

THE COST OF DECONTAMINATING AND RECYCLING PA2200 POWDER WASTE IN SELECTIVE LASER SINTERING TECHNOLOGY

Mocanu (Costache) Andreea Cristina¹, Marinescu Maria-Roxana², Buiu Octavian³,
Brîncoveanu Oana Andreea⁴, Doicin Cristian-Vasile⁵

¹ PhD student at Politehnica University of Bucharest, ² National Institute for Research and Development in Microtechnologies, IMT-Bucharest, cristina.mocanu@imt.ro

² National Institute for Research and Development in Microtechnologies, IMT-Bucharest, roxana.marinescu@imt.ro

³ National Institute for Research and Development in Microtechnologies, IMT-Bucharest, octavian.buiu@imt.ro

⁴ National Institute for Research and Development in Microtechnologies, IMT-Bucharest, oana.brincoveanu@imt.ro

⁵ Politehnica University of Bucharest, Romania, cristian.doicin@cont-edu.pub.ro

ABSTRACT: Additive Manufacturing (AM) technologies allow us to create three-dimensional objects using successive layers of material that are selectively laser sintered to create the object. This group of technologies has become an essential component of Industry 4.0, offering numerous advantages, including the reduction of material waste and the ability to customize products. The paper investigates the recycling of PA2200 powder waste following successful 3D printing experiments using Selective Laser Sintering (SLS) technology and provides a cost analysis of the associated processes. In addition, an analysis of scientific papers reporting the use of PA2200 - both "as new" and "recycled" - was conducted using the Web of Science database.

KEYWORDS: Additive Manufacturing, recycling, PA2200 powder, Selective Laser Sintering, Web of Science.

1. INTRODUCTION

As technology advances, equipment and materials are constantly evolving. Advanced materials that cannot be processed using traditional mechanical technologies have led to the development of non-conventional technologies [1, 2], such as the group known as additive manufacturing (AM). AM refers to a group of manufacturing processes and technologies that create parts layer by layer [3]. While initially used for prototyping, AM has become widely used for manufacturing finished products due to its ability to reduce material waste and customize products.

Today, AM is used across various industries, including the electrical, food, military, and medical sectors. This technology allows the development of personalized medicine, such as intracranial prostheses [4], scaffolds for craniomaxillofacial bones [5], and orthoses [6]. Additionally, using 3D scanners eliminates the need for CAD modeling, making the process more efficient.

There are different types of processes used in AM [7], including binder jetting, directed energy deposition, material extrusion, material jetting, powder bed fusion, sheet lamination, and Vat photopolymerization. According to the Web of Science database, the "Material Extrusion (MEX)" Figure 1 displays the number of published articles for the most popular categories: "Additive

category has the highest number of published articles (18,068) between 2016 and 2022, while the "Sheet Lamination (SHL)" category has the lowest (497).

The materials used in 3D printing technology are diverse, including polylactic acid (PLA), Acrylonitrile Butadiene Styrene (ABS), Thermoplastic Elastomers (TPE), polymers, ceramics, metals, Polycarbonate, and Polyethylene Terephthalate (PET).

2. 3D PRINTING USING SELECTIVE LASER SINTERING AS REFLECTED IN WEB OF SCIENCE

The recycling of PA2200 powder used in conjunction with selective laser sintering equipment is not well researched. The Web of Science (WoS) database was utilised to investigate this topic. WoS provides access to multiple databases for various academic disciplines and is the most prominent bibliometric database globally, followed by Scopus and Google Scholar (GS).

The following keywords were employed to determine the evolution of publications between 2016-2022: Additive Manufacturing; Selective Laser Sintering; 3D Printing; PA2200 Powder; Recycled PA2200 Powder.

"Manufacturing" and "3D Printing". Figure 2 shows the category with several moderate articles, and

Figure 3 demonstrates the category with the fewest articles published in WoS.

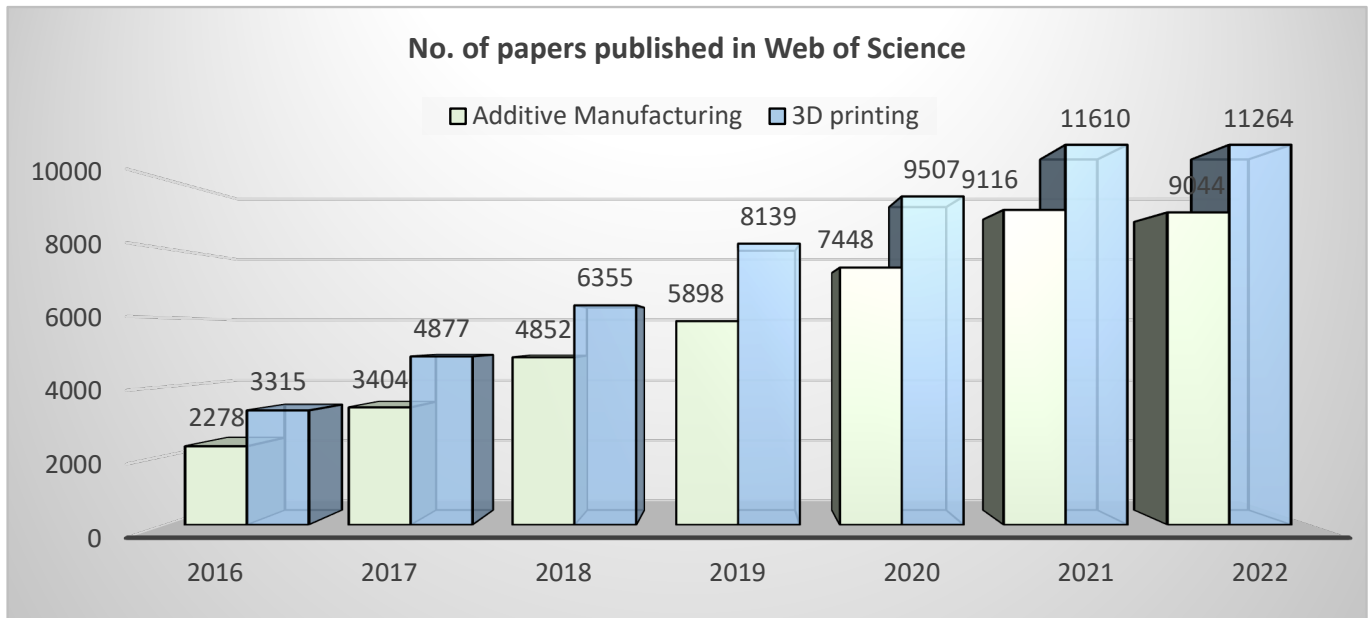


Figure 1. The categories with the highest number of published articles in Web of Science during 2016-2022

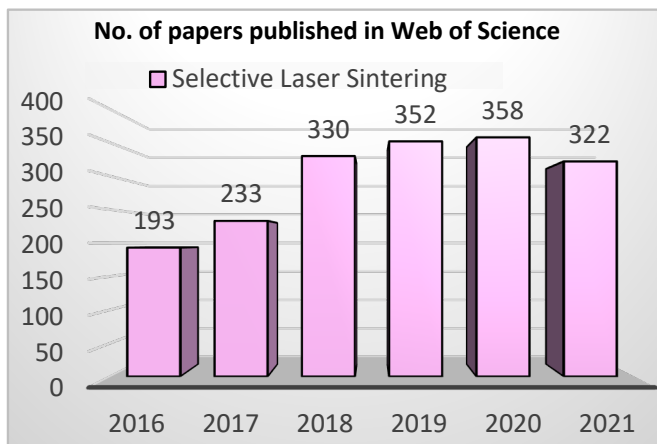


Figure 2. The average number of published articles in the Web of Science during 2016-2022

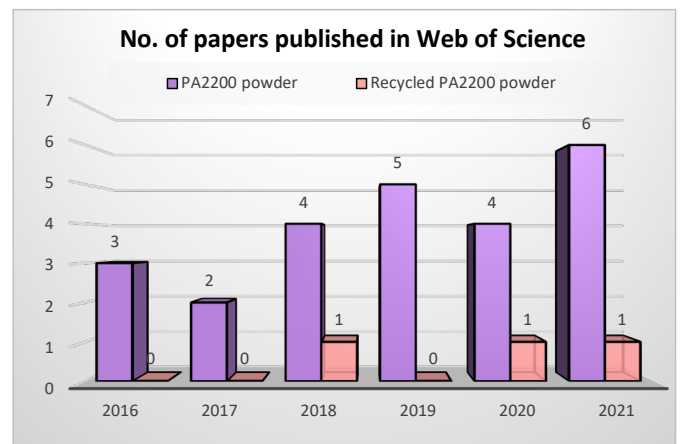


Figure 3. The fewest number of published articles in Web of Science during 2016-2022

It is obvious that the number of publications on “Additive Manufacturing” and “3D Printing” has increased significantly every year. This trend is also observed for “Selective Laser Sintering”, except for 2021 and 2022, where a slight decrease in the number of publications can be observed compared to the previous year.

The least number of publications is related to “Recycled PA2200 Powder”. From the studied data, articles on recycled PA2200 powder were only published in the last two years. One possible explanation for this could be the evolution of printers. Another explanation is the understanding and awareness of the adverse effects of microplastic pollution.

Nowadays, many printers use PLA filaments, and very few printers use PA2200 powder. Each of the 3D printing methods and the printers used has advantages and disadvantages, and certain printers are recommended for specific products. This may be a reason why the problem of recycling PA2200 powder has not received much attention.

Table 1 presents the top three Web of Science categories for each keyword corresponding to the data from Figures 1-3. The most popular category is "Materials Science Multidisciplinary," followed closely by "Engineering Manufacturing." The first four keywords have the most publications in the "Materials Science Multidisciplinary" category, while "Recycled PA2200 Powder" has no publications, so research in this field is necessary.

Table 1. Web of Science categories related to key words

No.	Keywords				
	Additive Manufacturing	Selective Laser Sintering	3D printing	PA2200 Powder	Recycled PA2200 Powder
1	Materials Science Multidisciplinary	Materials Science Multidisciplinary	Materials Science Multidisciplinary	Materials Science Multidisciplinary	Chemistry Multidisciplinary
2	Engineering Manufacturing	Engineering Manufacturing	Physics Applied	Engineering Manufacturing	Optics
3	Metallurgy Metallurgical Engineering	Physics Applied	Engineering Electrical Electronic	Engineering Mechanical	Polymer Science

Out of the 31 cumulative articles published from 2016 to 2022 related to "PA2200 Powder" and "Recycled PA2200 Powder," 74% were published in WoS indexed articles in Q1-Q4 areas, and the remaining 26% were published in WoS but without impact factor, as shown in Figure 4.

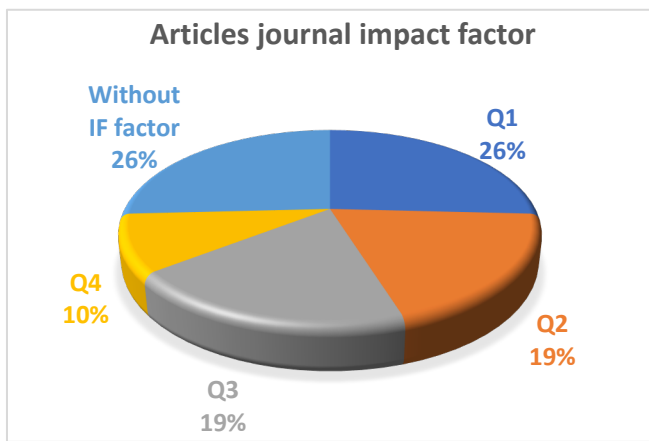


Figure 4. The impact factor for the articles from the categories "PA2200 Powder" and "Recycled PA2200 Powder" from the period 2016-2022

3. RESEARCH METHODOLOGY

The paper highlights the significance of recycling PA2200 powder, leftover after 3D printing and recovered from the anti-ex vacuum cleaner using Selective Laser Sintering (SLS) technology, as part of the Powder Bed Fusion (PBF) process, with the help of EOS Formiga P100 equipment.



Figure 6. EOS Formiga P100 equipment [11]

3.1 Modelling 3D Objects

All additive manufacturing (AM) techniques start with modelling a 3D object, slicing it into layers, and transferring the sliced object to machine controls. Then, specialized software packages are used to create the 3D model [8].

To print a 3D object using SLS technology, a CAD model is first generated and converted to Standard Tessellation Language (STL)/ Additive Manufacturing File Format (AMF). The STL/AMF file is then imported into the 3D printing software, where it is checked and corrected [9].

The STL model is sectioned (sliced) using specialized Scalable Link Interface (SLI) software. Figure 5 [10] shows the primary stages of creating 3D objects.

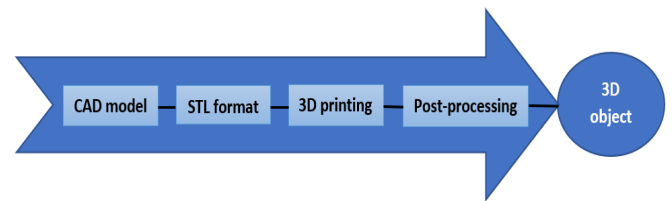


Figure 5. The Stages of Creating 3D Objects

Once the preparation stage is complete, the information is uploaded to the 3D printer (Figure 6), and the equipment begins to work. After obtaining the 3D object, a final post-processing step is carried out.

Figure 7 depicts a schematic representation of the printer's working process.

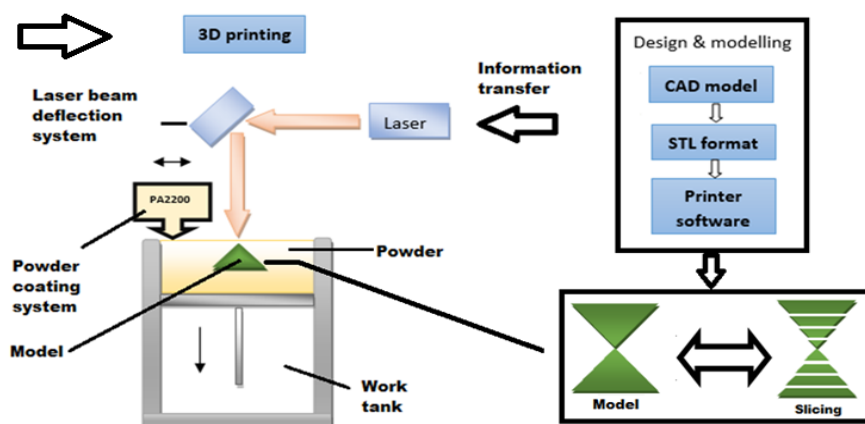


Figure 7. SLS working model

3.2 Laser Sintering Method (SLS)

Formiga P100 is a 3D printer that employs selective laser sintering technology. These printers work with materials in powder form, such as Polyamide 12 (PA 2200, PA 3200 GF, PA 2210 FR, PA 2201, Alumide), PS 2500, and PrimeCast 101. Thin layers of powdered material are deposited in the work tray of the 3D printer.

For SLS printers, deposited powder layers are heated by an infrared lamp. The infrared beam is directed onto the material until it heats just below the melting temperature, causing the powder grains to soften. Then, the laser beam intensity is adjusted to melt and shape the object only in the interest area. Once the layer is complete, the piston lowers and allows the deposition of a new layer of powder. This process is repeated until the object entire construction. The deposition system has a blade that gently presses the material to create a denser object after each deposited layer.

After the 3D object is ready, it needs post-processing. Post-processing involves removing dust grains leftover from deposition, removing support structures (mandatory for metals), and optional grinding or painting [10, 12].

Recycling PA2200 powder from printers is an activity that helps protect the environment. As the number of 3D printers sold increases, the amount of waste generated also increases. Therefore, recycling this powder can significantly reduce waste.

3.3 PA2200 Powder Waste and Recycling

3.3.1 The Material

The properties of PA2200 powder (polyamide 12) in the virgin form are characterized by good mechanical, thermal, and chemical resistance according to PA2200 data sheet, as shown in Table 2. The working chamber's dimensions are 250 × 200 × 330 mm³ [13].

Table 2. Properties of PA2200 [13]

Mechanical properties	Tensile modulus	1650 MPa
	Tensile strength	48 MPa
	Elongation at break	18 %
Thermal properties	Melting temperature	176 °C
	Heat deflection temperature (1.8 MPa)	70 °C
	Heat deflection temperature (1.8 MPa)	154 °C
Physical properties	Density	930kg/m ³

This experiment studied Polyamide PA2200 powder, produced by Electro-Optical Systems – EOS, Krailing, Germany [13]. Some initial results obtained from powder recycling were presented in [14]. The EOS Formiga P100 equipment was used to obtain these results [15].

To achieve satisfactory mechanical properties, various factors must be taken into account when 3D printing an object, including the thickness of the layer being constructed, the printing direction (PD), energy density, and laser beam parameters. The author of the paper "Rheological Properties of Polyamide PA 2200 in SLS Technology" [16] has found that layer thickness has a significant impact on the mechanical properties of printed models, with tested thicknesses ranging from 0.1-0.4mm. Therefore, a layer thickness of 0.1mm and an object orientation on the building platform of 0° are recommended.

When creating 3D objects from PA2200 powder (Figure 8-A), unused material found in the equipment tank is screened and larger grains are discarded, resulting in what is known as "contaminated material" (Figure 8-B). However, if this powder waste (Figure 8-C) is decontaminated using special solutions, it can be transformed into raw material. KOH was used as the primary solution to purify the powder, along with deionised water, isopropyl alcohol, and hydrochloric acid [14].



Figure 8. PA2200 Powder A – Reference material; B – Contaminated material; C – Decontaminated material

Figure 8 displays PA2200 powder A (reference material), B (contaminated material), and C (decontaminated material). Additionally, three samples consisting of reference material (Figure 9), contaminated powder (Figure 10), and purified powder (Figure 11) were analysed using FEI Nova Nano Scanning Electron Microscopy (SEM) 630 [15, 17].

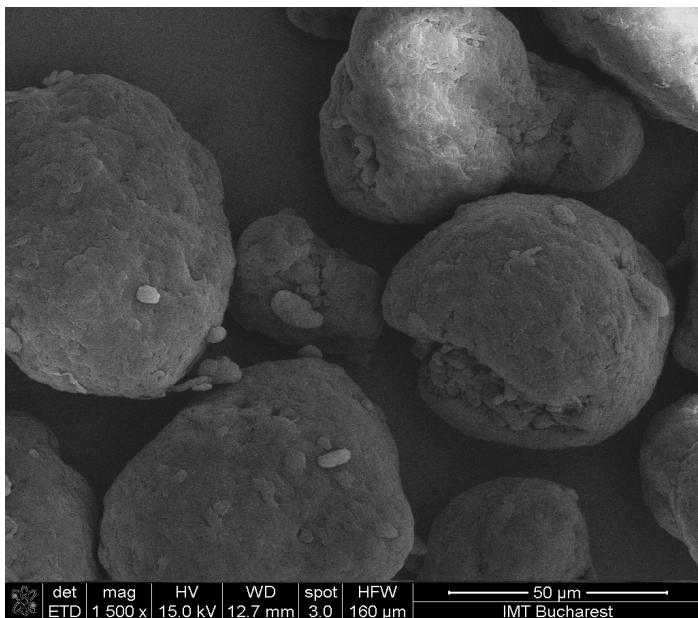


Figure 9. SEM image for the PA2200 reference material

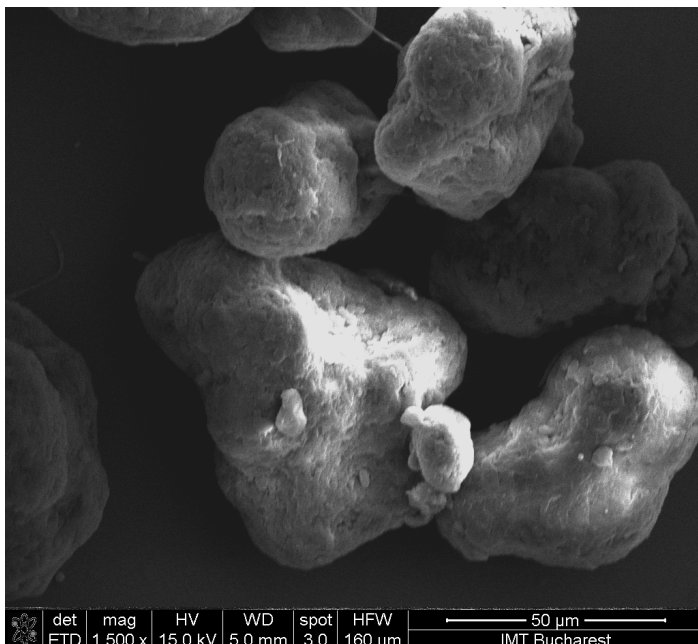


Figure 10. SEM image for the contaminated PA2200 powder

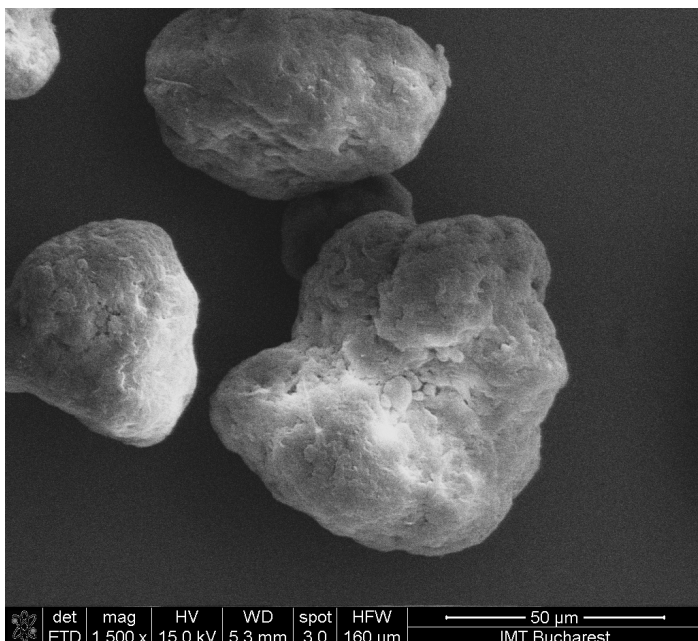


Figure 11. SEM image for the purified PA2200 powder

No significant differences were observed in the three SEM images, but it was noted that no dust particles were present in the decontaminated PA2200 powder. These results demonstrate that PA2200 powder can be decontaminated and recycled. Future research will investigate how PA2200 properties change after a higher number of KOH cycles.

In previous research, Yao B. et al. [18] examined various recycling times for PA2200 powders and found no significant differences between virgin and recycled powders in terms of powder size, shape, and distribution during the first recycling. Broken powders appeared due to thermal expansion during the cooling process from high temperatures, resulting in more defects in the interface and more unmolten powders in SLS parts built with aged powders that had been recycled more frequently. Wegner et al. [19] also demonstrated that aged powders have a detrimental effect on tensile strength. DePalma et al. [20] presented a mixture of recycled and new powders, while Magi P. et al. [21] recycled PA2200 in combination with other materials such as aramid, graphite, or Thermoplastic Polyurethane (TPU). The various combinations presented showed an unexpected but positive result, as there were no significant differences between virgin, recycled and combined PA-12.

3.3.2 Steps and Costs of Decontamination

PA2200 is obtained from Electro Optical Systems – EOS GmbH [13] and is priced at 60 EUR/kg, sold in 20 kg bags.

The process of removing dirt, inorganic contaminants, and biological contaminants from one kg of nylon powder involves several costs including material consumption, energy consumption, labour costs, and other expenses.

To decontaminate one kg of nylon powder, a solution of 5l of KOH 60% concentration (300 g KOH pills and 4700 ml deionized water) was prepared. The solution was then heated on a Selecta Combiplac hob (Barcelona) [22] with magnetic stirring at 80°C for two hours. Next, the polymer dispersion was washed with 5l deionized water and filtered five times to remove any traces of the KOH solution. A vacuum pump [23] was then used for 10 minutes to reduce the separation time of the solid mass from the suspension. Finally, the powder was washed with two litres of deionized water, 100 ml isopropyl alcohol (VLSI degrees, BASF), and 50 ml 1% hydrochloric acid and then introduced into a vacuum oven for 3 hours for drying [14].

All of the above costs culminate in a total cost of approximately 86.16 RON, which is equivalent to 17.80 EUR for 1 kg of decontaminated powder. The costs were calculated in RON and then converted to EUR and presented in Table 3.

If the industry that utilizes the printed objects allows it, such as guitar strings, using 1 kg of decontaminated PA2200 at the cost of only 17.80 EUR as opposed to the standard 60 EUR per kg can be considered.

Table 3. Costs (*The costs were calculated based on 2020 prices when the materials were purchased (June 2020 EUR = 4.84 RON))

KOH (99,8 % purity) e-chemicals [24]		Isopropyl alcohol (VLSI grade, BASF) from MicroChemicals [25]		Hydrochloric acid (1N) [26]		Deionized water [27]	Energy consumption [15]	Workforce salary [15]	TOTAL COSTS
Purchased quantity	Used quantity	Purchased quantity	Used quantity	Purchased quantity	Used quantity	Used quantity	Used quantity	Used quantity	
25 kg	300g	20 l	100 ml	1000 ml	50 ml	12 l	total cost	1 hour	1 kg decontaminated powder
208 RON	2,50 RON	195 RON	0,98 RON	29.75 RON	1.48 RON	24 RON	7,20 RON	50 RON	86.16 RON = 17.80 EUR.

4. CONCLUSIONS

We have started this work due to the fact that although recycling is a prevalent topic of interest, there are limited studies on recycling powder used in 3D printing. This was demonstrated by a case study that utilized the Web of Science database.

This paper aims to emphasize the importance of recycling and encourage its implementation globally. Plastic is the primary source of pollution on Earth, so even if the decontaminating and recycling of PA2200 powder represents a small percentage of recycled plastic, it can still have a significant impact.

From the real numbers obtained from the Web of Science database, it is evident that not many people are concerned about this subject. The PA2200 powder that is recovered and reintroduced in a new manufacturing cycle has modified properties due to the thermal process to which it was subjected during Selective Laser Sintering. The powder sample decontaminated and recycled using KOH solution, which comes from the same batch, showed no significant difference in shape or size. Further studies will explore recycling it several times using different solutions. Even though PA2200 loses some of its properties after several recycling times it is still suitable for making some products such as food packaging or dental floss. For these elements, the modified properties are not a priority.

It is essential to note that almost anything can be recycled with proper care.

5. ACKNOWLEDGEMENT

The authors would like to thank to the Romanian Ministry of Education and Research for the financial

support of the “NUCLEU” research program “MICRO-NANO-SIS PLUS”, Code: PN 19 16.

6. REFERENCES

- Ghiclescu, L., Pirnau, C., Enciu, C., Pirvu (Ene), G., Search for keywords in a hybrid technologies field, based on ultrasonically aided edm-ecm using the online environment. *Nonconventional Technologies Review*, Vol. 25, No. 3, pp. 37-42, (2021).
- Pirnau, C., Marinescu, M., Ghiclescu, L., Pirnau, M., The unconventional technologies reflected in web of science, *Nonconventional Technologies Review*, Vol. 24, No. 1, pp. 33-38, (2020).
- Jandyal, A., Chaturvedi, I., Wazir, I., Raina, A., Ul Haq, M.I., 3D printing – A review of processes, materials and applications in industry 4.0, *Sustainable Operations and Computers*, Vol. 3, pp. 33-42, (2022).
- Antoniac, I., Mohan, A., Semenescu, A., Doicin, C., Ulmeanu, M., Cavalu, S., Costoiu, M., Murzac, R., Doicin, I., Săceleanu, V., Mateș, I., Proteză intracraniană cu structuri de osteointegrare și acoperiri funcționale, Cerere de Brevet de invenție (înregistrată la OSIM cu numărul RO132417 (AO)- 2018-03-30).
- Jazayeri, H. E., Fahimipour, F., Dashtimoghadam, E. Tayebi, L., Collagen Grafted 3D-Printed Polycaprolactone Scaffolds for Craniomaxillofacial Bone Regeneration. *J. Oral Maxillofac. Surg.*, Vol. 75, no. 10, e402, (2017).
- Popescu, D., Marinescu, R., Sandache, Ș. O., Upper Limbs Orthoses Production in 3D Printing

- Points-of-Care, *International Conference on e-Health and Bioengineering (EHB)*, pp. 1-4, (2021).
7. Additive Manufacturing – General Principles – Terminology, available at <https://www.iso.org/obp/ui#iso:std:iso-astm:52900:ed-1:v1:en>, accessed on 24.07.2022
 8. Ulmeanu, M., Doicin, C.V., Baila, D.I., Rennie, A.E.W., Neagu, C., Laha, S., Comparative evaluation of optimum additive manufacturing technology to fabricate bespoke medical prototypes of composite materials, *Materiale plastic*, Vol. 52, No. 3, pp. 416 – 422, (2015).
 9. *ISO/ASTM 52915:2013. Standard specification for additive manufacturing file format (AMF) Version 1.1, link: <https://www.iso.org/standard/61944.html>, Published: 01.06.2023; accessed on 19.01.2022.
 10. Moagăr-Poladian, G., Tehnici de Rapid Prototyping pe bază de lumină, available at: <https://docplayer.net/54326875-Tehnici-de-rapid-prototyping-pe-baza-de-lumina-dr-moagar-poladian-gabriel-institutul-national-de-cercetare-dezvoltare-pentru-microtehnologie.html>, Published: 2012; accessed on 19.01.2022.
 11. ***EOS-P100-London, <https://www.3dprint-uk.co.uk/eos-p100-london/>, Published: 19.04.2013; accessed on 19.01.2022.
 12. Chua, C.K., Leong, K.F., (2014), *3D Printing and additive Manufacturing – Principles and Applications*, 4th Edition, World Scientific Publishing UK, (2017).
 13. ***EOS, available at: <https://store.eos.info/>, accessed on 19.01.2022.
 14. Costache, A. C., Moagăr-Poladian, G., Obreja, C.A., Tutunaru, O., Radoi, A., Pachiou, C., Chemical and physical study of waste PA2200 powder, *UPB Sci. Bull., Series B.*, Vol. 83, No. 1, pp. 175-186, (2021).
 15. ***IMT Bucuresti, Link: www.imt.ro; accessed on 19.01.2022.
 16. Koziar, T., Rheological Properties of Polyamide PA 2200 in SLS Technology, *Technical gazette*, Vol. 27, No. 4, pp.1092-1100, (2020).
 17. ***TGE-PLAT/IMT Bucuresti, *Ofertă de expertiză, servicii și echipamente pentru domeniile: microsenzori, componente fotonice, dispozitive și sisteme pentru unde milimetrice*, Ed. INCD pentru Microtehnologie – IMT București, available at: https://www.imt.ro/TGE-PLAT/doc/Brosura_TGE-PLAT_iunie2018.pdf,
 18. Yao, B., Li, Z., Zhu, F., Effect of powder recycling on anisotropic tensile properties of selective laser sintered PA2200 polyamide, *European Polymer Journal*, 1414, 110093, (2020).
 19. Wegner, A., Mielicki, C., Gronhoff, B., Witt, G., Wortberg, J., Determination of robust material qualities and processing conditions for laser sintering of polyimide 12, *Polymer Engineering & Science*, Vol. 54, No.7, (2013).
 20. DePalma, K., Walluk, M.R., Murtaugh, A., Hilton, J., McConky, S., Hilton, B., Assessment of 3D printing using fused deposition modeling and selective laser sintering for a circular economy, *Journal of Cleaner Production*, Vol. 264, No. 121567, (2020).
 21. Măgi, P., Krumme, A., Pohlak, M., Recycling of PA-12 in Additive Manufacturing and the Improvement of its Mechanical Properties. *Key Engineering Materials*, Vol. 674, pp. 9-14. (2016).
 22. ***J.P. Selecta S.A. equipments, available at <https://grupo-selecta.com/fr/>, accessed on 23.03.2019.
 23. ***One-stage vacuum pump with 2-port pressure gauge set, available at: https://www.vidaxl.ro/e/vidaxl-pompa-de-vid-cu-o-etapa-cu-set-de-manometre-cu-2-porturi/8719883868738.html?gclid=Cj0KCQiAxoiQBhCRARIsAPsvo-wa8A9_5r3jtCGy0ALOkDUE5R8COctFS4iIB_0dGBCUK-ozXzVWE9YaAghOEALw_wcB, accessed on 03.03.2022.
 24. ***Potassium hydroxide bag 25Kg, available at: <https://www.e-chimicale.ro/hidroxid-de-potasiu-sac-25kg.html>, accessed on 20.06.2020.
 25. ***Isopropyl alcohol 99% 20L, available at: <https://www.e-chimicale.ro/alcool-izopropilic-99-20l.html>, accessed on 20.06.2020.
 26. ***1N, 1L hydrochloric acid, available at: <https://remedlab.ro/produs/acid-clorhidric-1n-1l/>, accessed on 20.06.2020.
 27. ***Deionized purified water, pet bottle, 5L, available at: <https://www.dedeman.ro/ro/apa-purificata-deionizata-flacon-pet-5l/p/7026675?k=apa%20deionizata>, accessed on 20.06.2020.