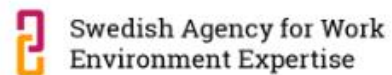


Konferencja m-nar. "Building awareness of safe work during additive manufacturing."
Elżbieta Dobrzyńska, 5th PEROSH Research Conference & Anniversary Event
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Bio sketch

Elżbieta Dobrzyńska, Ph.D. (Eng.) is a researcher at the Department of Chemical, Aerosol and Biological Hazards, Central Institute for Labour Protection – National Research Institute in Poland. The author of various publications including peer-reviewed articles in scientific journals. Her main scientific interests are focused on exposure to chemical substances at the workplace, particularly CMR and endocrine disruptors. She is also involved in trainings on chemical risk assessment methods and the development of CHEMPYL knowledge database.

"Building awareness of safe work during additive manufacturing"

The opportunities and progressive development of additive manufacturing technology is associated with an increasing demand for new materials which may pose health risk to their users. One example is, the printer's operator who may be exposed to the emission of particles and harmful chemical substances.

In CIOP-PIB, we have conducted research focused on the identification and analysis of the risks associated with the use of different types of materials in one of the best-known 3D printing technologies, i.e. FDM (fused deposition modelling). We have also initiated research on the effects of components used in 3D printing on the respiratory system on the blood-brain barrier cells. Measurements of particles and chemical emissions were carried out at selected workplaces and in a test chamber during the printer operation. Among the emitted compounds, mainly filament monomers, their degradation products and potential additives were identified. Thus, the measurements were carried out for different types of compounds like volatile organic compounds (VOCs), aldehydes and ketones, phthalates and particles. The work carried out so far, has shown that more than 90% of the particles emitted are at the nanoscale (< 115.6 nm). The emissions of ultra-fine particles may be of concern due to their negative health effects. The average number concentration of particles emitted during the operation of the 3D printer was measured to range from 482 - 60466 particles/cm³. The calculated TVOC values, depending on the filament used at the individual workplaces ranged from 673 - 4452 µg/m³. The total PAE concentration both in the inhalable fraction and in the gaseous phase did not exceed 5 µg/m³. Nevertheless, phthalates, as endocrine disruptors measured in air samples, increase the risk estimated at the printer operator's workplace. This research will contribute to increase the knowledge and understanding of both manufacturers and printer users regarding exposure to chemical agents and particles at workplaces.



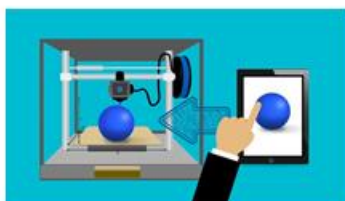
Building awareness of safe work during additive manufacturing.

ELŻBIETA DOBRZYŃSKA

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AM applications and opportunities



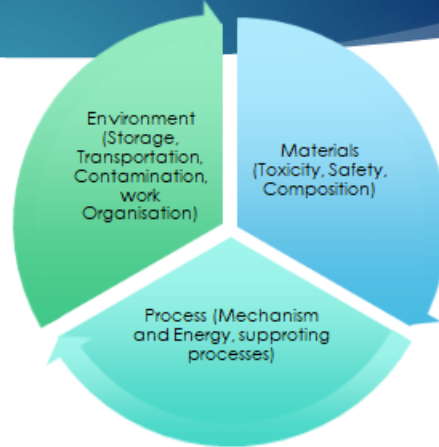
3D printing provides almost unlimited opportunities in every field of manufacturing from creating conceptual models to producing high-performance parts for aerospace or transportation.

Apart from the outstanding applications and opportunities, AM is still a source of new processes and new materials with little hazard and exposure data.

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Holistic approach to risk assessment

1. Identify the hazards
2. Evaluate the risk
3. Decide on control measures
4. Document RA and implement preventive measures



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Identification of hazards

- ▶ physical (noise, mechanical - machinery and moving parts, electric lighting, optical and laser radiation, electric current, electromagnetic fields, mechanical vibrations)

- ▶ psychophysical



- ▶ chemical (chemical substances and their mixtures, particles)

- **What pollutants are used or emitted during the printing process?**
- **What is the risk to human health from exposure to these chemicals and particles?**
- **What factors influence the type and scale of emissions?**

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Chemicals of concern in AM

- ▶ Chemical substances and their mixtures used before and after the printing process (pre- and post-processing)
- ▶ Materials used for printing as a feedstock (thermoplastics, polymers, resins etc.)
- ▶ Thermal decomposition products of raw materials and their additives – volatile organic compounds, phthalates, carbonyl compounds e.g. in FDM technology

Filaments used during printing	TVOC [$\mu\text{g}/\text{m}^3$]
ABS	995 – 4 452
PLA	673 – 2 835
FLEX	882 – 3 123
PETG	856 – 3 280

Example results of TVOC emission at workplaces

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Chemicals identified



- ▶ The VOCs identified at the selected workstations during FDM printing (e.g. styrene, ethylbenzene, toluene, xylenes and aldehydes) resulted from thermal degradation of the polymer itself. The others (cumene, phthalic acid esters) were result of chemical additives (dyes, plasticizers, flame retardants) degradation at a given temperature of printing
- Carcinogens (formaldehyde or 1,2 -dichloropropane) and reproductive agents (toluene, styrene) increase the risk estimated for the printer operator's workplaces and require appropriate preventive measures
- Substances that have a harmful effect on the skin or are absorbed through the skin, enforce dermal risk assessment

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Fine and ultrafine particles

The emissions of ultra-fine particles may be of concern due to their negative health effects. Our studies have shown more than 90% of the particles emitted are at the nanoscale (< 115.6 nm). The average number concentration of particles emitted during the operation of the 3D printer was measured to range from 482 - 60466 particles/cm³.

filaments	Particles diameter [nm]	Particles concentration [particle/cm ³]
ABS	16,1 – 81,0	539 – 130 786
PLA	28,1 – 60,6	4 839 – 17 528
FLEX	20,7 – 56,4	5 624 – 88 626
PETG	57,3 – 106,7	3 853 – 10 068

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Publications



Elżbieta Dobrzyńska, Dorota Kondej, Joanna Kowalska, Małgorzata Szewczyńska, **State of the art in additive manufacturing and its possible chemical and particle hazards—review**, Indoor Air, 2021, 31: 1733-1758. (IF = 5,77), <https://doi.org/10.1111/ina.12853>

Elżbieta Dobrzyńska, Dorota Kondej, Joanna Kowalska, Małgorzata Szewczyńska, **Exposure to chemical substances and particles emitted during additive manufacturing**, Environmental Science and Pollution Research 2022, 29, 40273–40278, (IF = 5,19), <https://doi.org/10.1007/s11356-022-20347-2>

Elżbieta Dobrzyńska, Dorota Kondej, **Ocena emisji cząstek na stanowiskach pracy operatorów stacjonarnych drukarek 3D**, Przemysł Chemiczny, (IF = 0,49), <https://doi.org/10.15199/62.2023.1.9>

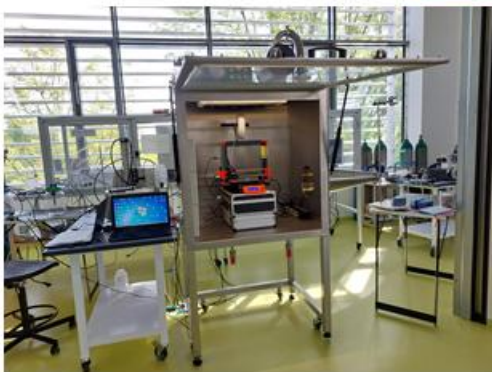
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Guidelines for AM practitioners



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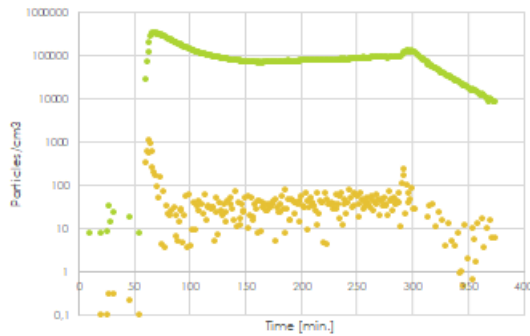
Ongoing research...



- ▶ Measurements of emissions of both particles and the chemicals identified in the previous studies are being carried out in a test chamber during the most popular FDM printer's operation.
- ▶ The test chamber was equipped with a designed air supply system and a system to maintain humidity within the required range. Tests were conducted using the SMPS (TSI Inc.) and APS (TSI Inc.) particle size analysis system to determine the number concentration, and size distribution of particles in the range of 20nm to 20µm.
- ▶ Chemicals were sampled on sorbent tubes and filters and analyzed using chromatographic techniques.

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Preliminary results on chemical analysis and particles measurements



- ▶ Particles were emitted during the process and an increase in their number concentration relative to the number concentration of background particles was observed.
- ▶ Preliminary tests showed that during a 4-hour printing process from ABS filament, the emission rate (Total Particle Emission) was about $7.65e^5$ particles.

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Toxicological studies

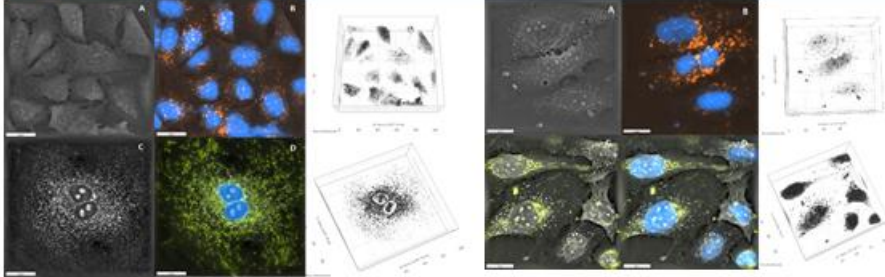
The human barrier cell lines: cerebral microvascular endothelial cells (hCMEC/D3) and lung cells (A549) will be exposed to samples collected during 3D printing or to selected commercial substances such as: dioctyl phthalate-DOP, dioctyl terephthalate DEHT, oxide iron(III) < 50 nm, oxide iron(II, III) < 50 nm. The changes in the cell viability will be assessed based on the metabolic capacity of cells (EZ4U test) and damage to cell membranes (NRU test). The caspase 3/7 activity and proliferation will be also evaluated in the real time.

- ▶ The in vitro toxicity of phthalate group substances (which are components of the filaments used) in a human lung cell line (A549) was also evaluated. The results show, the ability of the tested compounds to reduce cell survival, as well as to increase the activity of caspases 3/7.

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Toxicological studies

- The alterations in mRNA level for pro - inflammatory markers e.g. IL1- β , IL-8, and endoplasmic reticulum (ER) stress mediators (PERK, ATF6, IRE1a) will be examined using Real-Time PCR reactions.
- Holo- tomographic (HTM) visualizations of morphological changes in the cell structures will be also demonstrated.



The holo-tomographic visualizations of human blood - brain barrier cells (hCMEC/D3) (I) and human lung cells (A549) (II) after fluorescent staining. HTM images of cells showed: blue- nuclei, orange- lysosomes and yellow- ER structures/mitochondria. Scale bar: 20 μ m.

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Conclusions

- Building awareness of safe work with chemicals prevents many problems for printers operators and reduces health risks.
- Presented research contributes to increase the knowledge and understanding of both manufacturers and printer users regarding the exposure to chemical agents and particles at workplaces.
- The current project will contribute to safe work with different types of filaments with various parameters and from different manufacturers, making it easier for 3D printing users to choose less emissive materials

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THANK YOU FOR YOUR ATTENTION

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The CIOP-PIB is the Programme's main co-ordinator.

This presentation is based on the results of a research task no. 3.ZS.05 carried out within the scope of the sixth stage of the National Programme "Governmental Programme for Improvement of Safety and Working Conditions" supported within the scope of state services by the Ministry of Family and Social Policy.

The CIOP-PIB is the Programme's main co-ordinator.

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