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Review

Enzyme-Assisted Circular Additive Manufacturing as an Enabling Technology for a Circular Bioeconomy—A Conceptual Review

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Abstract: Additive manufacturing (AM) is a decisive element in the sustainable transformation of technologies. And yet its inherent potential has not been fully utilized. In particular, the use of biological materials represents a comparatively new dimension that is still in the early stages of deployment. In order to be considered sustainable and contribute to the circular economy, various challenges need to be overcome. Here, the literature focusing on sustainable, circular approaches is reviewed. It appears that existing processes are not yet capable of being used as circular economy technologies as they are neither able to process residual and waste materials, nor are the produced products easily biodegradable. Enzymatic approaches, however, appear promising. Based on this, a novel concept called enzyme-assisted circular additive manufacturing was developed. Various process combinations using enzymes along the process chain, starting with the preparation of side streams, through the functionalization of biopolymers to the actual printing process and post-processing, are outlined. Future aspects are discussed, stressing the necessity for AM processes to minimize or avoid the use of chemicals such as solvents or binding agents, the need to save energy through lower process temperatures and thereby reduce CO_2 consumption, and the necessity for complete biodegradability of the materials used.

Keywords: circular economy; additive manufacturing; enzyme; waste stream; bioeconomy

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1. Introduction

Over the last ten years, additive manufacturing (AM) has developed into a booming manufacturing sector with high growth rates and a wide range of applications, technologies [1,2] and materials ranging from, e.g., soft materials in medical applications [3] to metals [4], plastics [5] or even cement [6]. Although it is still a rather new manufacturing technology, AM too must meet the requirements of future economic activities whose key aspects are sustainability and, as a medium-term goal, suitability for a circular economy [7].

Due to its layer-by-layer production and the individual design of objects, AM is by definition a resource-conserving technology and thus already much more sustainable than established production technologies such as milling or injection molding [8]. However, additively manufactured objects typically have a short lifespan, which leads to large amounts of waste standing in the way of achieving a circular economy. The fact that plastics and metals are the dominant printing materials in terms of volume [9] further exacerbates this effect as large amounts of CO_2 are released during production of these printing materials. Other used plastics may be considered critical as they often contain hazardous substances [10,11]. Approaches to recycling material from printed objects into new printing materials have been developed [12]. But even these approaches can only solve the problem to some extent, as only a fraction of the printed material can be recycled. Thus, printing materials with significantly lower CO_2 emissions during production and a compatibility with the circular economy are necessary [12–14].

Interesting approaches towards sustainable AM can be found in the area of bio-based materials such as reinforcements of bio-composites with fibers [15] or nanocomposites [16] and even sustainable photopolymers [17]. Within this area, some printing materials are already commercially available, such as bio-polyester (bio-PE), polylactic acid (PLA) or lignin derivatives. However, CO_2 emissions during production are still high as they have to be synthesized in energy-intensive process steps from biological raw materials, such as starch in the case of PLA [18,19]. Furthermore, biodegradability is only ensured under very specific conditions, which are not achieved by most disposal facilities [20,21]. Compatibility with the circular bioeconomy is, therefore, difficult to realise. Thus, new types of work are needed to make AM fit for the circular bioeconomy. Bishop et al. [18,19] were able to show that the use of side streams from food and forestry industries makes a significant contribution to reducing the greenhouse gas emissions and is superior to the use of biomass produced specifically for this purpose, such as maize in the case of PLA [19]. The use of side streams from forestry and agriculture as a raw material for new printing material is, therefore, an obvious choice. However, in order to enter the circular bioeconomy, the printed objects need to be completely biodegradable.

When looking for ways to create structures and materials using biopolymer-based systems that are completely biodegradable, it is worth taking a look at other disciplines such as agronomy and food science. Here, material development and modification is often performed by enzymes covering a wide range of different classes of raw materials and polymers, ranging from lignins and fiber-based residues to protein-rich matrices [22–24]. Enzymes can be regarded as proteinogenic catalyzers that enable chemical reactions by lowering the activation energy. Thereby, the addition of other chemical substances or higher temperatures for the reaction to start is not necessary. During the reaction, enzymes are not exhausted and can be used multiple times. In combination with their substrate specificity and broad abundance, enzymes are versatile. The enzymes used in agronomy and food science are mostly technical enzymes that are available in large quantities and at reasonably low prices, which favors their use in material development for AM. Despite the good experiences with the use of enzymes in other processes, the knowledge on the applicability of these enzymes during production of bio-based printing material for AM is limited [13,25]. A transfer of these approaches to additive manufacturing has not yet been trialled but could contribute to making AM more sustainable and ready for the circular bioeconomy. In addition to their use in the production or crosslinking of printing material, enzymes are also used in industry for the purification [26], functionalization and chemical-physical [27] modification of biogenic material. In this way, it is possible to produce more sustainably by dispensing with chemicals and to expand the substrate spectrum, thus enabling entry into the circular value chain.

In this conceptual review, the state of the art concerning applications of biopolymers in AM with special emphasis on biopolymers originating from side streams is described. Further on, biogenic printing materials that are already produced using enzymes are compiled and their applicability in circular bioeconomy concepts that are in line with the European Commission's bioeconomy strategy [28–30] is discussed. Based on this, the technological concept of Enzyme-assisted Circular Additive Manufacturing processes (EnCAM) is presented, including the possible application of enzymes along the process chain in pre-treatment, functionalization and printing. Some final remarks on the future prospects of enzyme production and novel enzyme engineering approaches conclude the paper.

2. Methodology

The research process of this work follows the standard approach of real sciences according to Ulrich and Hill [31]. The aim of this work is, thus, to execute subjectively perceived sections of reality by describing and defining concepts, to abstract on the basis of individual cases and to develop alternative courses of action for the realization of future realities. By identifying essential issues of integrated bio-additive manufacturing design, a search string for a literature review according to the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines was developed. The results of the literature review were reviewed in relation to previous studies. Similar approaches are well-documented in the literature [32,33]. Figure 1 illustrates the procedure used.

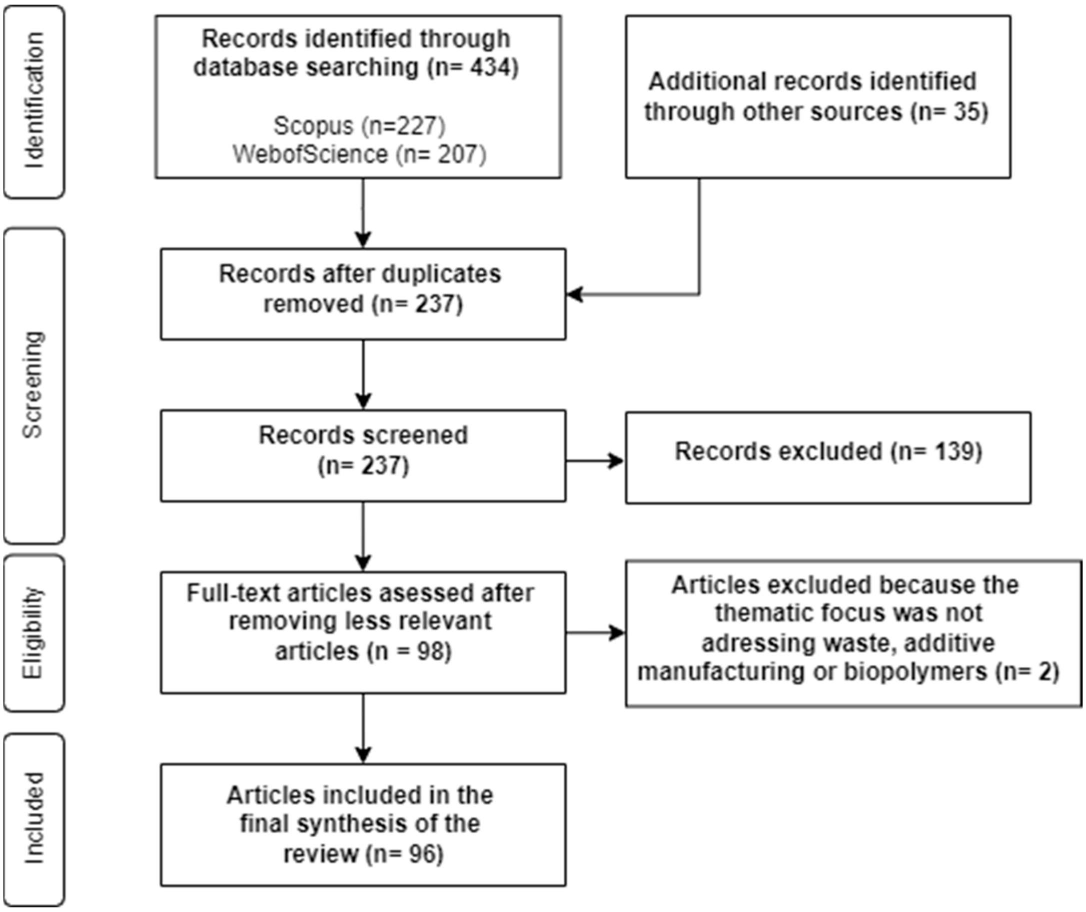

Figure 1. Systematic representation of the process for data search and collection according to the PRISMA guidelines.

3. Biopolymers in Additive Manufacturing

3.1. Areas of Application for Biopolymers in AM

Identifying application sectors for biopolymers in AM initially requires a classification of AM technologies. Classifying AM in the context of biological transformation is, however, semantically non-trivial. Currently, the literature widely refers to bioprinting, additive biomanufacturing, and additive manufacturing of biomaterials. However, there is no clear definition of these terms. The key term here is biomaterial. The term originates primarily from the healthcare industry and science and does not describe a substance that must necessarily be made of biological matter, but rather a substance that has been engineered to interact with biological systems, e.g., for therapeutic or diagnostic purposes. This is often achieved through bioimitation/biomimetics. In the context of biointegration, however, we are concerned with the processing of substances that consist at least in part of biological matter. These are referred to below as bio-based materials. This results in three possible fields of application for AM, which can be differentiated according to the basic technology and materials used:

1. Bioprinting is the versatile deformation of cellular tissue. This is, for instance, an application of cells, growth factors and biomaterials that are combined to create products that mimic the properties of natural tissue [34,35]. A distinction is made between three- and four-dimensional technologies. In 3D bioprinting, fabric is created

in three spatial dimensions and in 4D bioprinting, time is added, i.e., the ability to change over time by changing the product with the help of a programmable mat that reacts to environmental parameters (humidity, temperature, etc.) and thus changes its shape accordingly [36].

2. Traditional additive technologies applied with bio-based or bio-hybrid materials, i.e., any manufacturing process producing a three-dimensional object (workpiece) by layering the materials [37–39].
3. Additive biomanufacturing describes any bio-based printing technology that uses non-traditional additive manufacturing technologies or materials and products that mimic the properties of natural tissues. EnCAM is an early example of these types of AM technologies.

3.2. Biopolymers as Raw Materials for Circular Additive Concepts

The term "biopolymer" is widely used in natural and material sciences. However, the underlying meaning can differ substantially. Starting from the fundamental biological definition, biopolymers are polymers synthesised in cells of living beings, including very different types of molecules such as DNA, starch or hormones [40]. Seen from a material sciences point of view, the term "biopolymers" covers (1) polymers of biological origin that are biodegradable, (2) polymers generated from biological sources that are non-degradable, and (3) polymers generated from fossil fuels that are biodegradable to a large extent [41,42]. Considering further aspects such as the origin from waste streams and garden compostability, the classical representation [43] can be extended via a coordinate system with four quadrants, which allows a more differentiated assessment of biopolymers suitable for circular concepts (Figure 2).

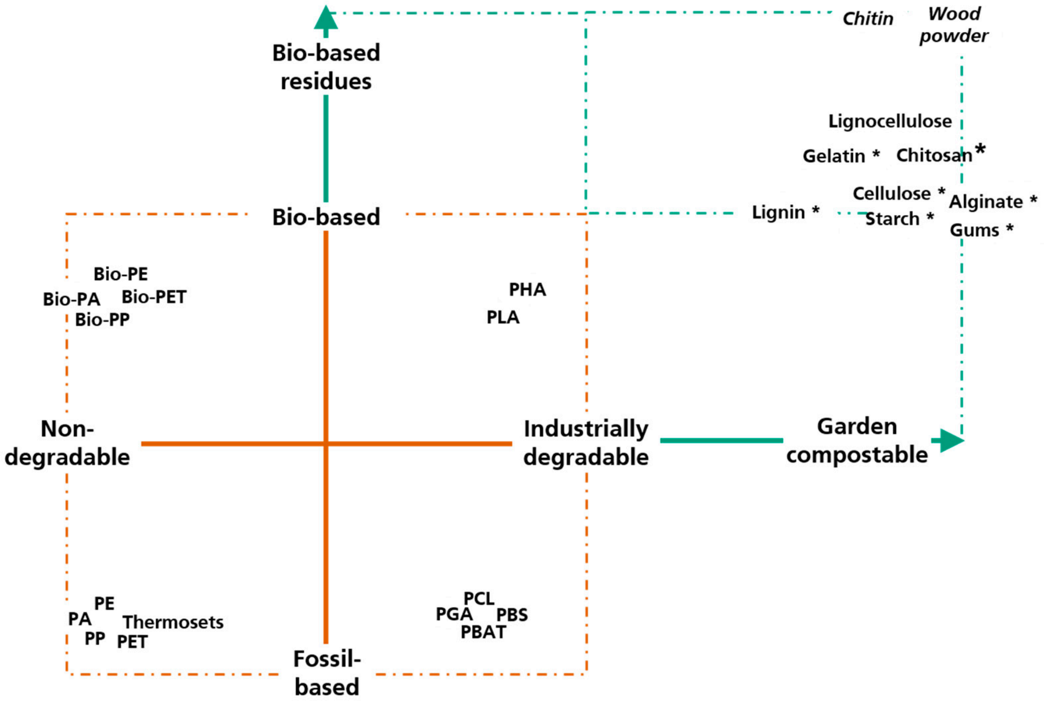

Figure 2. Classification of polymers used in material development summarized under the term "biopolymers" according to their degradability and origin. PE: Polyester; PP: Polypropylene; PET: Polyethylene; PA: Polyamide; PHA: Polyhydroxyalkanoates; PLA: Poly lactic acid; PCL: Poly capro lactone; PBAT: aromatic copolyesters; PBS: Aliphatic copolyesters; PGA: Polyesteramides. *: These biopolymers undergo intense pre-processing and are not considered in a focused manner with regard to concept development.

Such a representation is particularly useful with regard to their future availability and potential supply chain issues. For example, the short-term availability of biopolymers that can be obtained directly from side streams without extensive pre-processing, such as sawdust, is much more robust and convertible. In addition, upstream reprocessing of the side streams means both additional costs, e.g., for thermal energy, and higher resource consumption, e.g., for chemicals. This results in a higher price for the biopolymers and thus for the product printed from them, as well as a poorer life cycle impact. For use in a circular bioeconomy, biopolymers that are obtained from side streams and undergo as little pre-processing as possible should be favoured. These biopolymers can be found in the top right corner in Figure 2, highlighted in italics. It has to be considered that biogenic printing materials for applications in the medical sector are typically highly pre-processed and standardized due to medical device regulations [44].

Thus, even though originating from waste streams and being garden compostable, these biopolymers only partially fall under this designation and are marked with asterisks. In the following section, we will focus on biopolymers in the top right corner that can be applied in additive circular bioeconomy concepts. Further additive applications of biopolymers from the upper right corner that are not suitable for circular additive concepts are summarized in Table 1.

3.2.1. Chitin and Derived Biopolymers

After cellulose, chitin is the second most produced naturally occurring biopolymer in the world [45]. Chemically, chitin is a polysaccharide consisting of acetylglucosamine units linked together via β-1,4-glycosidic bonds. Depending on the origin, the chain length, folding and the degree of deacetylation vary. If less than 50% of the amino groups are acetylated, it is referred to as chitosan. Chitin is the main component of the cuticle of insects (e.g., beetles, flies), fungal cell walls (e.g., *Aspergillus niger*), and green algae [45,46]. It is also an essential component of various exoskeletons of marine arthropods such as crustaceans (e.g., crabs, shrimps) or squid. Chitin is characterized by special chemical and biological properties such as biocompatibility, non-toxicity and high adsorption capacity [46].

Currently, chitin is obtained mainly from waste from the fishery industry, and here primarily from crustacean shells. According to Nirmal et al. [47], the consumption of crustaceans and crabs such as shrimps will increase from 5.03 million tons in 2020, at a compound annual growth rate of 6.1%, up to 7.28 million tons in 2025. In the processing of shrimp for human consumption alone, 40–50% of the amount produced is waste, of which again up to 40% is chitin [47,48], corresponding to an annual quantity of up to 1 million tons depending on raw material and processing conditions. The same applies to chitin, which is produced during the production and processing of insects. The current amount of chitin waste from insect production is still comparatively low. However, the production volume for edible insects will increase from 227,700 tons in 2020 to 3.14 million tons in 2030, which corresponds to a compound annual growth rate (CAGR) of about 30% [49]. Depending on the insect species, the proportion of chitin produced varies between 30 and 50%, corresponding to 942–1569 kilotons of chitin. Further chitin sources relevant in terms of quantity are can be found in biofermentation. For example, *Aspergillus niger*, which is typically used in biofermentation for the production of citric acid and enzymes, contains 42% chitin in its cell wall constituents [50]. From the annual production of citric acid alone, up to 750.000 t of mycelium waste from *A. niger* accrues [51].

Despite this huge potential, only a small proportion of the chitin waste accruing worldwide is reused, e.g., for animal feed or chitosan production. The majority is disposed of in the environment. Crustacean waste, for example, is responsible for a large proportion of crustacean-related pollution in oceans and on shorelines [52–54]. Thus, the largest part of chitin currently accumulating is lost to the circulation system as a valuable raw material [47]. A solution for achieving direct utilization of chitin in the mass market is not present. Hence, using chitin as a printing material in additive manufacturing with a broad sales market could provide a remedy.

3.2.2. Wood Powder and Derived Biopolymers

Wood is one of the world's most widespread naturally occurring and most-used industrial raw materials. During the preparation and processing of wood, large quantities of wood waste are produced. About 50% of the harvested wood is processed into value-added products such as construction lumber, while the rest is waste [55]. The primary utilization route of wood waste is energy recovery, mostly in the form of pellets pressed from sawdust [56,57]. In recent years, however, the use of wood powders from wood waste in additive manufacturing has been increasingly investigated, and the usability of the whole powder, as well as its individual components, which are mainly cellulose and lignin, has been studied in detail (Table 1).

Cellulose is the most abundant biopolymer on earth and is found mainly in plants but can also be synthesized by bacteria, algae and fungi [58]. In plants, cellulose accounts for about one third of the dry mass and represents the main component of the cell wall. Chemically, cellulose is a homo-polymer of β-1-4 glycosidically linked glucose units forming long chains that are highly ordered and arranged into so-called cellulose microfibrils that provide tensile strength and have a stabilizing function in plant cell walls [59]. Moreover, cellulose is characterized by its hydrophilicity, chirality and biodegradability [58]. Due to these properties, high amounts of the fibrous raw material, i.e., pulp (mainly consisting of cellulose), are nowadays extracted from wood and other cellulosic materials in order to produce paper and paper products. In the 1960s, about 60 million tons of pulp were produced for the paper industry. Since then, the annual demand for pulp has increased extremely, and over the last two decades, an average of about 180 million tons of pulp have been produced annually [60]. In 2022, the global wood pulp market size was estimated at USD 162.3 billion, but it is expected to increase even further to USD 185 billion 2027 [61].

Since only cellulose is extracted from the plant material and further processed to be used in the pulp and paper industry, lignin is generated in high amounts as a waste product from this sector. In plant cell walls, lignin represents 15–40% of the dry mass and is embedded in the cellulose matrix to increase the stability of the cells, allowing plants to grow to huge sizes [62]. Lignin, the most common aromatic biopolymer on earth, consists of cross-linked guaiacyl, syringyl, and p-hydroxyphenyl monomers. Crosslinking of these units in plant cell walls occurs through oxidation of the lignin units by laccases/peroxidases, which causes a radical polymerization [63]. Around 50–70 million tons of lignin are produced annually as residual waste alone from the pulp and paper industry worldwide [64,65]. Nowadays, lignin is mostly burned in order to generate energy, thereby wasting a natural renewable feedstock with a high potential in terms of recycling and valorization that can be worth up to USD 750/metric ton depending on purity and origin [66,67]. Therefore, new possibilities and techniques, such as additive manufacturing, are needed in order to recycle valuable side streams such as lignin to use them in a sustainable circular bioeconomy.

3.2.3. Alginate and Gelatin

Alginate is a linear polysaccharide that consists of guluronic and mannuronic acids linked together via α-1,4-glycosidic bonds. The uronic acids are partially distributed in homopolymeric blocks, which results in the typical folding structure necessary for gelation [68]. Alginate is characterized by its good gelation capacity, for forming hydrogels, and high biocompatability. Thus, the main application areas are in the food and beverage industry as gelling or emulsifying agents, as well as in the biomedical field for wound dressings, drug delivery, and to a small extent, tissue engineering [69,70], including alginate-based bioinks (Table 1). In 2021, the global market volume was 44.5 kilotons with a value of 760 million USD. By 2030, this will increase to 59.1 kilotons and 1070 million USD, respectively, corresponding to a CAGR of 5% [71]. Typical sources of alginate are seaweeds such as *Lessonia trabeculate* or *Macrocystis pyrifera*, which can be either harvested from the wild or cultivated [72]. Apart from these methods, alginate can also be obtained via biofermentation using *Azotobacter vinelandii* or *Pseudomonas aeruginosa*. This bacterial alginate retains a higher molar mass and a higher degree of polymerization than alginate from seaweed but is, in turn, more expensive [70,73]. To date, industrial processes for obtaining alginate from waste streams have not been described.

Gelatin is one of the most widely used hydrocolloids in industry. It consists of a mixture of denatured and hydrolyzed proteins and peptides, which are obtained from collagen, a natural component of the extracellular matrix in many tissues of vertebrates and invertebrates [74]. Depending on the conditions of collagen hydrolysis, acidic or alkaline, type A or type B gelatin is obtained, which differ from each other in their isoelectric point and thus their area of application. Gelatine is characterized by its good water binding capacity, biocompatibility and poor mechanical and adhesive properties [75]. Practically, gelatin can be obtained from any vertebrate or invertebrate whose tissue contains collagen. However, the main source of collagen used for gelatin production is bovine and pig slaughterhouse waste [76]. A total of 98% of the gelatin produced is obtained from this source [77]. Gelatine is also obtained from fish processing waste, although the proportion is significantly lower [78]. Other approaches involve the extraction of gelatine from leather waste, although the tanning residues significantly limit the range of applications [79]. Among the hydrocolloids available on the market, gelatine dominates the market as it has the highest revenue share of all at 33.5% [80]. The majority of gelatin produced (56.7%) is utilised in the food and beverage industry, and about one third is used in the medical field, including in health care, wound healing and medications [81]. Applications in tissue engineering as part of bioinks are being intensively researched (Table 1) but only account for a very small proportion of current applications [82]. In 2023, the market value of gelatin was 6.5 billion USD, and the revenue forecast for 2030 is 13.2 billion USD with a CAGR of 10.1% [82]. The underlying market growth is primarily attributed to growth in the food and beverage sector [81].

Table 1. Overview of biopolymers used in additive manufacturing, including the material systems in which they are applied, the printing process and the prospective applications. FDM: fused deposition modeling, FLM: fused layer modeling, DIW: direct ink writing, SLS: selective laser sintering, BJ: binder jetting, PP: photo-polymerization, DLP. digital light processing, PBF: powder bed fusion, SL: stereolithography.

Material System	**Printing Process**	**Applications**	**Reference**
Chitin/Chitosan			
• Chitosan in acidic mixtures with basic bath solidification	DIW	Tissue engineering	[83–88]
• Dissolution into alkali aqueous solution	DIW	Tissue engineering	[89]
• N,O-carboxymethyl chitosan, Ca^{2+} crosslinking with polyphosphate	DIW	Tissue engineering	[90]
• Genipin crosslinking, crosslinking water-soluble	DIW	Immobilization of microorganisms	[91]
• Self-crosslinking chitosan, NaCl and phosphate buffer saline	DIW	Drug release	[92]
• Chitin with iota-carrageenan and tungsten trioxide	DIW	Tissue engineering	[93]
• Chitosan in Acrylamide	PP	Tissue engineering	[94]
• N-maleyl chitosan with gelatin methacrylamide	PP	Wound treatment (bone)	[95]
Cellulose			
• Nanofibrils reinforced with quince seed mucilage, CaCl$_2$-crosslinking	DIW	Soft tissue engineering	[96]
• Cellulose in alginate matrix and crosslinking in CaCl$_2$-solution	DIW	Cartilage tissue engineering	[97–99]
• Nanofibers treated with carboxymethylation and periodate oxidation, CaCl$_2$-crosslinking	DIW	Wound treatment	[100]
• Methylcellulose, κ-carrageenan with incorporated cellulose nanocrystals, KCl-crosslinking	DIW	General additive in bioink	[101]
• Cellulose nanocrystals with photoactive modified surface	DLP	General additive in bioink	[102]
• Cellulose nanocrystals in photopolymerizable monomers solution	DLP	Lightweight sustainable composite	[103]
Wood powder			
• Wood powder, methylcellulose lubricant and binder	DIW	Wood products	[104]
• Wood powder, diverse binders, e.g., PLA, TPU, copolyster	FDM, FLM,	Cost reducing material	[105]
• Wood powder; polyvinyl acetate and urea-formaldehyde as binder	DIW, SLS, BJ	Wood products	[106]
• Wood powder with PLA, silane coupling agent KH550 as plasticizer	FLM	Bio-based filler and coupling agent	[107]
• Wood powder, PLA as a binder	FDM	Bio-based filler and coupling agent	[108–110]
• Fragile perforated wood powder, crosslinking via binder liquid	FDM, BJ	By-product recycling	[111]
• Wood powder, PLA as a binder	BJ	Biodegradable ink	[112,113]
• Wood powder, copolyester as binder	SL	Higher mechanical strength	[114]
• Wood chips as bulk material and gypsum, methyl cellulose, sodium silicate, cement as binder	PBF	Cement alternative	[115]

Table 1. *Cont.*

Material System	Printing Process	Applications	Reference
Lignin			
• Lignin cross-linked with soft triblock copolymer Pluronic F127	DIW	Biomedical engineering	[116]
• Lignin modified with terminal carboxyl group incorporated in PLA	FDM	Increased tensile strenght	[117]
• Kraft lignin, organosolv lignin and lignosulfonate with PLA as binder	FDM	Biopolymer foaming	[118]
• Lignin with acrylonitrile-butadiene rubber and acrylonitrile-butadiene-styrene	FDM	Renewable material	[119]
• Dealkaline lignin as photoinitiator for polyacrylates	DLP	Packaging	[120]
Alginate			
• Alginate with hydroxyapatite, crosslinking via NaOH—bath solidification or $CaCl_2$	DIW	Bone tissue engineering	[88,121]
• Sodium alginate with collagen type I/agarose/gelatine, crosslinking via $CaCl_2$	DIW	Soft and hard tissue engineering	[122–125]
• Gelatin-sodium alginate-inks with bioactive glass particles	DIW	Tissue engineering	[126,127]
• Sodium alginate with soft polyacrylamide networks, crosslinking via $CaCl_2$	DIW	Tissue engineering	[128]
• Laponite/alginate bioinks, $CaCl_2$—crosslinking	DIW	Tissue engineering	[129]
• Pre-crosslinking with $CaCO_3$ and D-Glucono-δ-lactone, final crosslinking via $CaCl_2$	DIW	Tissue engineering	[123]
Gelatin			
• Enzymatic crosslinking of gelatine by tyrosinase and sonication	DIW	Tissue engineering	[130]
• Termed gelatin-sucrose matrix	DIW	Tissue engineering	[131]
• Crosslinking with glutaraldehyde and mix with cellulose and alginate	DIW	Biomedical devices	[132]
• As medium for agar scaffolds	DIW	Tissue engineering	[133]
• Hydrating gelatine substrate as a Ca^{2+} reservoir	DIW	Tissue engineering	[134,135]
• Yoghurt-gel ink with whey protein isolate	DIW	Food design	[136]

4. Discussion

The use of biopolymers as raw materials in additive manufacturing has been steadily increasing in recent years [137,138], which is helping to reduce the shortage of petroleum-based raw materials. However, the percentage of biopolymers derived from side streams that have not been processed or blended with other chemicals and that are garden compostable is low [138]. One reason for this is variation in raw material quality and quantity as well as the varying composition of impurities. For example, the content of chitin, proteins and other minerals in the shells of shrimps varies between 10 and 40% [45,46,48], which means that all subsequent processes have to be adjusted and additional costs, e.g., for more chemicals or due to longer downtimes, are incurred. However, if there were processes available by which biopolymers could be obtained from the side streams and further processed in a flexible and resource-saving manner, this could significantly improve the potential uses of biopolymers from side streams as raw materials for additive manufacturing. Furthermore, this could enable the transition from the linear economy, in which printed objects accumulate as waste after use, to a circular economy, in which printed objects are fully biodegradable and can, therefore, be integrated into the cycle.

4.1. Process Concept for Enzyme-Assisted Circular Additive Manufacturing

One concept that can help here is called enzyme-assisted circular additive manufacturing (EnCAM). Figure 3 shows schematically how AM can be integrated into the circular economy using EnCAM. A key feature of EnCAM processes is the use of enzymes along the entire process chain, starting with pre-treatment of side streams, through functionalization of the biopolymers to the additive printing process, including post-treatment. Enzymes consist of large biological molecules and can act as catalysts to accelerate certain chemical reactions. In principle, the catalyzed reaction can also take place without the respective enzyme, but much more slowly. Most enzymes are proteins and may contain co-factors, such as magnesium or iron ions. They are categorized into seven different classes depending on the catalyzed type of reaction: oxidoreduction, transfer, hydrolyzation, lyation, isomerization, ligation, or translocation [139]. Among these categories, there are various enzymes that catalyze covalent and non-covalent crosslinking reactions as well as the functionalization of biopolymers by means of grafting. However, their field of application is narrowly defined and limited to applications in the medical field, above all tissue engineering. Here they have the task of crosslinking the hydrocolloid systems used, e.g., gelatin, in order to achieve a higher and longer-lasting strength [130,132]. In EnCAM processes, however, the field of application of the enzymes is much broader. Here, they can reduce the necessary activation energy for pre-treatments, accelerate specific chemical reactions during functionalization or avoid the use of non-biodegradable chemicals such as photo-crosslinkers or hardeners during printing processes. Post-treatment steps, such as the removal of support structures or the smoothing of surfaces, can also be improved by the targeted selection of enzymes, e.g., hydrolases [140,141]. A schematic representation of the EnCAM concept is shown in Figure 4. The possibilities of using enzymes in pre-treatment, functionalization and printing processes are explained and discussed in more detail in Sections 4.2–4.4.

Another characteristic of EnCAM processes is the possibility to decouple the printing process spatially and temporally from the first two process steps, pre-treatment and functionalization. By dividing the production process into individual sub-steps that can be clearly separated from each other through the selective use of enzymes, it is possible to achieve greater flexibility and the possibility of decoupling. In concrete terms, this means that the enzymatically catalyzed reactions in the functionalization step have to be stopped at a defined point in time. There are various possibilities for this, whereby lowering the reaction temperature is the easiest to implement [142]. Further options are removal and consumption of a reaction product or the thermal or pH-induced inactivation of the enzyme. The latter is only successful if the reaction products are not affected [143]. After the reaction has been stopped, the intended temporal and spatial decoupling is decisive for the further procedure. If only a shorter time of decoupling is required, e.g., in order to achieve a more flexible production utilisation, the prepared intermediate product can be stored in batches and used as needed, similar to the procedure in semi-continuous production. During storage, it is important that the containers and the preceding product have been produced and are stored under high-standard anti-microbial conditions [144]. However, if decoupling is to take place over a longer period of time, e.g., to build up stocks, or if spatial decoupling is to occur, e.g., by supplying the printing material to a customer, drying of the functionalised biopolymer is necessary. Various methods, such as spray drying, roller drying or freeze drying, are available [145]. Depending on the composition of the matrix, e.g., if it contains fibers, the spray drying option is not available [146]. Furthermore, it must be taken into account that the thermal load during drying is kept as low as possible in order to avoid a subsequent negative change in the printing material, e.g., through the formation of Maillard products [145,147].

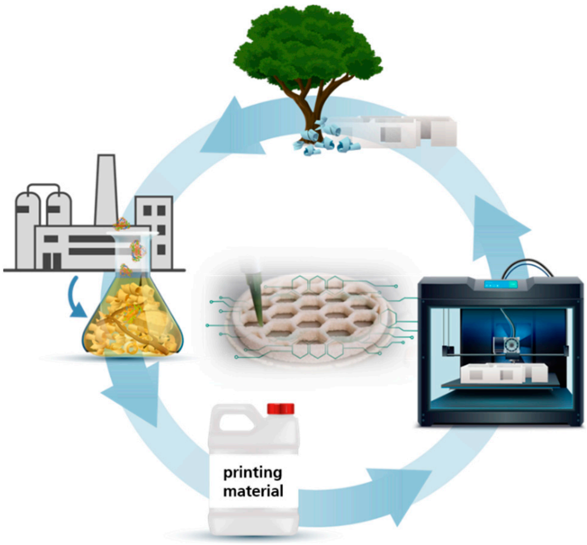

Figure 3. Schematic representation of how additive manufacturing can be integrated into a circular bioeconomy using the enzyme-assisted circular additive manufacturing processes approach.

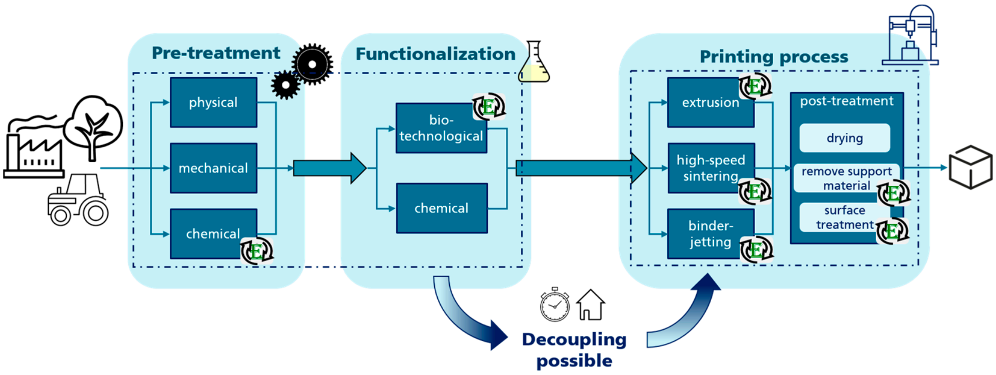

Figure 4. Schematic representation of the structure of enzyme-assisted circular additive manufacturing processes. The green symbols highlight the processing steps in which enzymes can be applied beneficially as catalysts.

4.2. Application Possibilities of Enzymes during Pre-Treatment

Using side streams from agricultural or food production as substrates typically implies the necessity of pre-treatment steps in order to ensure a homogeneous and standardized input stream. Thus, certain pre-treatment steps such as sifting, classifying or grinding have to be performed to remove impurities or obtain powders with a standardized particle size. Apart from these classical methods, further chemical pre-treatments are often applied. These processes are used to remove contaminants or certain functional groups [25,26].

Often, chemicals such as alkalis, acids or halogenide-containing substance mixtures are used. Their environmentally compatible disposal can be critical and very expensive. To achieve optimal reaction conditions, these processes must also be performed at elevated temperatures (>100 °C), which requires a supply of energy to the system.

The use of enzymes, on the other hand, makes it possible to work under moderate conditions and at lower temperatures. Enzymes can be used in different processes for upgrading biopolymers or side streams. For example, the biopolymer collagen is purified with the help of the enzyme pepsin [148]. Silber et al. [149] have shown, that wood residues possess a great potential for enzymatic valorization. For instance, nanocellulose is traditionally produced using enzymatic reactions with endoglucanases and cellulases [150]. Similar to the production of nanocellulose, the deprotonation of chitin can also be achieved by enzymatic methods utilizing various proteases [151,152]. Both, chitin and chitosan, are used in bioprinting. During the manufacture of chitosan, chitin can be deacetylated using chitosan deacetylase [26] or laccase [25]. Further purification can be performed using proteinase K for deproteinization [153].

4.3. Application Possibilities of Enzymes during Functionalization

Functionalization of biopolymers by using enzymes refers to the process of modifying biopolymer materials, such as cellulose or chitin, to enhance their properties. Through these modifications, biopolymers become more suitable for certain applications and help to improve the quality, stability and performance of the final product. During these processes, functional groups are attached to the surface or covalently bonded in the biopolymer matrix. Additional molecular groups can be added or removed to alter properties or add specific functionalities.

Apart from various applications within the medical and biomedical sector [154,155], enzymes are increasingly applied to modify and functionalize biopolymers originating from waste streams [27,153,156,157]. Examples of frequently used enzymes are lipases, which can be used to modify or remove fatty acids and lipids [158–160]. Depending on their substrate specificity, lipases can also polymerize and polycondense dicarboxylic acids to produce bio-based polymers [161]. Another group of enzymes frequently used are laccases, which can be used to graft phenolic amines on wood particles to build anchor groups for additional functionalization or remove those phenolic compounds [25,162,163]. Further, laccases can also be applied to hydrophobize bamboo [164] or other dietary fibers from plant waste [165] that can be applied as structuring fillers in AM printing material.

4.4. Application Possibilities of Enzymes during Printing Processes

As illustrated in Figure 4, the printing process consists of the actual printing step in which three-dimensional objects are created, as well as the post-treatment steps, including drying, removal of support structures and surface treatment. During the actual printing step, the focus lies on the formation of covalent bonds between individual molecules or particles, which can be catalyzed by crosslinking enzymes. In general, enzymes originating from the enzyme classes 1, 2, 3 and 6, which are oxidoreductases, transferases, hydrolases and ligases, can be used for this purpose.

Among biopolymers originating from side streams, proteinogenic polymer systems in particular are cross-linked by enzymes. For example, gelatin and collagen-containing matrices are usually cross-linked by transglutaminases, but tyrosinases or phosphatases can also be used [166,167]. If the proteinogenic matrices contain particles or fibers, they are also spatially fixed during crosslinking, so that additional physical crosslinking can occur [25]. Further examples for biopolymers originating from waste streams are lignins and chitosans. Both can be polymerized and thus chemically cross-linked by enzymes [168].

When selecting the printing process, different technologies utilize different dosage forms, either lyophilized or liquid preparations. Lyophilized preparations are particularly suitable for binder jetting, in which they can be pre-mixed with the powdered biopolymer, and then the liquid required for the chemical reaction can be selectively applied locally [106,111]. Classic application methods for liquid preparations are extrusion-based processes such as liquid deposition modeling, in which the enzyme and substrate come together before the actual printing [101,116]. The same applies to high-speed sintering, in which the enzyme and substrate powder are mixed with a little liquid before the actual sintering takes place.

During post-treatment, the removal of support structures that are required during the printing process to ensure geometrical stability is an important aspect. Especially in small and geometrically complex objects, the removal can be challenging. Since enzymes are very specific and stop their reaction once their substrate is depleted, an immersion in an enzyme-rich bath or their application in a spray can be very effective and help to reduce manual intervention. Current research in the field of biodegradation of plastics, such as polyethylene, polyethylene-terephthalate or other microplastics [169–171], demonstrates the potential of this approach. The surface of the printed object can also be treated with enzymes to improve its characteristics and functionality. In contrast to non-biological polymers, the surfaces of objects printed with biopolymers can be directly grafted by enzymes [172]. The spectrum of functional groups that can be applied ranges from oligonucleotides and antibodies for bio-sensing and microarray applications [173–175] to antimicrobial substances to prevent degradation [176] and phospholipids that can ensure greater biocompatibility [177,178].

5. Future Directions for Enzyme-Assisted Approaches in AM

The expansion of the enzyme portfolio through enzyme design and the discovery of new ecosystems and donor organisms will extend the breadth of additive manufacturing using enzymatic catalysis to other biogenic and non-biogenic materials and raw materials. Currently, the market for industrial enzymes of all kinds is estimated at USD 6 billion and will grow at 6% CAGR over the next few years [161]. On the one hand, the market is demanding a growing variety of enzyme applications in food and beverages, pharmaceuticals, detergents, cosmetics and in biofuel production. The growing demand for enzymes due to increasing environmental standards and regulations on the use of chemicals is also expected to drive the market growth for industrial enzymes [162]. On the other hand, there is is a market push in which expansions in the application base and new product innovations—such as AM—will offer numerous new possibilities for the application of biocatalysts. The market push is based on the availability of improved and new properties of enzymes. The following innovative approaches to improving or rediscovering enzymes are envisaged:

1. Protein engineering by recombinant production via the diversity generation strategy: The aim here is to improve the efficiency of the process by genetically altering the amino acid sequence of either an already-available enzyme or the formulation of an advanced enzyme activity. Therefore, the originally observed disadvantages of native enzymes can be overcome by using enzyme engineering tools. Some evolutionary strategies are applied to support this optimization procedure:
    a. Direct evolution by random mutagenesis to produce enzyme variants with recombination techniques. Machine learning (ML) and artificial intelligence (AI) help to select the characterized generations [163,164].
    b. A rational design approach in which computerized design is used to perform targeted mutagenesis so that new proteins with increased stability, desired interactions and enzymatic functions can be developed [165,166].
    c. Enzyme performance is critically influenced by the microenvironment. Therefore, the mechanistic study of immobilized enzymes is useful for developing improved biocatalysts. The study consists of the characterization of their effects on the properties of the enzymes associated with the particular microenvironment in the solid material. Key performance parameters are investigated. These include the enzyme activity, catalytic rate, and stability, which strongly depend on substrate and product concentrations, as well as the pH, ionic strength, reac-

    tion equilibrium and effective mass–action ratio in the solid particle, which can be influenced by changes in the critical concentrations [167,168].

    d. Cell-free systems consist of in vitro biochemical technologies extracting enzymes from outside the organism where they were originally located. Cell-free systems complement traditional cellular systems. Cell-free synthetic biology methods are useful in pathway prototyping for testing and optimizing biosynthetic pathways before implementation in live cells and scale-up, as well as for pathway-operation design and debugging in bio-circuitry [179,180]. The de novo biosynthesis of cellulose and chitin in cell-free systems has been shown to be possible. Generating covalent binding of material fragments of cellulose or chitin in the context of additive manufacturing would be a possible next step [181,182].
    e. A more advanced step than just improving proteins through random or targeted substitution within the 20 standard amino acids is to develop artificial amino acids and incorporate them into the gene sequence as artificial proteins with new properties. The development of completely new product classes, whose chemical synthesis was previously not possible through conventional protein engineering using the 20 standard amino acids, is expected [183,184].

2. Screening strategies with high throughput screening using functional genomics, microbiome screening and looking for extremophiles:
    a. In the search for biocatalysts, especially for biomaterials, microbiome research enables the discovery of ever new enzymes. Insects, in particular, represent a very diverse group of organisms that can adapt to extremely different environmental conditions. Some of them, the herbivorous insects, have developed highly specialized systems that allow them to use a variety of plants as food sources. In the decomposition of leaves, stems and roots, the composition of the insect gut flora plays a decisive role for the development of food, but also for the decomposition of plastics and toxins [185–187].
    b. The search for specific metabolic activities in extremophilic organisms may reveal extremophilic enzyme functions that operate under extreme conditions such as high temperature and high ion concentrations, even in non-aqueous organic solvents. This would enable the design of a new generation of enzyme catalysts [188,189].
    c. New types of nanozymes will be able to replace biocatalytic reactions of natural enzymes at low cost. “Nanozymes” are “nanomaterials with enzyme-like characteristics” [190]. Their unique characteristics over natural enzymes and even conventional artificial enzymes are as follows: suitability for mass production; robustness to harsh environments; high stability; possible long-term storage; recyclability; adjustable activity; size-, shape-, structure-, or composition-dependent properties; and responses to external stimuli (e.g., light) [191,192]. Many non-metallic materials, especially carbon-based nanomaterials, possess peroxidase activity, one of the non-specific catalytic options for lignin-based material fusion in AM processes.

6. Conclusions

In the course of the sustainable transformation of technologies, additive manufacturing plays a crucial role. Yet, its full potential is not exploited. The use of biological components, in particular, represents a new dimension that is currently still in the early stages of development and has various challenges to overcome before it can be considered sustainable and contribute to circularity.

In this paper, we thus presented a new technology concept—enzyme-assisted circular additive manufacturing (EnCAM)—that uses fully biodegradable printing materials from biogenic side streams. The core of the concept is the use of enzymes along the process chain, starting with the preparation of the side streams, through the functionalization of the biopolymers to the actual printing process and post-processing. The use of enzymes makes it possible to minimize or eliminate the use of chemicals such as solvents or binders, save energy through lower process temperatures, thereby contributing to reducing CO_2 consumption and ensuring the complete bio-degradability of the printed objects. Consequently, entry into the decentralized circular bioeconomy is possible.

For now, this paper merely introduces the basic concept; further research is necessary to prove the feasibility of the approach in practice. Future research should focus on investigating criteria that biogenic side streams have to meet so that they can be used as raw material in EnCAM processes. Furthermore, model processes that cover the whole process chain starting with exemplary side streams should be set up in lab-scale. In addition, it is essential to determine relevant local side streams and to identify systems for sorting and pre-treatment. Moreover, the economic and circular advantages of the approach, including costs of enzyme production, waste reduction and life cycle assessment, must be demonstrated in the medium-term by means of a comprehensive assessment of various application scenarios as well as stakeholder analysis in order to convince decision-makers to adopt such systems and pave the way to a circular bioeconomy.

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