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Review Article

Polylactic Acid Based Biocomposite for 3D Printing: A Review

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Abstract

Three-dimensional (3D) printing technology facilitates the direct creation of intricate objects from computer-aided digital designs. This method offers an efficient means to integrate all essential components by leveraging biomaterials, advanced printing techniques, and innovative cell delivery methods. As 3D printing becomes increasingly prevalent in research, commercial, and domestic spheres, the demand for high-quality polymer filaments continues to rise. Biopolymers, which are widely accessible, low- or nontoxic, biodegradable, biocompatible, chemically versatile, and inherently useful, hold significant potential for diverse applications including biomedicine, food, textiles, and cosmetics. Recent studies have examined the 3D printing of polylactic acid (PLA) using biopolymers such as cellulose, lignin, chitosan, starch, collagen, and gelatin. These biodegradable composites outperform non-biodegradable counterparts in various applications, enhance the properties of PLA, and offer environmental benefits. Thus, a thorough understanding of the 3D printing process for these biocomposites is essential for their production. This review classifies PLA/biopolymer 3D printing materials, details the materials and processing technologies, and discusses their applications. Furthermore, it explores the roles and characteristics of specific filler materials in PLA-based biocomposites and their effects as fillers.

Keywords

3D-printing, Biocomposite, Biopolymers, Polylacid

1. Introduction

3D printing is a technology called additive manufacturing, in which 3D products can be created based on the designed 3D model by depositing materials layer by layer in the 3D printing apparatus [1, 2]. It is also considered a technology that drives the world's rapid development and has an overwhelming impact on our daily lives. 3D printing is a new technology utilized in numerous sectors, including as: (i) in the sphere of research for restricted prototype manufacturing or for prototyping; (ii) to use digital models acquired from several medical imaging modalities (ultrasound, computer

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tomography, and magnetic resonance imaging) to generate three-dimensional biological structures in medicine; (iii) in the automotive as well as the aerospace sector for the production of prototypes and spare bodies; (iv) In the fields of architecture and construction, as well as the fashion and food industries, additive manufacturing has gained considerable traction owing to its appealing benefits. These advantages encompass a reduction in consumables, the ability to customize object geometry, cost-effectiveness, and the prompt fabrication of objects as and when required. [3-6]. Unlike traditional fabrication methods, which assemble individual parts to create a complex structure, 3D printing allows predefined slices of the desired object to be printed in layers (bottom to top). This allows for the rapid manufacturing of complex objects almost completely free from design complexity, giving designers significant freedom to create novel and unproven geometric designs [7, 8]. The initial stage of the printing process is usually the use of computer-aided design to create the desired model shape. The development of 3D printers was predicated on additive layer manufacturing techniques like fused deposition modeling (FDM) [7-12] selective laser sintering (SLS), and stereolithography 3D scaffolds for tissue engineering [13-16]. Fused deposition modeling, or FDM, is currently the most appealing 3D printing method for composite material fabrication. Applied to a wide range of materials, including metals, polymers, ceramics, and other materials, 3D printing is an incredibly adaptable production technology. Bio-based products and materials for analytical, dental, medical, orthopedic, consumer testing, and food applications are among the bioproducts that are anticipated to be part of the $1.82 billion global market for 3D printing by 2022 [11]. Making bio-filaments for FFF 3DP usingbiodegradable and/or renewable resource-based materials, is receiving much greater attention. For filament additive processing, polymer materials like acrylonitrile-butadiene styrene (ABS), polylactide (PLA), polyamide (PA), thermoplastic elastomer (TPE), and polylactic acid are commonly utilized. [17, 11]. The so-called "polymer of the 21st century," poly (lactic acid) (PLA is one of the most dynamic polymers that supports a green and circular economy and is used in a wide range of applications because of its remarkable features. Its biodegradability has allowed it to advance significantly in the 3D printing industry [18]. Generally, PLA is more renewable and currently in use, and it has been authorized for numerous biomedical applications and others [14, 15, 19-23]. However, the need for a variety of products can no longer be met by ordinary virgin PLA filament as 3DP technology develops quickly to integrate into industries like tissue engineering, textiles, and apparel. In order to enhance the physicochemical characteristics of PLA for 3DP, several scientists have started including biomass raw materials into the PLA matrix. [24]. Thus, by combining neat PLA with other biomass, its properties can be improved: polysaccharides found in natural gum, starch, collagen, gelatin, cellulose, and latex found in natural rubber. Because of its cheap cost and PLA's boosting capacity, this seems like a good option. The consequences of adding biopolymer resources to PLA, characterization, applications, and prospects for high-value bio-derived materials are all examined critically in this review study that focuses on PLA-based 3D printing.

2. Synthesis of Polylactic Acid

Polylactic acid (PLA) is the typical raw material used in technology for 3D printing, and its preparation has paramount importance for its full commercialization. It has good mechanical properties, undergoes biodegradation, and can be prepared from renewable resources that contain nontoxic organic acids (α-hydroxy acids), including tartaric, citric, glycolic, lactic, and malic acids. However, the most common monomer used for the preparation of PLA is lactic acid, which can be obtained from either renewable or non-renewable resources [26] in Figure.1. The environmental issues and the cost associated with the conversion of non-renewable resources such as petrochemicals into lactic acid make it not a preferred route. Thus, huge attention is given to abundant and renewable resources at this time. The synthesis of PLA involves either direct condensation or ring-opening polymerization. The successful synthesis is the basis for the interesting properties, market conditions, and wider applications of PLA. Low melting temperatures are one of the interesting features of PLA, which makes it the most suitable material for 3D printing [27, 28].

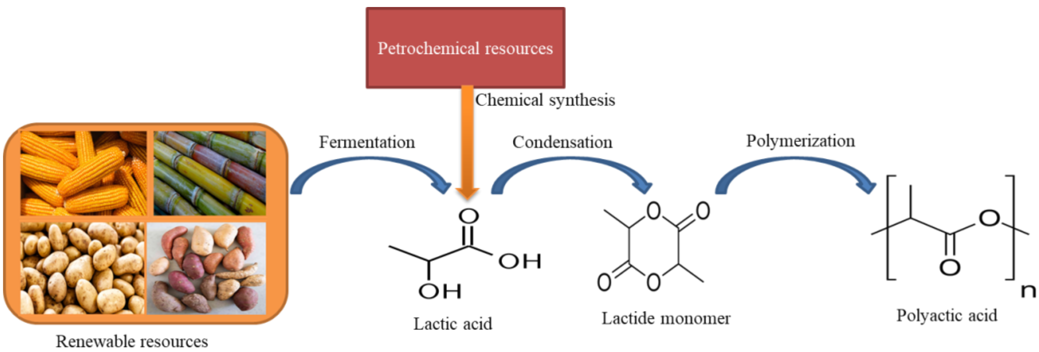

Figure 1. *Synthesis of polylactic acid from different resources.*

Based on the recent findings, PLA is the most promising material that has the potential to substitute the market-dominating man-made thermoplastic polymers. The interesting properties of PLA, such as its low energy consumption because of its flexible structure and low melting point, make it the most important polymer in 3D printing or additive manufacturing [29].

3. The 3D Printing of Polylactic Acid

PLA has been extensively researched as aliphatic polyester for various biomedical and packaging purposes owing to its exceptional biocompatibility, biodegradability, transparency, impressive mechanical strength and modulus, as well as its ease of processing through extrusion, injection molding, or casting techniques. rewrite. PLA has been widely studied as an aliphatic polyester for numerous biomedical and packaging applications due to its outstanding biocompatibility, biodegradability, transparency, strong mechanical properties, and ease of processing via extrusion, injection molding, or casting technique. Commercial 3D printers use this polymer material extensively. Additionally, PLA is an excellent material for 3D printing because it has a low coefficient of thermal expansion and does not adhere to the printing surface. Because of its excellent biological performance, it is widely used, particularly in the biomedical field (e.g., as scaffolds for tissue engineering). Poly (lactic acid) has attracted a great deal of interest in biopolymer research because of its exceptional biocompatibility and sustainability [15, 20, 21, 25, 26]. With the emergence of novel processing methods utilizing additive manufacturing technologies, commonly referred to as 3D printing, the utilization of PLA has experienced a significant expansion in the aforementioned field [14]. Figure 2 illustrates the chemical structure of polylactic acid.

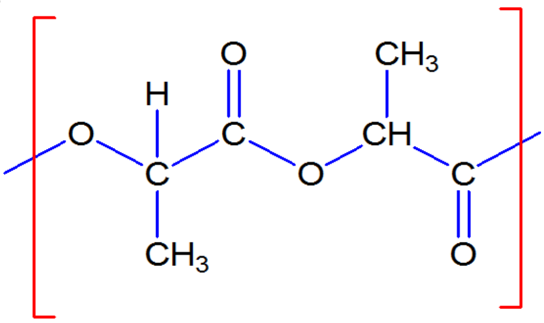

Figure 2. Chemical structure of polylactic acid.

3.1. The 3D Printing of Polylactic Acid Composites

In order to produce PLA, specific reaction parameters like temperature and pressure are needed, which leads to an increase in energy consumption. Additionally, concerns have been raised about the potential impact on food shortages due to the use of corn-based PLA. By adding additives to PLA, not only can consumption be reduced and worries about food scarcity alleviated, but costs can also be lowered compared to using pure PLA. The poor mechanical and thermal qualities of PLA result in limited technical applications. It was also mentioned that PLA cannot properly mimic nature (e.g., natural bone structure, cells, colonization). Therefore, to broaden its applicability for both engineering and biomedical applications, it needs to incorporate biofillers (biopolymers) such as cellulose, lignin, starch, chitosan collagen, and gelatin. Thus, to overcome those drawbacks, PLA binds with different biopolymers.

3.1.1. The Poly Lactic Acid - Cellulose Based Bio Composite for 3D Printing

Within the biosphere, cellulose is the most prevalent biopolymer. It is present in algae, plants, marine animals, fungi, and bacteria the most prevalent biopolymer within the biosphere [27, 28]. Natural bio-based cellulose crystals (CC) have the potential to be useful nanofiller in PLA, altering its mechanical and biodegradable characteristics. CC is considered be the most prevalent organic chemical on Earth and has recently gained importance as a raw material in the commercial world. [5, 29, 30]. Micro- or nano-crystalline cellulose, hemicellulose, and short and long lignocellulose fibers in terms of their fiber dimensions can enhance the properties of PLA [27].

The crystallinity, mechanical characteristics, and degradability of the PLA matrix can all be slightly enhanced by nanocellulose filler (CNF) [24, 30, 31]. However, evenly dispersing the cellulose throughout the PLA matrix is a significant challenge involved in adding cellulose reinforcements to PLA. The hydrophilic nature of cellulose and the hydrophobic nature of PLA pose challenges to the uniform dispersion of the material, as cellulose tends to aggregate and loses its tensile strength—a crucial attribute for 3D printing. Thus, in order to enhance the dispersion of cellulose into the PLA matrix, PLA and cellulose were ground to a fine particle size, and different compatibilizers were used [24, 30, 32]. Wang et al. [24] use polyethylene glycol 600 (PEG600) as a smoothing agent to develop CNF-filled PLA bio-composite filaments for 3D-FDM printing with CNF as filler. In this investigation, CNF was initially separated using high-pressure homogenization in conjunction with enzymatic hydrolysis. Then, using PLA as the matrix and CNF as the filler, melt extrusion was used to create CNF/PLA filaments. The mechanical capabilities, water absorption capabilities, and thermal stability of biocomposite filaments and 3D-printed items were examined. Results indicated that CNF improved the PLA/PEG600/CNF composite's thermal stability. The CNF-filled PLA biocomposite filament exhibited a 33% increase in tensile strength and a 19% elongation at break when compared to unfilled PLA FDM filaments, indicating improved compatibility for desktop FDM 3DP. The research revealed new potential for high-value utilization of CNF in 3DP in consumer product applications. PEG600 is not only working as a plasticizer but also as an adhesive in the filament preparation procedure. With PEG600 added, the PLA filament's tensile strength decreased and its elongation at break increased. This is because PEG600 has a plasticizing effect. Nicoleta Adriana Frone and others attempted to use decimal peroxide (DCP) as a cross-linking agent in a single-step reactive blending process to enhance the 3D printing behavior of polylactic acid (PLA), poly (3-hydroxybutyrate) (PHB), and cellulose nanocrystals (NC). The addition of DCP improved the interfacial adhesion and dispersion of NC in nancomposites. PLA's crystallinity increased from 16 percent in the PLA/PHB blend to 38 percent in the DCP cross-linked blend and 43 percent in the cross-linked PLA/PHB/NC nanocomposite as a result of the nucleating activity and crystallization favoring by NC and DCP. Furthermore, after extrusion and 3D printing, PLA/PHB blends and nanocomposites exhibited an increase in the onset degradation temperature, even with more than 10◦C, according to the thermo gravimetric analysis. PLA/CNC biopolymer nanocomposites are made by mechanically combining PLA and CNC. Prior to mechanically mixing PLA and CNC, drying CNC is done to eliminate air bubbles. This improves the mechanical characteristics of the 1 weight percent cellulose nanocomposite. In comparison to pure PLA, the tensile strength has increased by 18%, and the tensile modulus has also increased by 50%, which helps 3D printing achieve high mechanical strength. [30]. Cellulose nanocrystals (CNC) were obtained using maleic anhydride (PE-g-MA) grafted polyethylene as a coupling agent, which helped to increase the PLA crystallinity degree and reduce the complex viscosity. CNC and the coupling agent can act as nucleating agents on the mixture [33]. Frone et al. investigated a study on silane-treated CNF with PLA. Research results demonstrated that PLA composites containing untreated CNFs had a higher degree of crystallinity even if the treated CNFs had better dispersion. [34]. The chemical structure of poly (lactic acid) and cellulose is shown in Figure 3.

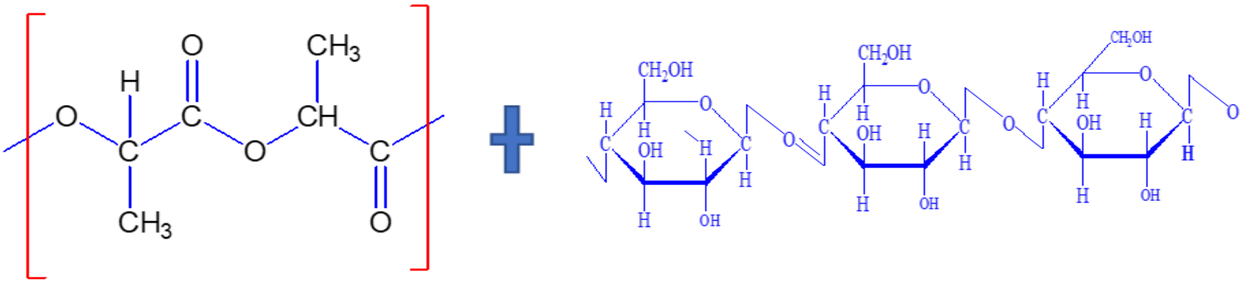

Figure 3. *Chemical structure of poly (lactic acid) and cellulose.*

Another PLA biocomposite was made from poplar wood fibers. The biocomposite was evaluated in terms of cost-effectiveness and environmental friendliness. The developed materials were used for 3D printing and the effects of poplar fibers on the properties of the bio-composite were investigated. Temperature, speed, and layer thickness are examples of operating parameters that have been carefully optimized. Under ideal circumstances, the printing speed, temperature, and layer thickness are 40 mm/s, 220 ℃, and 0 point 2 ℃, respectively. The study discovered that the goal of the biocomposite applications determines which printing parameters to use [35]. Table 1 lists the biocomposite for 3D printing that is based on cellulose and polylactic acid.

Table 1. *3D printing bio-composite based on cellulose and poly-lactic acid.*

Base	Fillers	3D printing Technique	Processing	Application	Ref
PLA	Natural jute fabric	Fused deposition modeling (FDM)	-	Reinforce different 3D object in different research area.	[39]
PLA	Microcrystalline cellulose (MCC)	Deposition modeling technique	solvent casting and twin-screw extrusion	Biomedical, automotive, and construction sectors.	[28]
PLA	Sisal fibers nanocellulose, nanocellulose	Fused filament fabrication (FFF)	Melt extrusion	Textile and Apparel Product Applications and others	[36, 40, 24, 32]

Base	Fillers	3D printing Technique	Processing	Application	Ref
PLA	Kenaf cellulose fibers (KF)	Modeling via fused deposition (FDM)	MELT-extrusion	Biomedical and tissue engineering	[37]
PLA	Cellulose nanocrystals (NC) with poly (3hydroxybutyrate) (PHB)	Fused Deposition Modeling (FDM)	compression molding, extrusion, and 3D printing	high standards of engineering applications	[38]
PLA	Bacterial cellulose (BC) does not require the removal of contaminants like lignin and hemicellulose.	Fused deposition modeling	Pickering emulsion approach	Food packaging, biomedicine, and other areas	[41]

3.1.2. Poly-lactic Acid – Lignin-Based Bio-composite for 3D Printing

One of the most prevalent organic polymers on Earth, behind cellulose, lignin is regarded as a waste product in a number of industrial operations, including the paper industry and biofuel production. The poly lactic acid lignin based bio composite bio for 3D printing is shown in Table 2. Lignin is an excellent candidate for biocomposites, both with and without modification, thanks to its high abundance, low cost, biodegradability, high carbon content, aromatic nature, and reinforcing capabilities [42, 43]. The high temperature of transition and high brittleness (high flow resistance) of pure lignin composites limits their production. [42]. Therefore, lignin is combined with other polymers that enhance its melting and flow properties. Recently, hardwood organogold lignin [44] and softwood kraft lignin [45] were used to produce filaments for FDM based on acrylonitrile-butadiene-styrene and PLA polymers, respectively. Other than burning lignin for energy, blending lignin with PLA to produce composite filaments for 3D printing is a promising bio-based option that could increase the utilization of lignin [43]. The use of lignin as a raw material in the production of biopolymers contributes to its utilization. Furthermore, adding lignin to PLA decreases the amount of PLA required and reduces the overall cost of the filaments. The addition of 15 wt% rice straw (US$0.28/kg) to the ABS filament resulted in a reduction in the overall cost of filament production, including additional processing costs [44]. Pairon et al. developed a reinforced polylactic acid biocomposite using lignin derived from oil palm empty fruit bunches (OPEFB) for 3D printing applications. 0.1% (w/w) lignin in PLA/lignin biocomposite filaments enhanced the mechanical strength and surface morphology achieved by the filament extruder and then used for 3D printing. The PLA/lignin biocomposite sample exhibited increases of 11% in elastic modulus, 7% in ultimate strength, and 10% in elongation at break [46]. S. Hong et al. prepared PLA biocomposites, reinforced with chemically (anhydride group) modified lignin. The modified lignin (original lignin and COOH-lignin) was successfully incorporated into a poly (lactic acid) matrix through a typical melt blending process. It was found that the interfacial adhesion performance between the lignin filler and the PLA matrix for COOH-lignin was better than that of pure lignin. By incorporating COOH-lignin into PLA biocomposites, the cost of producing PLA 3D printing filaments can be lowered without altering their thermal and mechanical properties [47]. The chemical structure of poly (lactic acid) and lignin for producing PLA-lignin biocomposite is shown in Figure 4.

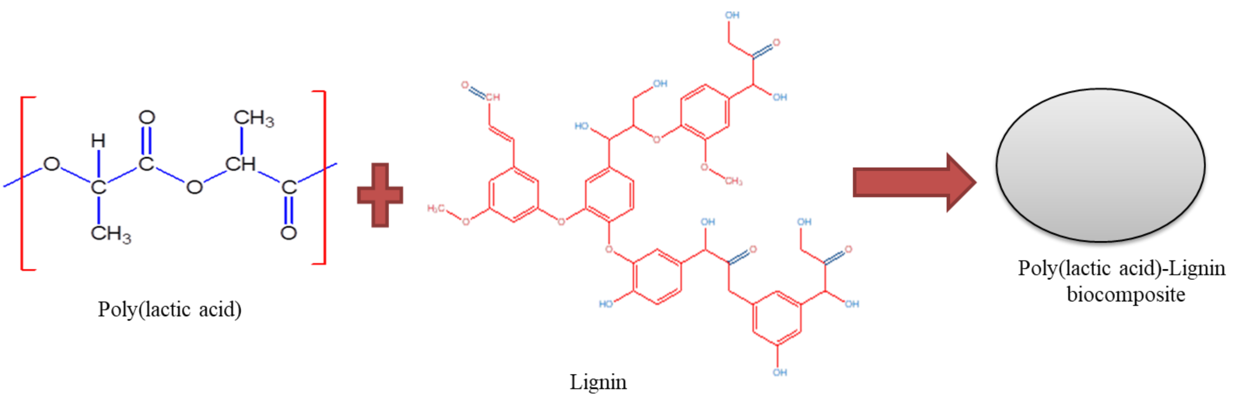

Figure 4. *Chemical structure of poly (lactic acid) and lignin to produce PLA-lignin biocomposite.*

Table 2. *Poly lactic acid - lignin Based bio composite bio for 3D printing.*

Base matrix	Filler	3D printing Technique	Processing	Application	References
PLA	OPEFB Lignin	Not mentioned	Extrusion	-	[46]
PLA	Lignin organosolv, Lignin	FFF	Extrusion	Has the potential for repurposing it for high-value niche applications, neculating agent for PLA crystallization.	[42, 47, 48]
PLA	Kraft Lignin, Organosolv Lignin and Lignosulfonate	Not described	Extrusion	Highly applicable for foaming purpose	[49]

3.1.3. Poly Lactic Acid - Chitosan Based Bio Composite for 3D Printing

Chitosan is a biopolymer of cationic polysaccharides that is second in abundance. It is chemically produced through partial alkaline deacetylation of chitin, which is sourced from the exoskeletons of crustaceans and arthropods, as well as the cell walls of fungi. Table 3 presents the polylactic acid-chitosan-based biocomposite for 3D printing. It has a lot of fascinating qualities, such as the capability to create a gel, increased adsorption, exceptional biodegradability, a very high level of biocompatibility, and non-cytotoxicity [50, 51]. Chitosan promotes better cell adhesion, proliferation, and differentiation because it has a polymeric structure with glucosamine. However, the mechanical behavior of pure chitosan is extremely poor. For this reason, chitosan and PLA matrix must be combined [52]. Furthermore, the chitosan-PLA biocomposite is biocompatible with cells. Chitosan as a reinforcement for PLA to fabricate polymer scaffolds considering morphological features in analyzing the efficiency and performance of 3D printing techniques for tissue engineering [52-57]. Mania. S. and others explored the potential for co-extrusion of the PLA pellet with chitosan powder to create antimicrobial filaments for use in FDM 3D printing, a technology used to create implants or other biomedical tools. Based on his assessment, the PLA filaments' porosity was enhanced and their density was lowered upon the addition of chitosan [58]. Wang and associates. investigated the application of chitosan to a 3D-printed PLA scaffold and the resulting formation of hydroxyapatite (HA). A 3D-printed PLA scaffold's surface has been effectively used to ensnare chitosan. Due to the rapid growth of HA just one day after printing, in vitro mineralization showed that 3D-printed PLA/chitosan scaffolds have a high potential for use in biomimetic environments. The modified 3D printed scaffold was also shown to be biocompatible with human fibroblast cells through in vitro cell culture studies. [53]. Chitosan, along with keratin derived from hair and feathers, serves as reinforcement for PLA to create 3D printable polymer composite scaffolds. Hair and feathers as fibers and chitosan alter polymer behavior before milling to produce a less stiff material, or in particular to cause a reduction in stiffness comnpared to raw PLA [55]. M. Hassan and K. Koyama investigated the effect of adding chitin microparticles to PLA on its thermal stability, physical-mechanical properties and microstructures. Increasing the chitin loading enhanced the stiffness of PLA, with the storage modulus rising from 3.21 GPa for pure PLA to 3.48 GPa for PLA with 3% chitin microparticles. The findings indicate that chitin can be used for reinforcement, improving the moisture barrier properties, stiffness, and tensile strength of PLA [59]. Compatibilizers such as grafted maleic anhydride increase the interfacial adhesion between PLA and chitosan and improve the mechanical properties of the PLA/CS composite strip. The CS powder is mixed with PLA and subsequently grafted with maleic anhydride (MA) to form PLA-g-MA/CS. This process enhances the interfacial adhesion and improves the mechanical properties of the PLA/CS composite strip. The resulting material is anticipated to offer superior functionality and enhanced cytocompatibility in biomedical applications compared to PLA alone or pure PLA [57].

Julia L. et al. reinforced poly (lactic acid) with chitin fibers using an ionic liquid (IL)-based method in which they co-dissolved chitin and poly (lactic acid) in 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]). The chitin to PLA ratio influenced the fibers' tensile strength and flexibility. Strength (112 vs. 71 MPa) and stiffness (5.9 vs. 4.2 GPa) were noted for a chitin to PLA ratio of 1:0.3, and the mechanical strength of the composite was dependent on the chitosan to PLA mixing ratio [60]. The chemical structure of poly (lactic acid) and chitosan to produce PLA-chitosan biocomposite are shown in Figure 5.

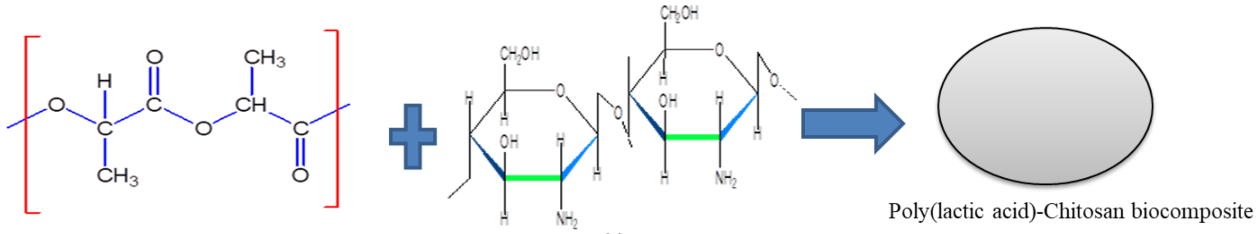

***Figure 5**. Chemical structure of poly (lactic acid) with chitosan to make PLA-chitosan biocomposite.*

***Table 3**. Poly lactic acid - chitosan based bio composite for 3D printing.*

Base	Fillers	3D Printing Technologies	Processing	Application	References
PLA	Chitosan Powder	Fused deposition modeling	Melting extrusion	Used in biomedical sector in manufacturing of bacteriostatic products	[58]
PLA	Chitosan with acetic anhydride	-	Extrusion	To enhance the antibacterial property of 3D filament	[57]
PLA	Keratin and chitosan:		Extrusion	Production of highly reproducible scaffolds for tissue engineering possibly extendible to bone regeneration.	[55]
PLA	Chitin fiber	wet-jet spun	extrusion	Not mentioned	
PLA	chitosan powder particles	Fused deposition modeling	Extrusion	biomedical applications,	[52]

3.1.4. Poly Lactic Acid - Starch Based Bio Composite for 3D Printing

In 3D food printing, starch is frequently utilized as a thickening or gelling agent and as a rheological modifier. Starch is a readily available, renewable raw material that, like cellulose, has a large number of hydroxyl groups in its structure, which provide an active site for functionalization [61, 62]. By blending starch with PLA, it has been shown that the biodegradability property of the composite has been improved, reducing the cost of PLA. However, a significant challenge in physically blending PLA and starch is their lack of miscibility, which limits the enhancement of formulations for 3D printing. To address this, compatibilizers like maleic anhydride (MA) or polyethylene glycol (PEG) are used to improve the interfacial adhesion between the two polymers [63]. Hyrynask. A. et al. synthesized self-made bio-based polylactide (PLA)/thermoplastic potato starch (TPS) filament for the purpose of the FFF 3D printing technology, resulting in a considerable improvement in hydrophilicity, susceptibility to hydrolytic degradation, and thus enhancement of computability in contrast to that of commercial PLA printouts [7].

3.1.5. Poly Lactic Acid - Collagen Based Bio Composite for 3D Printing

Multiple studies have demonstrated the widespread use of PLA in the 3D printing process due to the scaffold's good mechanical integrity and controllable pore size, both of which affect the in vivo stimulation of the formation of new tissue [64]. Although PLA is used in various tissue engineering and biomedical applications, it has several drawbacks, including hydrophobic properties and the absence of a bioactive side chain, which result in low cell affinity and proliferation. Without the addition of other bioactive fillers, PLA also exhibits poor mechanical properties. To enhance the functionality of surface groups and decrease the hydrophobicity of PLA, various strategies have been explored. These include covalent bonding, physisorption, and creating a surface-penetrating network through modification [52, 53]. In addition, there are several bioactive materials that can be used as coating materials, such as polydopamine, chitosan, collagen and gelatin [46, 64, 53, 54]. Collagen is a versatile biomaterial for nervous tissue. It has been previously used to repair small gaps in the nervous systems of various animals and has demonstrated the ability to repair, heal, or regenerate damaged or injured organs and contaminated tissue. It has been used as a filling material for nerve pathways, increasing the superiority of peripheral nerve regeneration in longer gaps [68]. Collagen performs better in tissue regeneration when combined with other biopolymers such as PLA. M. Hamza et al. modify the 3D printed polylactic acid scaffold on the surface by immobilizing the collagen via the surface entrapment method. The in vitro mineralization of the 3D PLA/collagen scaffold demonstrates significant potential for biomimetic applications, with rapid HA formation observed within just 7 days [69]. V. Martin et al. Developing novel multifunctional 3D printed poly (lactic acid) scaffolds by incorporating these bioactive compounds onto PLA surfaces, whereby bioinspired surface coatings are capable of reducing bacterial biofilm formation while simultaneously supporting human bone marrow-derived mesenchymal stem cells (hMSCs). strong microbiological effect against the formation of a biofilm by the pathogenic S. aureus, while it has no cytotoxic effect on hMSC activity [64-67]. The chemical structure of poly (lactic acid) and collagen to produce PLA-collagen biocomposite are shown in Figure 6.

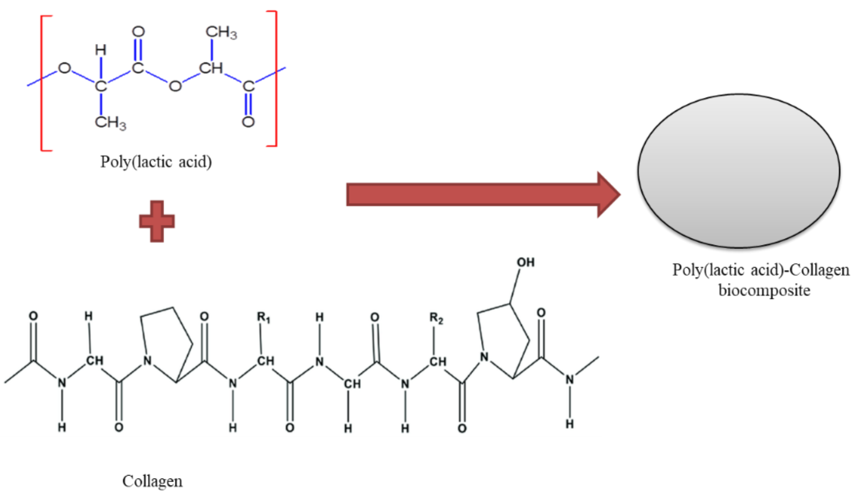

Figure 6. *Chemical structure of poly (lactic acid) and collagen to produce PLA-collagen biocomposite.*

3.1.6. Poly Lactic Acid - Gelatin Based Bio Composite for 3D Printing

Gelatin is a naturally occurring protein that is obtained from the hydrolysis of collagen and exhibits am-photeric activity with respect to alkaline and acidic amino acid functional groups. It encourages cell attachment with biodegradable qualities and minimal immunogenicity [70], is non-cytotoxic, water-soluble, biocompatible, has high water retention, and can breakdown entirely in vivo. [71]. The chemical structure of polylactic acid and gelatin to produce a PLA-gelatin biocomposite is shown in Figure. 7. Considering this, PLA and gelatin composites provide the benefits of both materials. They maintain mechanical properties while also delaying degradation to synchronize with the rate of tissue repair and regeneration. Electrospun nanofibers composed of polymer materials exhibit favorable properties, including porosity, water retention, tissue compatibility, and mechanical strength. These attributes make them highly suitable for use in tissue repair applications, such as skin, dura mater, muscles, bones, and cartilage.. In addition, electrospinning gelatin with some other natural or synthetic polymers is usually more advantageous because it has optimal biological, mechanical and kinetic properties and acts as an important component of some functional scaffolds.

Studies show that the gelatin/PCL/collagen mixture inserted into the gelatin matrix acts as a bridge in the 15 mm gap in sciatic nerve rats. Due to its increased biocompatibility, nanoscale gelatin is often used as a material for the regeneration of nervous tissue. For example, the cell suitability of gelatin-coated nanoparticles on acetate or PLA scaffolds is greater than that of uncoated scaffolds. The gelatin/chitosan/PEDOT hybrid scaffolds increase neurite growth and promote proliferation and cell adhesion [51] H. Chen et al. produced the PLA/gelatin nanofiber membrane for in-situ skin defect repair in a flash using a self-designed, 3D-printed handheld electrospinning device, both in vitro and in vivo. Experiments have shown that PLA/gelatin has superior material properties and biocompatibility, confirming that it is a perfect material for skin repair and may be used in the future to repair skin defects. [71]. R. Rarima and G. Unnikrishnan use thermally influenced, non-solvent-induced phase separation to create porous structured poly (lactic acid)/gelatin foams. In this study, gelatin, which is hydrophilic and biocompatible but not foamable on its own, was used as an additive to create a porous structure in a mechanically stable poly (lactic acid) matrix. They found that the amount of gelatin affects crystallinity, which in turn affects the rate of degradation of the foams, and that the presence of gelatin and the porosity created in situ within the matrix improve the controlled release of a hydrophilic drug (metformin hydrochloride). Thus, PLA/gelatin composites have high levels of biodegradability and cell viability, making them ideal for various biomedical applications. Rachmadiani et al. create a PLA-based scaffold that is coated with hydroxyapatite gelatin, which may be utilized as a scaffold for reconstructing the mandible. It is used to reconstruct tumors that could potentially lead to bone fractures or damage. The researchers discovered that hydroxyapatite can enhance the PLA scaffold's bioactive qualities when added to the PLA 3D printing scaffold. The PLA-HA scaffold's mineralization can be enhanced and its osteoinductive qualities can be enhanced by adding hydroxyapatite to the PLA scaffold surface to promote cell differentiation and proliferation. Furthermore, mixing gelatin into the PLA scaffold can increase the hydrophilic properties, so that the hydrophobic properties of PLA and gelatin can be enhanced, which are used to increase biocompatibility and support cell proliferation [72]. A biocomposite of poly (lactic acid) microstructure and nanocomposite gelatin-forsterite fiber layers was developed using fused deposition modeling (FDM) and electrospinning (ES), which was used for bone tissue engineering applications. Due to the inclusion of forsterite nanopowder in the gelatin matrix, a unique PLA microfibre scaffold made with FDM and ES demonstrated an elastic modulus that was 52% greater than that of the pure scaffold [73].

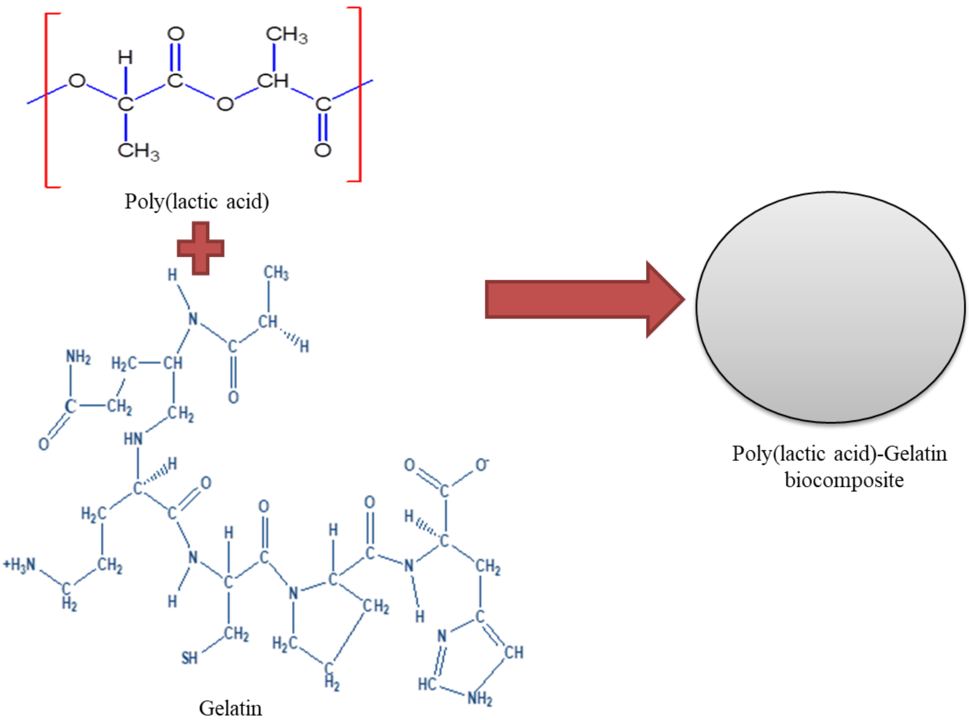

Figure 7. *Chemical structure of poly (lactic acid) and gelatin to produce PLA-gelatin bio composite.*

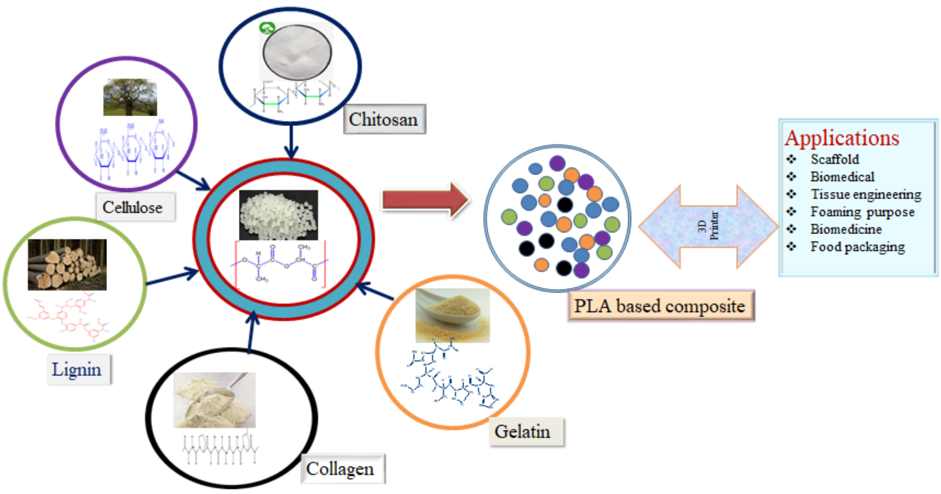

Figure 8. *PLA (Polylactic Acid) with Fillers for 3D printing.*

3.2. Application of 3-D Printed PLA Based Bio Composite

3D printed composites using PLA (Polylactic Acid) are utilized in a variety of fields due to their environmentally friendly and flexible nature

3.2.1. Biomedical Application

3D images of tissues and organs have improved in resolution and informational value with the advent of Computed Tomography (CT) and Magnetic Resonance Imaging (MRI) technologies [74].

Using the obtained imaging data, 3D printing technology might create patient-specific tissues and organs with complex 3D microarchitecture. Poly lactid acid based composite material are currently used for printing in the field of biomedical applications are naturally derived PEG, Nano fillerss, Nano-hydroxyapatite, Mg, gelatin polyvinyl alcohol (PVA, etc. Addition of PEG has shown to be advantageous to produce high-resolution PLA-based scaffolds at low temperature, the result reavls that knowing the effect of PEG in the final scaffolds properties is of great importance not only from the fabrication point of view but also from the structural and physico-chemical one as it is known that scaffolds success is ruled by their surface, structural and degradation properties [75]. Scaffolds made from PLA and PLA nanocomposites with conductive (PLA/CNF) and magnetic (PLA/Fe_2O_3) fillers were created using Fused Filament Fabrication (FFF) 3D printing. The study analyzed how these fillers affected in vitro biodegradation and bioactivity. The results revealed that the PLA/CNF sample exhibited significantly improved bioactivity (~5.32%) compared to neat PLA (~2.9%). Additionally, the PLA/Fe_2O_3 samples showed the highest biodegradation rate, likely due to internal microporosity confirmed by micro-CT, surpassing both neat PLA and PLA/CNF samples in this regard [76]. The study investigated the impact of incorporating Magnesium (Mg) WE43 into PLA as filament feedstock for Fused Deposition Modeling (FDM) 3D printing. The findings indicate that Mg composite filaments are printable and show promise as composite biomaterials for 3D-printed bone implants [77]. Metal-PLA composites, such as copper-filled PLA, bronze-filled PLA, and steel-filled PLA, have been evaluated for their suitability in 3D printing scaffolds. Disk-shaped samples with linear infill patterns and varying line spacings of 0.6, 0.7, and 0.8 mm were tested. The findings revealed that bronze-filled material exhibited the highest porosity for identical line spacings, while steel-filled material had the lowest. Additionally, steel-filled PLA polymers demonstrated good cytocompatibility, eliminating the need for biomolecule coatings [78].

3.2.2. Electronics

Utilizing 3D printing technology can result in electronic prototypes that are geometrically acceptable and need less development time. 3D-printed PLA-based bio composites are increasingly being explored for electronics applications due to their biodegradability and versatility. To improve conductivity, the addition of multi-walled carbon nanotubes (MWNTs) and high-structured carbon black (Ketjenblack) (KB) to polylactic acid (PLA) was investigated. The results demonstrated that when the extruder temperature rises, the conductivity of extruded filaments falls at low filler amounts. However, conductivity is unaffected by extruder temperature at greater filler levels. Furthermore, as the cross-sectional area increases, the resistance of the 3D printed tracks drops rapidly. This demonstrates how these composites can be used to create conductive parts for a range of applications [79].The structure, electrical characteristics, and thermal behavior of 10 polymer compositions based on multi-walled carbon nanotubes (MWCNT), low-cost industrial graphene nanoplates (GNP), and polylactic acid (PLA) were investigated. Both mono-filler systems (PLA/MWCNT and PLA/GNP) with 0–6% filler content were included in these compositions. By merging the two carbon nanofillers with varying geometric forms and aspect ratios, hybrid bi-filler nanocomposites were created with improved filler dispersion. The analysis showed that evenly distributed nanofillers produced a microstructure that could greatly improve heat and electron transmission, as well as maximize the electrical and thermal characteristics [80]. Incorporating carbon black (CB) conductive particles into a PLA matrix has been studied to assess the mechanical, electrical, and thermal behaviors of 3D-printed polymeric composites. This integration of conductive particles within the polymer matrix enables programmable conduction paths through the printing process. The electric properties of these composites are closely linked to thermo-mechanical processes, offering a promising approach for designing materials with tailored electrical conductivity [81].

4. Conclusions

PLA-based biopolymers stand out as promising candidates for future 3D printing applications across various fields. Extensive research indicates that these biopolymers hold significant potential to replace conventional petroleum-derived plastics. Effective printing strategies and innovative material designs are vital for producing a range of industrial, biomedical, and construction materials. Despite early efforts to tailor printing systems for PLA-based structures, challenges remain due to PLA's limited mechanical properties. To achieve the desired functionalities, it is essential to incorporate new bio-based fillers such as cellulose, chitosan, lignin, starch, collagen, and gelatin. Additionally, chemically modifying existing bio-based polymers is crucial for enhancing their biocompatibility and printability, ultimately realizing the full potential of PLA in advanced applications.

Abbreviations

3D	Three Dimensional
PLA	Polylactic Acid (PLA)
FDM	Fused Deposition Modeling
CC	Cellulose Crystals
CNF	Cellulose Nano Filler

Author Contributions

Kasahun Tsegaye Mekonnen: Conceptualization, Data curation, Writing – original draft

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Ethics Approval

Not applicable.

Consent to Participate

All authors read and approved the final review paper.

Declarations

This article explores the advancements and applications of polylactic acid (PLA) biocomposites in 3D printing. The purpose of this article is to examine the properties, processing techniques, and potential uses of PLA-based biocomposites, highlighting their benefits and challenges in various industries. Our main argument is that PLA-based biocomposites hold significant potential to replace conventional petroleum-derived plastics. We will cover aspects such as mechanical properties, biocompatibility, and environmental impact. By incorporating new bio-based fillers and chemically modifying existing polymers, we aim to enhance the functionalities of PLA in advanced applications. The insights provided in this article are essential for researchers, manufacturers, and environmental advocates interested in sustainable materials.

Consent for Publication

All authors agree to publish in Journal of Science PG

Conflicts of Interests

The authors declare no conflicts of interest.

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