Three-Dimensional Printing of Multifunctional Composites

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Contributor: Beata Anwajler , Anna Witek-Krowiak

Additive manufacturing, with its wide range of printable materials, and ability to minimize material usage, reduce labor costs, and minimize waste, has sparked a growing enthusiasm among researchers for the production of advanced multifunctional composites. Over the past few decades, our environment has witnessed a significant accumulation of plastic waste, mainly due to human economic activities. Plastic pollution negatively affects the ecosystem and global warming, so our society urgently needs solutions to counteract these effects. Therefore, the closed-loop economy principle is fundamental to reducing the amount of non-biodegradable petroleum-based waste.

multifunctional composites | biodegradability composites | 3D printing | AM technology | biomass | methods assessing biodegradability | natural fillers | biofibers | biocomposites

1. Multi-Material 3D-Printed Polymer Composites

Based on the International Organization for Standardization (ISO) and the American Society for Testing and Materials (ASTM) standard 52.900:201 [1], 3D printing techniques are divided into seven categories consisting of binder injection (BJ), directed energy deposition (DED), material extrusion (ME), material sputtering (MJ), powder bed fusion (PBF), sheet lamination (SL), and vat photopolymerization (VP) [2][3]. Each AM method has its specific applications based on its advantages. For example, selective powder bed fusion techniques are best suited for producing intricate and accurate parts. On the other hand, if we care about the highest deposition rate due to the raw material, filament AM methods, commonly used for large-scale production of components, will be the most suitable [4]. The multifunctionality of composites [2][3][4] combines different properties in a single material or structure. This allows them to perform two or more functions, such as optical, magnetic, electronic, thermal, or structural, making the resulting composites suitable for the applications in which they will be used. This has the advantage of achieving autonomy, adaptability, self-sufficiency, and weight reduction. Combining two or more properties in a single material is desirable in all engineering fields, from robotics to life sciences, to serve as embedded structural health monitoring from cradle to death or as structural energy storage. Accordingly, the interest of researchers in multifunctional and multi-material polymer-based composites continues to grow, especially in nanoscale materials, biomimetics, structural energy composites, etc. [3][5][6]. The main advantage of 3D printing in this context is the ability to deposit the required materials precisely in specific areas of the structure, reducing manufacturing costs and time of the target composites. This gives rise to different materials and methods for creating multi-material systems. Based on the available literature, we can distinguish two methods for

manufacturing multifunctional composites. These include 3D printing of composites and 3D printing of multiple materials. The difference between the two lies in how the composition of the printed composites is combined. The first method combines materials before printing, while the second uses 3D printing techniques to combine materials [3]. It primarily uses polymers and other functional inorganic or organic materials to combine multiple materials into a functional whole. Several methods are used to obtain multilayer materials, including multiwire/multilayer printing, core/coaxial rugation, and embedded printing [3][5].

Three-Dimensional Printing of Composites

In 3D printing of composites, a matrix of polymers is combined with specific additives to produce materials with improved structural or functional properties. The resulting properties cannot be achieved by using any of the components alone [3][7][8]. Functional fillers consisting of inorganic particles or fibers are used as additional materials. A characteristic feature of this method is that the composites are prepared beforehand and then used in the 3D printing process in the same way as the pure material. As mentioned earlier, adding foreign filler particles to the polymer matrix enables high printing accuracy with improved mechanical and functional properties. Such materials are known as polymer matrix composites (MPCs). Most of the current research is focused on developing new composite materials with reinforced particles, fibers, nanomaterials, and ceramics and their use in additive manufacturing processes [3][8][9][10]. The main objective of scientific research is to improve the printability of the material matrix, to mechanically strengthen the material matrix, to impart new properties to the composite (e.g., thermal, electrical, and magnetic properties), or to build a porous structure as a final element [3].

Research to improve the printability of the material matrix has mainly focused on using various types of nano/microparticles, including nanosilica, nanoclay, and micro-NaCl, as functional fillers. It has been shown that the physical and chemical interactions between the polymer matrix and the filler that occur during fabrication provide an opportunity to improve the viscosity of the material system [3].

As pure, homogeneous materials, polymeric materials typically have limited mechanical properties, limiting their potential applications. In contrast, combining different materials to achieve desired mechanical properties has recently become a promising method to overcome this problem. The literature shows many impressive results in developing new particle and fiber-reinforced materials. The most commonly mentioned nano/microparticles and fibers include nanosilica, nanoclay, aluminum/aluminum oxide (Al_2O_3), and C/SiC fibers [3][11].

Depending on the range of functionality, multifunctional materials can be divided into homogeneous and locally functionalized categories. In homogeneous 3D-printed composites, the conformal property is uniformly distributed throughout the printed part. Conversely, in locally functionalized 3D-printed composites, the desired functionality is restricted to a specific area of the structure.

Adding a functional component to a polymer matrix material is now a promising solution. There is a lot of emphasis in the literature on the production of multifunctional composites, i.e., those in which the matrix material has complex functions, i.e., conductivity, magnetism, and reactivity to the environment (e.g., heat, solvent). Conductivity is

essential for flexible and wearable electronics. Conductive organic/inorganic additives such as carbon nanotubes (CNTs), graphene, and polypyrrole are mainly used for this purpose. These 3D-printed conductive polymer composites have shown great potential in electronics [12][13][14][15][16].

Various carbon nanomaterials, such as carbon nanotubes (1D) and graphene (2D), have long been used as secondary phases to produce homogeneous, conductive composites (electrical properties) [17]. Carbon nanotubes (CNTs) are cited in reviews [14][18][19][20][21][22][23][24][25][26] as one of the most promising candidates in 3D printing for modifying inks or filaments to develop multifunctional structures. A common goal of all research on CNTs has been to successfully incorporate the conductive phase into the polymer (create a continuous conductive network) without exceeding the viscosity limit above which the ink or filament cannot be printed. In addition to CNTs, graphene [19][27][28][29][30][31][32][33] and graphene oxide (GO) [34] have also been used to prepare nanomodified inks for 3D printing.

2. Biodegradable Polymers in 3D Printing

An analysis of published papers by researchers in the field of biodegradable materials and 3D printing technology was conducted. As a result, it was found that interest in the topic has been very evident over the last six years (**Figure 1**), and it is also noteworthy that the number of citations has increased more dramatically than the number of publications. In addition, PLA (more than 40%) and PCL (35.5%) dominate among the polymers studied, with other polymers accounting for a total of 25% of the cases analyzed (**Figure 2**).

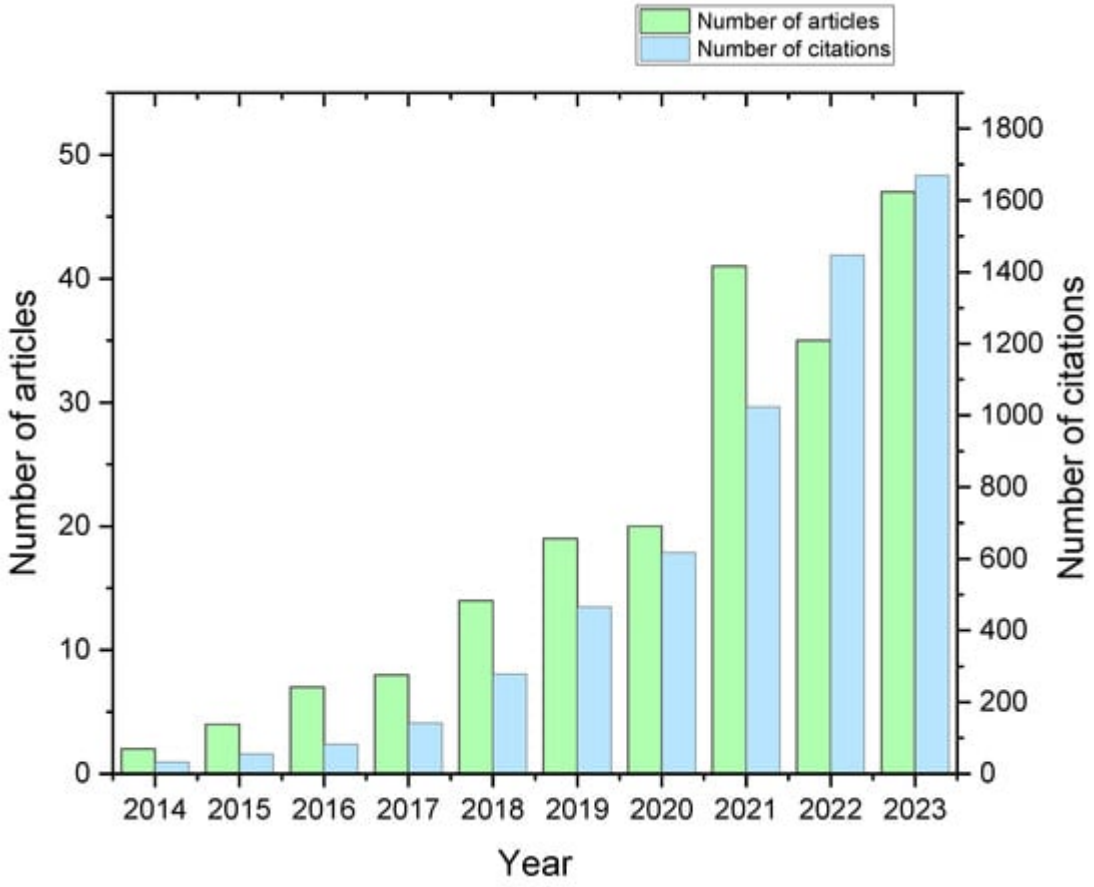

Figure 1. Number of publications from 2014–2023 containing selected methodology keywords (biodegradation AND (3D print) AND ((polylactic acid) OR PLA) OR (polyhydroxyalkanoate OR PHA) OR ((polybutylene succinate) OR PBS) OR ((poly lactic-co-glycolic acid) OR PLGA) OR ((polybutylene adipate terephthalate) OR PBAT) OR (polycaprolactone OR PCL) OR starch).

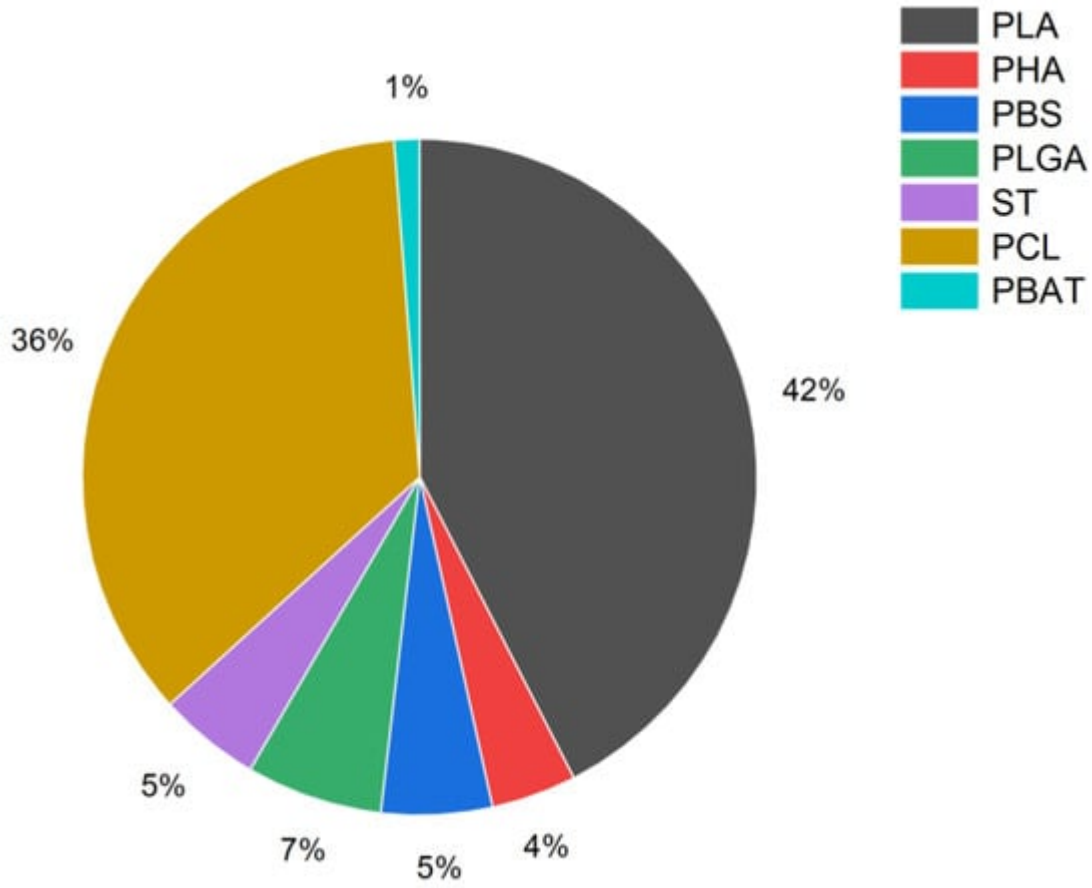

Figure 2. Share of specific polymers in search results selected methodology keywords (biodegradation AND (3D print) AND ((polylactic acid) OR PLA) OR (polyhydroxyalkanoate OR PHA) OR ((polybutylene succinate) OR PBS) OR ((poly lactic-co-glycolic acid) OR PLGA) OR ((polybutylene adipate terephthalate) OR PBAT) OR (polycaprolactone OR PCL) OR starch).

Polylactic acid (PLA) is the most commonly used raw material in the FDM 3D printing process due to its biodegradability and environmentally friendly properties, but the use of pure PLA polymer in the FDM approach is limited due to its disadvantages such as mechanical weakness, dissolution rate in water, etc. [5]. Lactic acid can be synthesized with high efficiency from the microbial fermentation of sugars. Sugars can be obtained from sustainable or renewable plant materials. Because it can be made from renewable carbon and is biodegradable, PLA has tremendous value because other high-performance plastics, such as polyethylene and polypropylene, are not biodegradable and are made from ethylene and propylene derived from fossil fuels. Although PLA is biodegradable, it is not renewable as it emits ~1.3 kg CO_2 equivalent/kg of synthesized plastic. Therefore, it is suggested that preparing PLA composites with appropriate additives is a feasible method to improve the properties of 3D-printed PLA parts obtained via the FDM approach [35].

2.1. Methods for Evaluating the Biodegradability of Composites Produced Using 3D Printing Technologies

Degradation of polymer composites can occur under abiotic factors such as light, temperature, humidity, and chemical treatment. Biodegradation is a series of complex transformations that materials undergo in the presence of microorganisms and their metabolites. Compounds (enzymes and acids) produced by microorganisms aid the degradation process under environmental factors (temperature, oxygen, humidity, sunlight, etc.). The biodegradation rate is strongly dependent on the composite structure in question; monolithic blocks will biodegrade more slowly, and a highly porous polymeric structure will behave differently if the accessibility of the surface is much greater.

To determine whether a composite is biodegradable, appropriate biodegradation tests are required. The choice of specific tests depends on the type of composite, its application, the expected environment in which it will be placed, and industry standards and regulations. Biodegradation tests are performed under natural conditions (aqueous or soil environment) or under controlled conditions (composting or anaerobic digestion). The choice of environment is critical because each environment has different physicochemical conditions and is inhabited by different microflora. It has been shown that the same polymeric material can biodegrade at completely different rates under other conditions [36]. Microorganisms colonize the surface of polymer prints and cause the materials to degrade into shorter chains of oligomers and monomers. Polymers change their physicochemical properties as their molecular weight decreases. The overall biodegradation of materials also includes the assimilation and mineralization of molecules that are the product of decomposition by microorganisms (**Figure 3**). Thus, depending on the availability of oxygen, water, CO_2, methane, and inorganic salts, the final products are different from partial degradation, which results in persistent microplastics [36]. This situation requires control of the resulting degradation products, as their presence in the environment can cause significant damage to ecosystems.

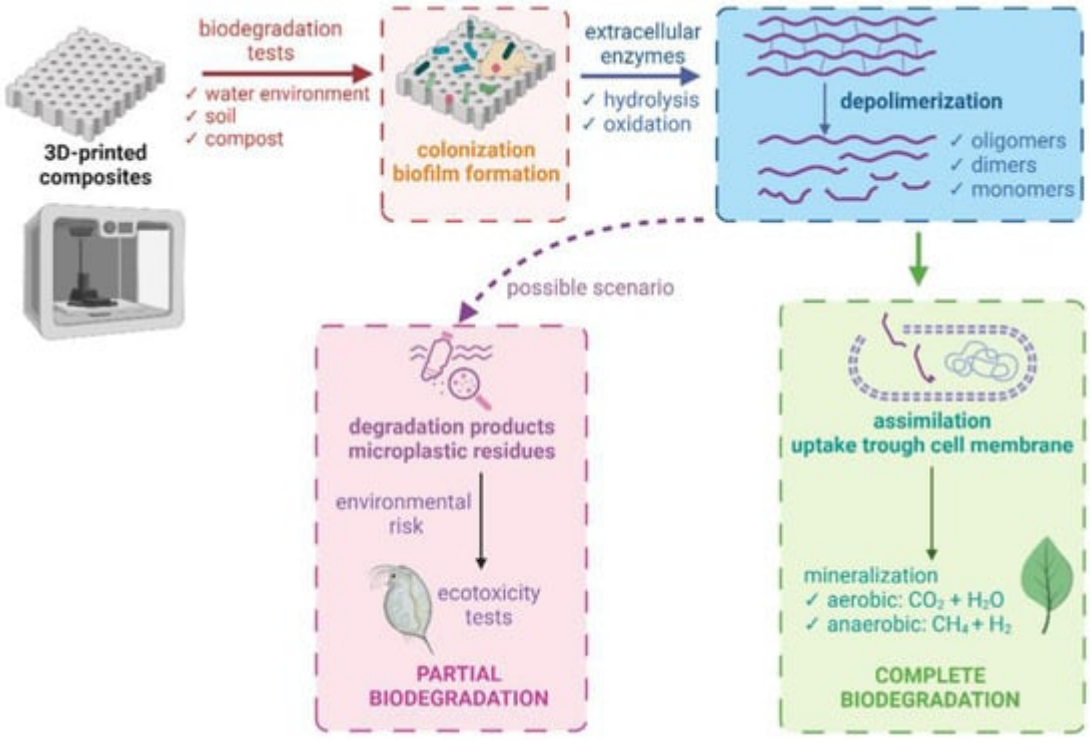

Figure 3. Biodegradation mechanisms (created with Biorender.com). Based on [6].

Products defined as biodegradable within 6 months will biodegrade more than 90% of their weight, while compostable products should decompose 90% in 3 months 4 [5]. However, the laboratory conditions under which biodegradation tests are conducted differ significantly from real-world conditions; the process parameters of laboratory conditions are predictable and selected to decompose materials relatively quickly. The introduction of the same material into the environment may significantly increase the biodegradation time due to the nature of the environment and its conditions.

The natural environments in which biodegradation can occur vary widely, mainly in terms of temperature, water content, and the number of microorganisms capable of degradation (**Figure 4**). In most cases, we carry out processes under controlled laboratory conditions, where we greatly accelerate the possibility of biodegradation by ensuring the best process conditions. A number of different methods can be used to assess the degree of biodegradation. These methods include measuring carbon dioxide release during material mineralization, monitoring weight loss, examining surface changes (through visual or microscopic observations), and analyzing changes in composite structures. Evaluating changes in material structure involves analyzing changes in the molar mass of the polymer, using thermal techniques such as TG and DSC, evaluating mechanical properties, and using spectroscopic methods. For degradation in aqueous environments, the evaluation extends to the analysis of components released into solution from the sampled materials.

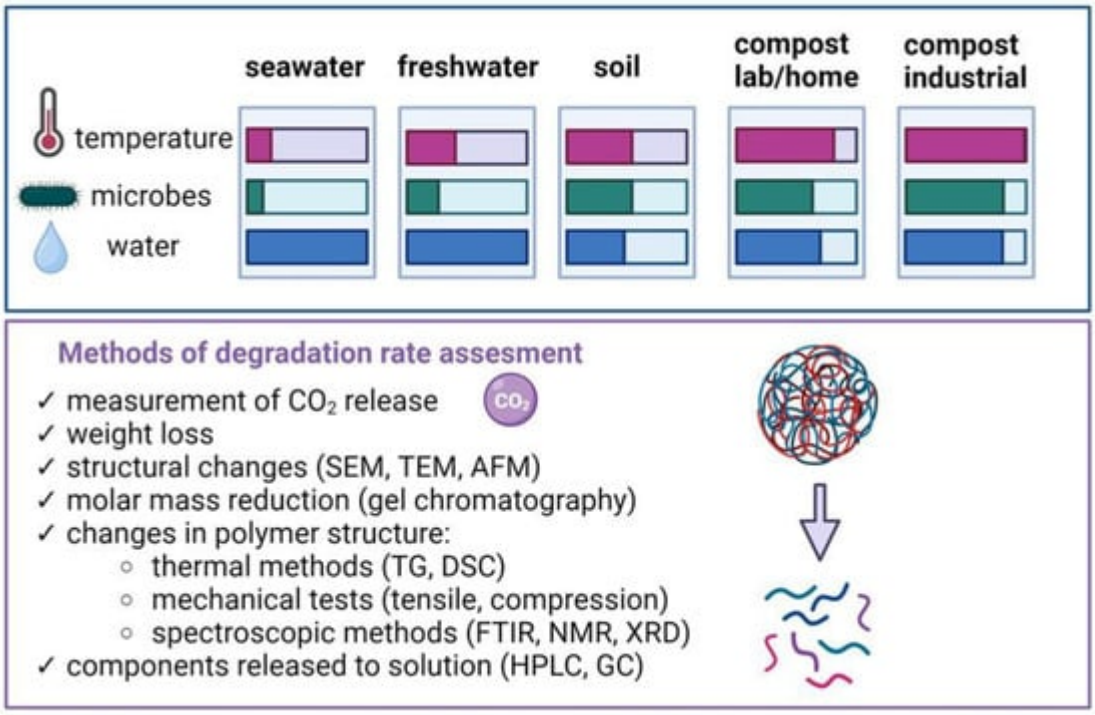

Figure 4. Various environments and methods to evaluate biodegradability (created with Biorender.com). Based on [6].

2.2. Biodegradation of Composites in Aquatic Environments

The degradation of composite materials can occur in the natural environment (surface water) or in an environment that mimics natural conditions.

2.2.1. Biodegradation in Freshwater and Seawater

A large volume of plastics enters surface waters and oceans, making these environments important recipients and sites of potential biodegradation of these materials. Aquatic environments contain relatively few microorganisms compared with other environments. Aquatic environments also have a lower temperature, which means that materials collected in water will degrade much more slowly than in other habitats. There are several standards for biodegradation in aquatic environments. For example, ISO 18830:2016 [37] and ISO 19679:2020 [38] deal with biodegradation measurements under controlled conditions of seawater and sediment, with the former measuring oxygen uptake and the latter measuring the amount of CO_2 released [39].

Some materials begin to degrade very rapidly in an aquatic environment. Of note is the PCL/wool composite, which begins to degrade within the first few days of entering the seawater environment. Higher wool content in the composite results in higher measured biological oxygen demand values. The study was extended to 5 months of seawater testing, during which changes in the prints (dark spots) were visually observed. The changes depended on the amount of wool used and the thickness of its fibers, which may be due to the lower amount of cuticle in thicker wool, which is more susceptible to degradation [40]. The seawater tests have been extended to include biodegradation tests in a compost environment (for filaments). The biodegradation of pure PCL in a compost

environment is negligible, typically less than 1%. The presence of natural additives (undyed wool fabric waste) accelerates biodegradation up to 10 times, resulting in more than 10% degradation in 3 months, depending on the size of wool fibers of two different diameters [40]. Studies indicate that the size of biomass immobilized in polymer matrices is one of the key parameters responsible for biodegradability.

2.2.2. Degradation Tests in Buffer Solutions for Medical Applications

Specific polymers are degraded in aqueous environments that mimic their future applications, such as medical applications. Such biomaterials should be safe for organisms, degrade at a certain rate, and yield non-toxic and non-inflammatory products. In vitro, room temperature, and accelerated (aging at elevated temperatures) methods estimate their biodegradation susceptibility. Materials used as implants can be tested in environments that mimic physiological environments according to ISO 10993-13:2010 [41]. Evaluation of the biodegradability of PBAT/chitosan blends confirmed the possibility of using replicas of this composite as a biodegradable cardiac occluder device [42]. Degradation of PLA scaffolds in a PBS buffer environment showed that the three-dimensional structure of the print is essential for the degradation rate. Prints with random porosity degraded the fastest, followed by cubic and gyroid [43]. It is also worth monitoring other parameters than just the change in mass of the prints, which can confirm the existence of specific degradation mechanisms of biomaterials. Interesting results have been obtained by researchers who have tested molecular weight changes during degradation. Numerous studies show that the mechanical strength of printed structures is also an important parameter, especially for tissue engineering applications. Degradation of PCL prints reinforced with natural fibers showed a significant effect of fibers on mechanical parameters (tensile and elasticity). The presence of biomass causes a faster degradation of the constructs due to the degradation of biological material. However, the values of tensile strength and modulus of elasticity are still higher than those of unreinforced PCL for up to 2 weeks [44].

Accelerated degradation at elevated temperatures resulted in a significant decrease in molecular weight without significant loss of bulk. This was explained by water diffusion into the interior of the polymer and gradual hydrolysis preceding chain degradation [45]. The accelerated degradation in an aqueous environment indicates the importance of temperature; at 50 °C, the degradation of PLA/PHA prints took much longer than at 70 °C, resulting in larger fragments. The printing direction also seems to have a significant effect; samples printed in the horizontal direction eroded, causing cracks, while samples printed in the vertical direction disintegrated completely. The presence of PHA in the PLA/PHA blend leads to a decrease in deformation during hydrolytic degradation [46].

2.3. Biodegradation of Composites in Soil Environments

Soil is a diverse type of environment that varies in granularity, porosity, water-holding capacity, aeration, pH, and composition of different fractions (sand, silt, and clay) [47]. An important parameter is temperature, which depends on the season and climatic conditions. Soil is home to various microorganisms, such as bacteria and fungi, which significantly impact the degradation of materials introduced into the environment. Standard methods for testing the biodegradation of plastics in soil are implemented by burying the materials in the soil at the appropriate temperature and humidity to ensure microbial activity and monitoring the release of carbon dioxide corresponding

to the decomposition of the material. Methods involving mass loss and/or evaluation of properties of decomposed samples, such as morphology, structure, and surface analysis, and mechanical properties, are also used. The effects of degradation residues on living organisms are also analyzed using ecotoxicity tests.

PLA-based composites enriched with TPS and plant biomass (Astragalus residues) showed significant weight loss (21.4%) after more than 4 months. The authors performed additional mechanical property measurements at this time, confirming the prints' flexural strength reduction. Thermal analysis of the degraded samples revealed interesting results. The thermal stability of the composites improved, which may indicate the rapid degradation of starch and fibers in the soil, increasing the number of PLA crystalline domains in the composite [48]. Hydrophilic additives that can absorb water improve the biodegradability of PLA. The addition of thermoplastic starch and wood resulted in higher biodegradation efficiency. The activity of microorganisms initiates surface changes and allows access to the inner areas of the print, which promotes swelling and makes more space available in the composites. It has also been observed that the degree of filling of the material supports accelerated degradation [49]. Similar observations have been reported for PLA by adding rice hulls [50]. The compression pattern can influence the degree of biodegradation of polymeric materials, as demonstrated for PLA/PHA acoustic absorbers with added wood fiber. Honeycomb shapes have been shown to degrade more slowly than systems with a denser (rectilinear) structure, perhaps through better moisture uptake [51].

Blends of biodegradable and non-biodegradable polymers are excellent raw materials for 3D printing, giving products better functionality. The presence of a biodegradable polymer in the blend does not guarantee good degradation of the prototype, so it is always necessary to test these properties under real conditions. The presence of non-biodegradable polymers (HDPE and PP) in blends with biodegradable polymers causes a significant reduction in degradation, probably as a result of covering the surface of the prints with a non-biodegradable layer that resists bond cleavage, making enzymatic hydrolysis of the whole material more difficult [47]. Adding non-biodegradable polymers to PLA can improve the mechanical strength of prints. A blend of PLA and PP at the lowest possible level (7.5%) with the addition of a compatibilizer (PE-g-MAH) was designed. A full print optimization was performed using table temperature, nozzle temperature, and biodegradation time as independent variables. The system's response was the mechanical tensile strength and weight change in the prints. Printing temperature was a statistically significant parameter with an optimum printing temperature of 171 °C. High biodegradation resistance of the proposed compound was observed [52].

2.4. Biodegradation in a Composter

Composting is an important alternative to landfills as an option for decomposing microorganism-sensitive materials. It can be implemented in backyard, laboratory, or industrial settings. Composting is influenced by several factors, such as temperature, humidity, pH, feedstock composition (C/N ratio), and microbial content and diversity. Large-scale composting is much more efficient and can operate under thermophilic conditions, up to 70 °C, with higher humidity and oxygen availability. Compost is a high microbial environment. The content of the bacterial population in compost can reach 109 CFU/g [6][53]. Composting can be carried out both on a small scale and under industrial

conditions, but in the latter case, the most common response to biodegradation is the visual evaluation of the prints.

As a representative of polyesters, PLA is degraded by chemical hydrolysis, which favors the degradation of this polymer in high-humidity environments. Biodegradation of PLA in a composting environment where temperature and humidity are at a high level shortens the biodegradation time compared with, for example, decomposition in soil [54]. For the PLA/PHB blend, better biodegradation results were obtained using lab-scale composting than for printing from pure PLA. Enzymatic degradation of polyesters can be realized by the action of microbial enzymes and hydrolysis, with the presence of polyhydroxy acids of microbial origin assisting the degradation process. Prints with the potential application of cosmetic packaging showed better degradability because they contain additional cosmetic residues (paraffin), an additional carbon source for microbes, and residual water, which accelerates PLA degradation [55]. PLA and PHB polymer impressions can exhibit very different biodegradability. PHB shows relatively rapid mineralization (84.6%) compared with the PLA50/PHB50 composite (biodegradation of 85%) in composting tests, indicating that PHB is more susceptible to the microbial enzymes of the compost. In the same test, the degradation of PLA prints yielded a surprisingly low result (21.7%); the extrusion and printing process may affect structural changes within this polymer [47]. PBAT, as a representative of polyesters containing an aromatic group, has a significantly reduced susceptibility to chemical hydrolysis compared with aliphatic esters [56].

An attempt to FDM 3D print small biodegradable pots from PCL with the addition of collagen hydrolysate proved to be an excellent solution, ensuring complete material degradation within 30 days. The authors tested the biodegradability of PCL/HA blend filaments against a reference material, cellulose, with significantly better results [57]. The addition of plant biomass, soybean waste, to PLA resulted in the printing of pots suitable for planting in soil. The developed formulations were tested on plants (tomato seedlings), but the degree of biodegradation of the material in the soil was not tested [58].

2.5. Ecotoxicity of Composite Degradation Products

Biodegradable polymers can cause the accumulation of decomposition products in the environment. Complete mineralization of samples by microorganisms results in the release of water, carbon dioxide, or methane and is an environmentally friendly solution. However, incomplete degradation leads to the accumulation of oligomers, monomers, or other decomposition product forms in the environment, which affects soil-living organisms. Therefore, an essential complementary element of biodegradability research should be the study of the ecotoxicity of polymer composite decomposition products.

There are no clearly defined standards for biodegradable polymers to assess their effects on aquatic and terrestrial organisms. The European standard EN 13432 [59] for assessing compostability supplements biodegradability tests with tests on plants [6]. To estimate the impact of polymer degradation products, it is worth using screening tests that consider toxicity standards for aquatic invertebrates (daphnia) and plant phytotoxicity tests. Reports from scientists studying the toxicity of bioplastics indicate that while biopolymers (PLA and PHA) are harmless to the larvae of the sea urchin *Paracentrotus lividus*, additives such as plasticizers may pose a threat in this area [60].

Available literature on biodegradation of 3D-printed composites does not provide any information on this topic and the set of additives used to produce prints is very wide.

References

1. ISO/ASTM 52900:2021(en); Additive Manufacturing—General Principles—Fundamentals and Vocabulary. International Organization for Standardization: Geneva, Switzerland, 2015.
2. Nugroho, W.T.; Dong, Y.; Pramanik, A. 3D printing composite materials: A comprehensive review. In Composite Materials; Elsevier: Amsterdam, The Netherlands, 2021; pp. 65–115.
3. Zhou, L.; Fu, J.; He, Y. A Review of 3D Printing Technologies for Soft Polymer Materials. Adv. Funct. Mater. 2020, 30, 28.
4. Li, N.; Huang, S.; Zhang, G.; Qin, R.; Liu, W.; Xiong, H.; Shi, G.; Blackburn, J. Progress in additive manufacturing on new materials: A review. J. Mater. Sci. Technol. 2019, 35, 242–269.
5. Bhagia, S.; Bornani, K.; Agarwal, R.; Satlewal, A.; Ďurkovič, J.; Lagaňa, R.; Bhagia, M.; Yoo, C.; Zhao, X.; Kunc, V.; et al. Critical review of FDM 3D printing of PLA biocomposites filled with biomass resources, characterization, biodegradability, upcycling and opportunities for biorefineries. Appl. Mater. Today 2021, 24, 101078.
6. Chandna, P.; Nain, L.; Singh, S.; Kuhad, R.C. Assessment of bacterial diversity during composting of agricultural byproducts. BMC Microbiol. 2013, 13, 99.
7. Bodkhe, S.; Ermanni, P. 3D printing of multifunctional materials for sensing and actuation: Merging piezoelectricity with shape memory. Eur. Polym. J. 2020, 132, 109738.
8. Bekas, D.G.; Hou, Y.; Liu, Y.; Panesar, A. 3D printing to enable multifunctionality in polymer-based composites: A review. Compos. B Eng. 2019, 179, 107540.
9. Jakus, A.E. An Introduction to 3D Printing—Past, Present, and Future Promise. In 3D Printing in Orthopaedic Surgery; Elsevier: Amsterdam, The Netherlands, 2019; pp. 1–15.
10. Li, Y.; Ren, X.; Zhu, L.; Li, C. Biomass 3D Printing: Principles, Materials, Post-Processing and Applications. Polymers 2023, 15, 2692.
11. Salmoria, G.V.; Klauss, P.; Paggi, R.A.; Kanis, L.A.; Lago, A. Structure and mechanical properties of cellulose based scaffolds fabricated by selective laser sintering. Polym. Test. 2009, 28, 648–652.
12. Kurimoto, M.; Yamashita, Y.; Ozaki, H.; Kato, T.; Funabashi, T.; Suzuoki, Y. 3D printing of conical insulating spacer using alumina/UV-cured-resin composite. In Proceedings of the IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP), Ann Arbor, MI, USA, 18–21 October 2015; IEEE: New York City, NY, USA, 2015; pp. 463–466.

13. Kowalewska, E.; Ficek, M.; Formela, K.; Zieliński, A.; Kunuku, S.; Sawczak, M.; Bogdanowicz, R. Tailoring of Optical Properties of Methacrylate Resins Enriched by HPHT Microdiamond Particles. Nanomaterials 2022, 12, 2604.
14. Wang, X.; Jiang, M.; Zhou, Z.; Gou, J.; Hui, D. 3D printing of polymer matrix composites: A review and prospective. Compos. B Eng. 2017, 110, 442–458.
15. Zheng, Y.; Huang, X.; Chen, J.; Wu, K.; Wang, J.; Zhang, X. A Review of Conductive Carbon Materials for 3D Printing: Materials, Technologies, Properties, and Applications. Materials 2021, 14, 3911.
16. Calamak, S.; Ermis, M. In situ silver nanoparticle synthesis on 3D-printed polylactic acid scaffolds for biomedical applications. J. Mater. Res. 2021, 36, 166–175.
17. Jariwala, D.; Sangwan, V.K.; Lauhon, L.J.; Marks, T.J.; Hersam, M.C. Carbon nanomaterials for electronics, optoelectronics, photovoltaics, and sensing. Chem. Soc. Rev. 2013, 42, 2824–2860.
18. Kim, H.C.; Hahn, H.T.; Yang, Y.S. Synthesis of PA12/functionalized GNP nanocomposite powders for the selective laser sintering process. J. Compos. Mater. 2013, 47, 501–509.
19. Guo, S.; Yang, X.; Heuzey, M.-C.; Therriault, D. 3D printing of a multifunctional nanocomposite helical liquid sensor. Nanoscale 2015, 7, 6451–6456.
20. Ghoshal, S. Polymer/Carbon Nanotubes (CNT) Nanocomposites Processing Using Additive Manufacturing (Three-Dimensional Printing) Technique: An Overview. Fibers 2017, 5, 40.
21. De Leon, A.C.; Chen, Q.; Palaganas, N.B.; Palaganas, J.O.; Manapat, J.; Advincula, R.C. High performance polymer nanocomposites for additive manufacturing applications. React. Funct. Polym. 2016, 103, 141–155.
22. Yan, J.; Zhi, G.; Kong, D.; Wang, H.; Xu, T.; Zang, J.; Shen, W.; Xu, J.; Shi, Y.; Dai, S.; et al. 3D printed rGO/CNT microlattice aerogel for a dendrite-free sodium metal anode. J. Mater. Chem. A Mater. 2020, 8, 19843–19854.
23. Agarwala, S.; Goh, G.L.; Goh, G.D.; Dikshit, V.; Yeong, W.Y. 3D and 4D printing of polymer/CNTs-based conductive composites. In 3D and 4D Printing of Polymer Nanocomposite Materials; Elsevier: Amsterdam, The Netherlands, 2020; pp. 297–324.
24. Peng, M.; Shi, D.; Sun, Y.; Cheng, J.; Zhao, B.; Xie, Y.; Zhang, J.; Guo, W.; Jia, Z.; Liang, Z.; et al. 3D Printed Mechanically Robust Graphene/CNT Electrodes for Highly Efficient Overall Water Splitting. Adv. Mater. 2020, 32, 23.
25. Dul, S.; Gutierrez, B.J.A.; Pegoretti, A.; Alvarez-Quintana, J.; Fambri, L. 3D printing of ABS Nanocomposites. Comparison of processing and effects of multi-wall and single-wall carbon nanotubes on thermal, mechanical and electrical properties. J. Mater. Sci. Technol. 2022, 121, 52–66.

26. Mora, A.; Verma, P.; Kumar, S. Electrical conductivity of CNT/polymer composites: 3D printing, measurements and model-ing. Compos. B Eng. 2020, 183, 107600.
27. Zanchetta, E.; Cattaldo, M.; Franchin, G.; Schwentenwein, M.; Homa, J.; Brusatin, G.; Colombo, P. Stereolithography of SiOC Ceramic Microcomponents. Adv. Mater. 2016, 28, 370–376.
28. Suwanprateeb, J. Improvement in mechanical properties of three-dimensional printing parts made from natural polymers reinforced by acrylate resin for biomedical applications: A double infiltration approach. Polym. Int. 2006, 55, 57–62.
29. Marconi, S.; Alaimo, G.; Mauri, V.; Torre, M.; Auricchio, F. Impact of graphene reinforcement on mechanical properties of PLA 3D printed materials. In Proceedings of the IEEE MTT-S International Microwave Workshop Series on Advanced Materials and Processes for RF and THz Applications (IMWS-AMP), Pavia, Italy, 20–22 September 2017; IEEE: New York City, NY, USA, 2017; pp. 1–3.
30. Ding, H.; Barg, S.; Derby, B. Direct 3D printing of graphene using capillary suspensions. Nanoscale 2020, 12, 11440–11447.
31. Guo, H.; Lv, R.; Bai, S. Recent advances on 3D printing graphene-based composites. Nano Mater. Sci. 2019, 1, 101–115.
32. Silva, M.; Pinho, I.S.; Covas, J.A.; Alves, N.M.; Paiva, M.C. 3D printing of graphene-based polymeric nanocomposites for biomedical applications. Funct. Compos. Mater. 2021, 2, 8.
33. Tang, X.; Zhou, H.; Cai, Z.; Cheng, D.; He, P.; Xie, P.; Zhang, D.; Fan, T. Generalized 3D Printing of Graphene-Based Mixed-Dimensional Hybrid Aerogels. ACS Nano 2018, 12, 3502–3511.
34. Lin, D.; Jin, S.; Zhang, F.; Wang, C.; Wang, Y.; Zhou, C.; Cheng, G.J. 3D stereolithography printing of graphene oxide reinforced complex architectures. Nanotechnology 2015, 26, 434003.
35. Liao, J.; Brosse, N.; Pizzi, A.; Hoppe, S.; Zhou, X.; Du, G. Characterization and 3D printability of poly (lactic acid)/acetylated tannin composites. Ind. Crops Prod. 2020, 149, 112320.
36. Choe, S.; Kim, Y.; Won, Y.; Myung, J. Bridging Three Gaps in Biodegradable Plastics: Misconceptions and Truths About Biodegradation. Front. Chem. 2021, 9, 671750.
37. ISO 18830:2016; Plastics Determination of Aerobic Biodegradation of Non-Floating Plastic Materials in a Seawater/Sandy Sediment Interface Method by Measuring the Oxygen Demand in Closed Respirometer. International Organization for Standardization: Geneva, Switzerland, 2016.
38. ISO 19679:2020; Plastics—Determination of Aerobic Biodegradation of Non-Floating Plastic Materials in a Seawater/Sediment Interface—Method by Analysis of Evolved Carbon Dioxide. International Organization for Standardization: Geneva, Switzerland, 2020.
39. Pires, J.R.A.; Souza, V.G.L.; Fuciños, P.; Pastrana, L.; Fernando, A.L. Methodologies to Assess the Biodegradability of Bio-Based Polymers—Current Knowledge and Existing Gaps. Polymers

2022, 14, 1359.

40. Haque, A.N.M.A.; Naebe, M. Material Extrusion of Wool Waste/Polycaprolactone with Improved Tensile Strength and Biodegradation. Polymers 2023, 15, 3439.
41. ISO 10993-13:2010; Biological Evaluation of Medical Devices Part 13: Identification and Quantification of Degradation Products from Polymeric Medical Devices. International Organization for Standardization: Geneva, Switzerland, 2010.
42. Wang, S.; Xing, Q. Preparation and in vitro biocompatibility of PBAT and chitosan composites for novel biodegradable cardiac occluders. e-Polymers 2022, 22, 705–718.
43. Karimipour-Fard, P.; Pop-Iliev, R.; Jones-Taggart, H.; Rizvi, G. Design of 3D scaffold geometries for optimal biodegradation of poly(lactic acid)-based bone tissue. AIP Conf. Proc. 2020, 2205, 020062.
44. Hedayati, S.K.; Behravesh, A.H.; Hasannia, S.; Bagheri Saed, A.; Akhoundi, B. 3D printed PCL scaffold reinforced with continuous biodegradable fiber yarn: A study on mechanical and cell viability properties. Polym. Test. 2020, 83, 106347.
45. Ghosh Dastidar, A.; Clarke, S.A.; Larrañeta, E.; Buchanan, F.; Manda, K. In Vitro Degradation of 3D-Printed Poly(L-lactide-co-glycolic acid) Scaffolds for Tissue Engineering Applications. Polymers 2023, 15, 3714.
46. Ausejo, J.G.; Rydz, J.; Musioł, M.; Sikorska, W.; Sobota, M.; Włodarczyk, J.; Adamus, G.; Janeczek, H.; Kwiecień, I.; Hercog, A.; et al. A comparative study of three-dimensional printing directions: The degradation and toxicological profile of a PLA/PHA blend. Polym. Degrad. Stab. 2018, 152, 191–207.
47. Choe, S.; Kim, Y.; Park, G.; Lee, D.H.; Park, J.; Mossisa, A.T.; Lee, S.; Myung, J. Biodegradation of 3D-Printed Biodegradable/Non-biodegradable Plastic Blends. ACS Appl. Polym. Mater. 2022, 4, 5077–5090.
48. Ni, Z.; Shi, J.; Li, M.; Lei, W.; Yu, W. FDM 3D Printing and Soil-Burial-Degradation Behaviors of Residue of Astragalus Particles/Thermoplastic Starch/Poly(lactic acid) Biocomposites. Polymers 2023, 15, 2382.
49. Lee, D.; Sun, Y.; Youe, W.J.; Gwon, J.; Cheng, H.N.; Wu, Q. 3D-printed wood-polylactic acid-thermoplastic starch composites: Performance features in relation to biodegradation treatment. J. Appl. Polym. Sci. 2021, 138, 50914.
50. Tsou, C.-H.; Yao, W.-H.; Wu, C.-S.; Tsou, C.-Y.; Hung, W.-S.; Chen, J.-C.; Guo, J.; Yuan, S.; Wen, E.; Wang, R.-Y.; et al. Preparation and characterization of renewable composites from Polylactide and Rice husk for 3D printing applications. J. Polym. Res. 2019, 26, 227.

51. Sekar, V.; Putra, A.; Palaniyappan, S.; Eh Noum, S.Y.; Sivanesan, S.; Jiun, Y.L. Additive manufactured acoustic absorbers made of wood-fiber composites with modified infill patterns. Wood Mater. Sci. Eng. 2023.
52. Harris, M.; Harris, M.; Mohsin, H.; Potgieter, J.; Ishfaq, K.; Archer, R.; Chen, Q.; De Silva, K.; Le Guen, M.-J.; Wilson, R.; et al. Partial Biodegradable Blend with High Stability against Biodegradation for Fused Deposition Modeling. Polymers 2022, 14, 1541.
53. Sekar, V.; Palaniyappan, S.; Noum, S.Y.E.; Putra, A.; Sivanesan, S.; Sheng, D.D.C.V. Acoustic absorbers made of wood fiber composites developed by compression molding and additive manufacturing. Wood Res. 2023, 68, 68–82.
54. Bher, A.; Mayekar, P.C.; Auras, R.A.; Schvezov, C.E. Biodegradation of Biodegradable Polymers in Mesophilic Aerobic Environments. Int. J. Mol. Sci. 2022, 23, 12165.
55. Rydz, J.; Sikorska, W.; Musioł, M.; Janeczek, H.; Włodarczyk, J.; Misiurska-Marczak, M.; Łęczycka, J.; Kowalczuk, M. 3D-Printed Polyester-Based Prototypes for Cosmetic Applications—Future Directions at the Forensic Engineering of Advanced Polymeric Materials. Materials 2019, 12, 6.
56. Kaya, H.; Arıcı, Ş.; Bulut, O.; Bilgili, F.; Ege, D. CNT incorporation improves the resolution and stability of porous 3D printed PLGA/HA/CNT scaffolds for bone regeneration. Biomed. Mater. 2023, 18, 055028.
57. Balogová, A.F.; Trebuňová, M.; Ižaríková, G.; Kaščák, Ľ.; Mitrík, L.; Klímová, J.; Feranc, J.; Modrák, M.; Hudák, R.; Živčák, J. In Vitro Degradation of Specimens Produced from PLA/PHB by Additive Manufacturing in Simulated Conditions. Polymers 2021, 13, 1542.
58. Seggiani, M.; Altieri, R.; Puccini, M.; Stefanelli, E.; Esposito, A.; Castellani, F.; Stanzione, V.; Vitolo, S. Polycaprolactone-collagen hydrolysate thermoplastic blends: Processability and biodegradability/compostability. Polym. Degrad. Stab. 2018, 150, 13–24.
59. PN-EN 13432:2002; Packaging Requirements for Packaging Suitable for Recovery through Composting and Biodegradation Testing Program and Evaluation Criteria for Final Approval of Packaging. Polish Committee for Standardization: Warsaw, Poland, 2002.
60. Uribe-Echeverría, T.; Beiras, R. Acute toxicity of bioplastic leachates to Paracentrotus lividus sea urchin larvae. Mar. Environ. Res. 2022, 176, 105605.