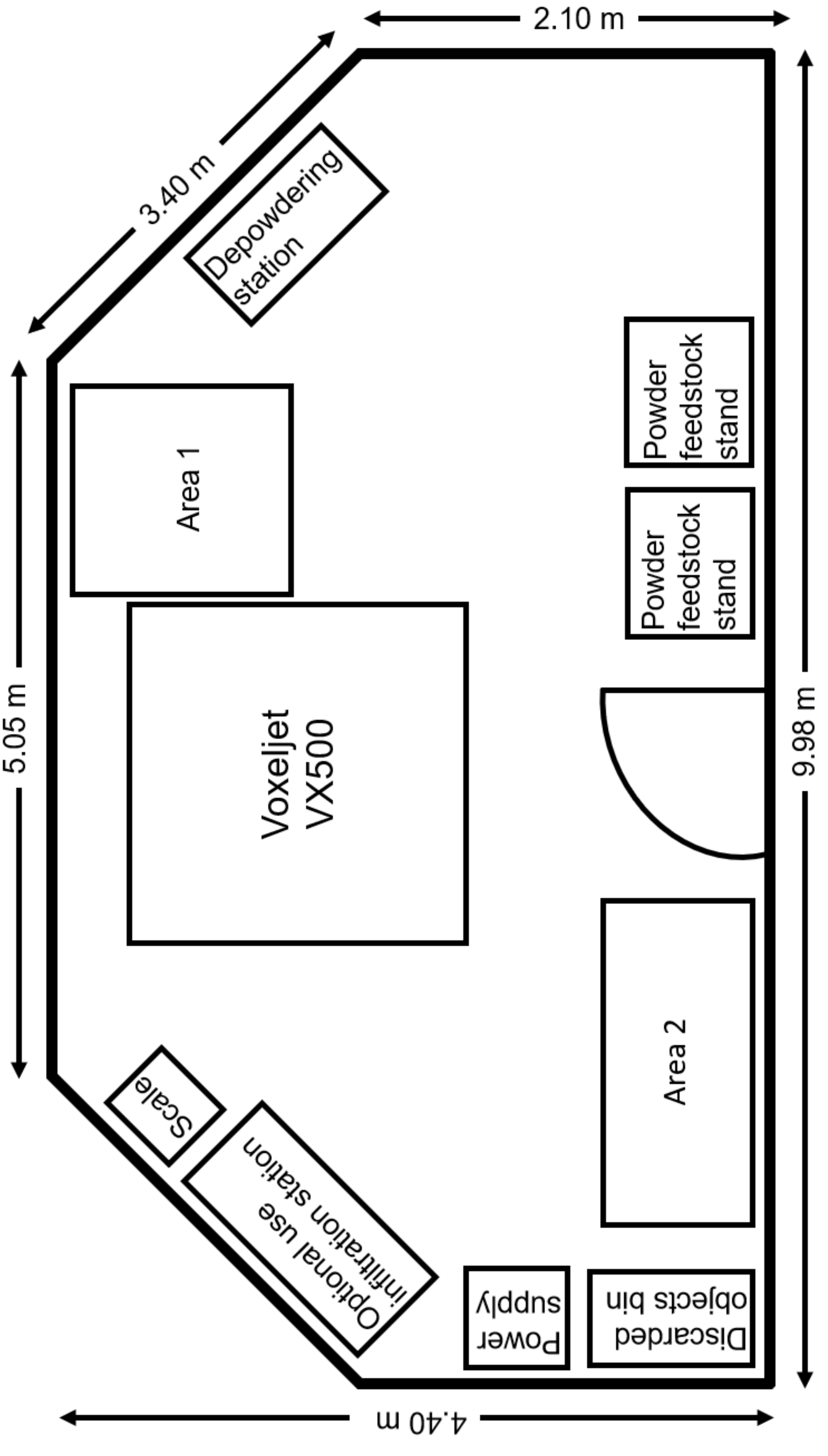
Khorram Niaki M, Nonino F. (2017) Additive manufacturing management: a review and future research agenda*.* IJPR*;* 55: 1419-1439.

Prasad TS, Devaiah M. (2018) Manufacturing of die using rapid prototyping technique. IUP J Mech Eng; 11: 69-79.

ANNEXURE A

Binder jetting utilising PMMA AM room – Floorplan

The AM room had a triangular shaped double-height ceiling of 4.66 m.



ANNEXURE B

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Research Ethics Regulatory Committee
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ETHICS APPROVAL LETTER OF STUDY

Based on approval by the North West University Health Research Ethics Committee (NWU-HREC) on 27/11/2018, the NWU Health Research Ethics Committee hereby approves your study as indicated below. This implies that the North-West University Research Ethics Regulatory Committee (NWU-RERC) grants its permission that, provided the special conditions specified below are met and pending any other authorisation that may be necessary, the study may be initiated, using the ethics number below.

Study title: Particle emissions and respiratory exposure to hazardous substances associated with additive manufacturing utilising poly methyl methacrylate.
Study Leader/Supervisor (Principal Investigator)/Researcher: Ms S du Preez
Student: S van der Walt

Ethics number:

N	W	U	-	0	0	1	2	3	-	1	8	-	A	1
Institution				Study Number						Year			Status	

Status: S = Submission; R = Re-Submission; P = Provisional Authorisation; A = Authorisation

Application Type: Single study
Commencement date: 2018/11/27 **Risk:** Minimal
Expiry date: 2019/11/30
Approval of the study is initially provided for a year, after which continuation of the study is dependent on receipt and review of an annual (or as otherwise stipulated) monitoring report and the concomitant issuing of a letter of continuation.

Special in process conditions of the research for approval (if applicable):

- Please provide the HREC with the final versions of the questionnaires to be included in the study
- Please provide the names of the research assistants when they become known as well as their CV's and signed codes of conduct

General conditions:

While this ethics approval is subject to all declarations, undertakings and agreements incorporated and signed in the application form, the following general terms and conditions will apply:

- *The study leader/supervisor (principle investigator)/researcher must report in the prescribed format to the NWU-HREC:*
  - *annually (or as otherwise requested) on the monitoring of the study, whereby a letter of continuation will be provided, and upon completion of the study; and*

- *without any delay in case of any adverse event or incident (or any matter that interrupts sound ethical principles) during the course of the study.*
- *The approval applies strictly to the proposal as stipulated in the application form. Should any amendments to the proposal be deemed necessary during the course of the study, the study leader/researcher must apply for approval of these amendments at the NWU-HREC, prior to implementation. Should there be any deviations from the study proposal without the necessary approval of such amendments, the ethics approval is immediately and automatically forfeited.*
- *Annually a number of studies may be randomly selected for an external audit.*
- *The date of approval indicates the first date that the study may be started.*
- *In the interest of ethical responsibility the NWU-RERC and NWU-HREC reserves the right to:*
  - *request access to any information or data at any time during the course or after completion of the study;*
  - *to ask further questions, seek additional information, require further modification or monitor the conduct of your research or the informed consent process;*
  - *withdraw or postpone approval if:*
    - *any unethical principles or practices of the study are revealed or suspected;*
    - *it becomes apparent that any relevant information was withheld from the NWU-HREC or that information has been false or misrepresented;*
    - *submission of the annual (or otherwise stipulated) monitoring report, the required amendments, or reporting of adverse events or incidents was not done in a timely manner and accurately; and / or*
    - *new institutional rules, national legislation or international conventions deem it necessary.*
- *NWU-HREC can be contacted for further information or any report templates via Ethics-HRECApply@nwu.ac.za or 018 299 1206.*

The NWU-HREC would like to remain at your service as scientist and researcher, and wishes you well with your study. Please do not hesitate to contact the NWU-HREC or the NWU-RERC for any further enquiries or requests for assistance.

Yours sincerely

Digitally signed by Wayne
Towers
Date: 2018.12.04
11:50:51 +02'00'

Prof Wayne Towers
Chair NWU Health Research Ethics Committee

Current details: (22351930) M:\DSS1\8533\Monitoring and Reporting Cluster\Ethics\Certificates\Templates\Research Ethics Approval Letters\9.1.5.4.2 HREC Ethical Approval Letter.docm
3 December 2018

File reference: 9.1.5.4.2

ANNEXURE C

Woorde wat werk / Working Words

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LANGUAGE EDITING STATEMENT

2019 – 11 - 18

I, Jannetje Levina De Kock hereby declare that the mini-dissertation

Particle emissions and respiratory exposure to hazardous chemical substances associated with additive manufacturing utilising poly methyl methacrylate

by

Sylvia van der Walt

for submission to the

the NWU

in the Niche area Occupational Hygiene and Health Research Initiative (OHHRI)

- has been edited for language correctness and spelling.
- has been edited for consistency (repetition, long sentences, logical flow)

No changes have been made to the document’s substance and structure (nature of academic content and argument in the discipline, chapter and section structure and headings, order and balance of content, referencing style and quality).

J L DE KOCK

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