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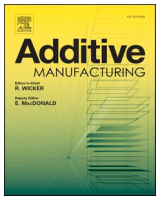

Review

Lignin-based additive materials: A review of current status, challenges, and future perspectives

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ABSTRACT

Additive manufacturing, using three-dimensional (3D) printing technology, is considered revolutionary in manufacturing, pharmaceutical, food, and biomedical industries, as it provides a platform for constructing a wide range of tailored object geometries. This rapidly growing technology mainly uses renewable natural polymers combined with synthetic materials to achieve the printability with desired features of the printed 3D structures. Among different polymers, lignin is receiving immense consideration as a renewable bio-based raw material for manufacturing high-performance 3D printed products owing to its amorphous macromolecular structure and antioxidative, antimicrobial, and other beneficial properties. Lignin is a natural organic polymer found in all plants, particularly wood and tree bark, with few exceptions like bryophytes. It accounts for about 30% of the total biomass worldwide, ranking it as the second most abundant renewable material after cellulose. Despite such advantages, the complex polymeric and amorphous structure of lignin is a great challenge to its utilization in 3D printing for the manufacturing of high-value-added products. This review summarizes the use of lignin in the preparation of ink for the 3D printing of different materials, such as degradable composites, hydrogels, and 3D thermoplastic materials. This review discusses the potential merits and limitations of different types of lignin and their innate features in the preparation of 3D printed materials. The challenges and future perspectives for use of lignin in the preparation of ink for 3D printing are also discussed to underscore the critical issues and opportunities.

1. Introduction

Lignin is a biopolymer that binds cellulose and hemicellulose fibers and provides stiffness to plants. Lignin is the second most abundant polymer after cellulose because 3×10^{11} metric tons of lignin is present worldwide, with yearly biosynthesis of approximately 2×10^{11} metric tons. [1,2]. At the industrial level, lignin is considered as the nucleating agent, copolymer, or filler for enhancing the mechanical and thermal properties of different synthetic and bio-derived thermoplastic polymer matrices. Therefore, creating products from lignin offers an approach towards sustainable development of materials to benefit the future circular economy [3–7].

Additive manufacturing by using 3D printing technology gained momentum earlier in the 1980 s and provided major manufacturing resolutions to meet the requirements of engineered materials. The introduction of lignin to the additive-manufacturing technology resulted in the emergence of a new field of lignin valorization, i.e., lignin-based 3D printing [8,9]. 3D printing refers to the fabrication of solid materials via layer-by-layer deposition of ink in a premeditated fashion. This technology provides a platform for fabricating structures for use in tissue engineering [10,11], biological scaffolds [12,13], and targeted drug delivery [14]. Typically, the success of the 3D printing process for the fabrication of biological scaffolds is dependent on three main factors: the selection of materials for the preparation of ink (demonstrate optimal rheological properties, mechanical strength, and thermal stability, as well as possess functional groups for crosslinking), the type of viable cells, and the selection of an appropriate printer. Furthermore, these materials should be non-toxic, biocompatible, and biodegradable, when the 3D-printed scaffold is used for biological applications. To this end, different natural polymers, such as various bacterial polysaccharides, have been widely evaluated for their potential in the formulation of inks for 3D printing due to their anti-infective and film-forming properties

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[15,16]. This technology is a fast-growing revolutionary manufacturing approach that is becoming more and more widespread due to its ability to achieve free-form manufacturing of complex geometries and structures and to achieve breakthroughs in manufacturing efficient and cost-effective materials for use in industrial fields, such as food [17], surgery [18], prosthetics [19], dentistry [20], forensic [21]. At present, various polyolefin plastics and engineered plastics such as acrylonitrile-butadiene-styrene (ABS), poly (lactic acid) (PLA), poly (vinyl alcohol) (PVA), thermoplastic polyurethane (TPU), and other bioplastics are used in 3D printing [22–25]. The aliphatic and aromatic hydroxyl groups are the major constituents and active sites of technical lignin enabling it to be directly used as polyols in the production of polyurethane thermoplastic and in 3D printing technology.

This review briefly discusses the structural features and applications of lignin and summarizes the recent developments in the preparation of lignin-based ink for 3D printing materials and products. It discusses the complex molecular structure of lignin and highlights the discrepancies caused by the amorphous nature of lignin that overshadows its industrial value. It also presents future development trends of using lignin in the emerging 3D printing technology for transitioning the material industry to sustainability and overcoming the problems associated with petroleum-based composites for the development of sustainable green resources (e.g., composites and hydrogels, environmental remediators, and photoelectrochemical hydrogen evolution materials) for medical, pharmaceutical (including wound dressing and healing), and sustainable production of clean energy. Finally, it provides a perspective on future research on lignin valorization through 3D printing technology.

2. Structure and depolymerization of lignin

2.1. Chemical composition of lignin structure

Lignin is a complex and irregular biopolymer containing randomly crosslinked phenylpropanoid units (i.e., coniferyl, sinapyl, and coumaryl alcohol), and is found in plant secondary cell walls. These monolignol units provide the base for the formation of lignin building blocks, i.e., *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) (Fig. 1) [26].

These building blocks are connected through several types of linkages [27]. Fig. 2 represents the main linkages of lignin structure, such as biphenyl ether, aryl ether, dibenzodioxocin, and phenylcoumaran.

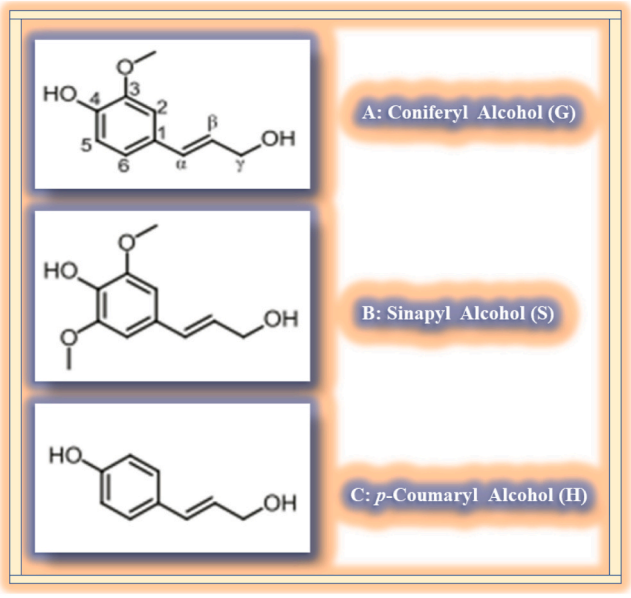

Fig. 1. Structure of three monolignol precursors. (A) Coniferyl-Alcohol, (B) Sinapyl-Alcohol, and (C) *p*-Coumaryl-alcohol.

The presence of these monomers in lignin depends upon the plant species and taxa, as these are present in all types of plants except bryophytes. Crops and grasses mostly contain coumaryl alcohol, while hard and soft wood contains sringyl and coniferyl alcohols [28]. The main lignin units are differentiated from each other in their degree of chemical substitution in the aromatic ring. The hydroxyl and other functional groups in the chemical structure of lignin confer the possibility to react with catalysts to proceed with its partial degradation/biodegradation. Additionally, for intermediation reaction and modification in lignin chemical structure, the double bond in the alkyl propane segment plays a key role [29].

2.2. Lignin depolymerization

In nature, lignin is an aromatic biopolymer, which forms different kinds of linkages with hemicellulose and cellulose, such as benzyl ether (wood's primarily bonds, links together lignin propane unit (α-carbon) and carbohydrates hydroxyl groups), benzyl ester (links β-diaryl lignin unit (α- or γ-carbon) to the side chain of xylan (carboxyl of 4-O-methyl-glucuronic acid), and phenyl glycoside (the linkage between lignin phenolic hydroxyl groups with cellulose, and hemicellulose anomeric hydroxyl groups) bonds [30]. Although lignin increases the thermal and mechanical properties of polymer blends. However, because of its low reactivity, inherent physicochemical properties, unpleasant odor in the resulting blends, lignin's immiscibility with most polymers, and high molecular weight with heterogeneous structure, limiting the range of applications [30–32]. According to the literature, lignin has low reactivity due to the presence of several functional groups (aliphatic hydroxyl, phenolic hydroxyl, and methoxyl) in its chemical structure [31,32]. Demethylation of lignin could effectively increase the reactivity of lignin by forming catechol moieties in the lignin macromolecule. Other methods, including reduction, oxidation, and hydrolysis, have also been studied to improve the reactivity of lignin as well as to produce phenolic compounds from lignin [33]. The miscibility of lignin with other polymers could be improved via hydrogen bonding. Therefore, we can say depolymerization/modification of lignin can enhance the availability of lignin and expose more reactive sites for further value-added materials production. Depolymerization of lignin can be achieved via different processes, mainly chemical, and biological [34–38]. For instance, the biologically synthesized lignin through the introduction of adenosine triphosphate binding cassette (ABC) transporters to engineered plants can translocate to the apoplast. Coumrayl-alcohol expression in yeast can be transported via Arabidopsis ABC transporters (AtABCG29). Laccase and per-oxidase enzymes are capable of polymerizing lignin into monolignol radicals via the radical-radical coupling reaction after entering the cell wall matrix [39–42]. According to our previous articles, partial degradation of lignin was achieved by treating it with laccase from *Bacillus ligniniphilus* L1 [42–44]. The partially degraded lignin was used as the nucleating agent for 3D printing applications. The partial degradation of lignin occurred via carbon-carbon coupling, incorporation of the hydroxyl group into the benzene rings, methylation/demethylation reaction, decarboxylation, cleavage of ether bonds, and breakdown of carbon-carbon aliphatic bonds in lignin side chains, as well as through oxidation of carboxyl group on the carbon-alpha linkage. These milestone research findings represent an opportunity for lignin valorization in 3D printing with biodegradable and degradable polymer blends. Structural characterization and composition analysis of lignin is carried out by different methods, mainly nuclear magnetic resonance, gas chromatography/mass spectroscopy, time-of-flight secondary ion mass spectrometry, Fourier-transformed infrared spectroscopy, and gel chromatography [45–47]. Although much has been explored about the structural characterization and composition of lignin, its depolymerization, and conversion into the desired compounds are yet to be fully elucidated, which is important for the rational design of the modified lignin for improving the lignocellulosic feedstock and developing lignin-based 3D printed

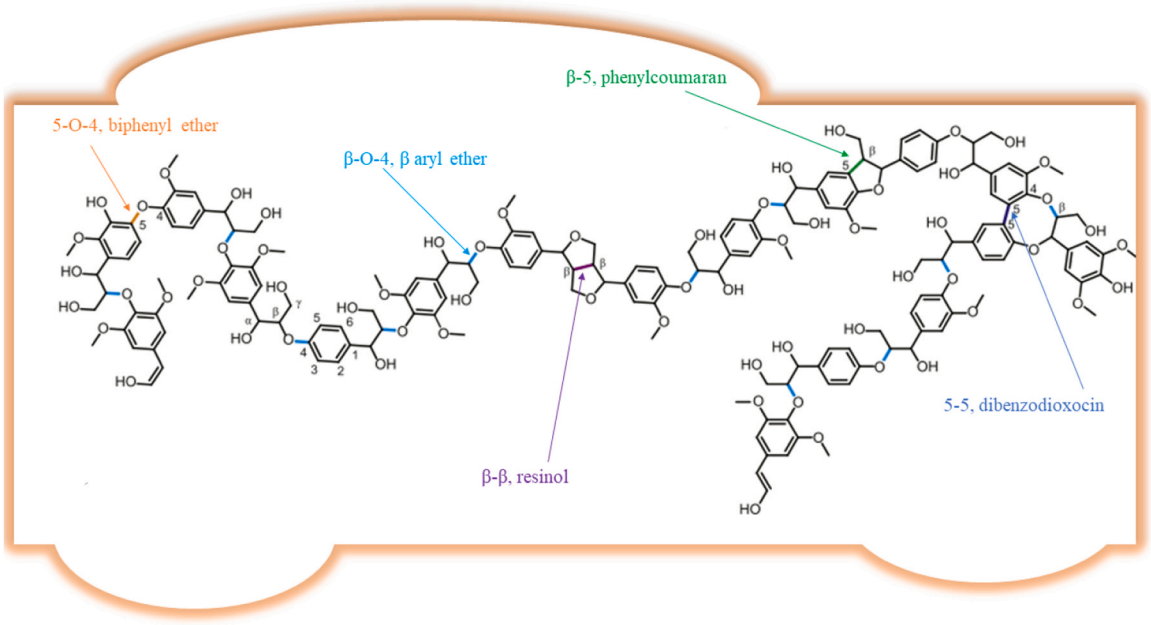

Fig. 2. Illustration of the building blocks of lignin structure connected via several linkages, the main linkages of lignin structure are represented in several colors. The β–O–4 unit (light blue), normally constitutes 40–85% of the total linkages depending on the wood species. The other β–β (Violet), 5–5 (Purple), β–5 (Green), and 5–O–4 (Orange) together account for the remaining 15–60% of interunit linkages.

materials and products.

3. Lignin extraction

The lignocellulosic biomass (cellulose, hemicellulose, and lignin) has been known as an energy resource. Among them, cellulose and hemicellulose are well-known polysaccharides, which can be used in many applications in several fields. However, lignin, which is mostly generated as a by-product in pulp and paper industries, is mainly burned in industrial boilers, underestimating its enormous potential. The main reason for this limited use of lignin, is its high dispersity and the difference in types and number of functional groups, because of different origins and isolation processes of lignin. Therefore, it is very important to establish different isolation and extraction methods [48,49]. Various methods of chemical, mechanical/physical, and biological nature have been adopted for the extraction of lignin [50–56]. Different mechanical

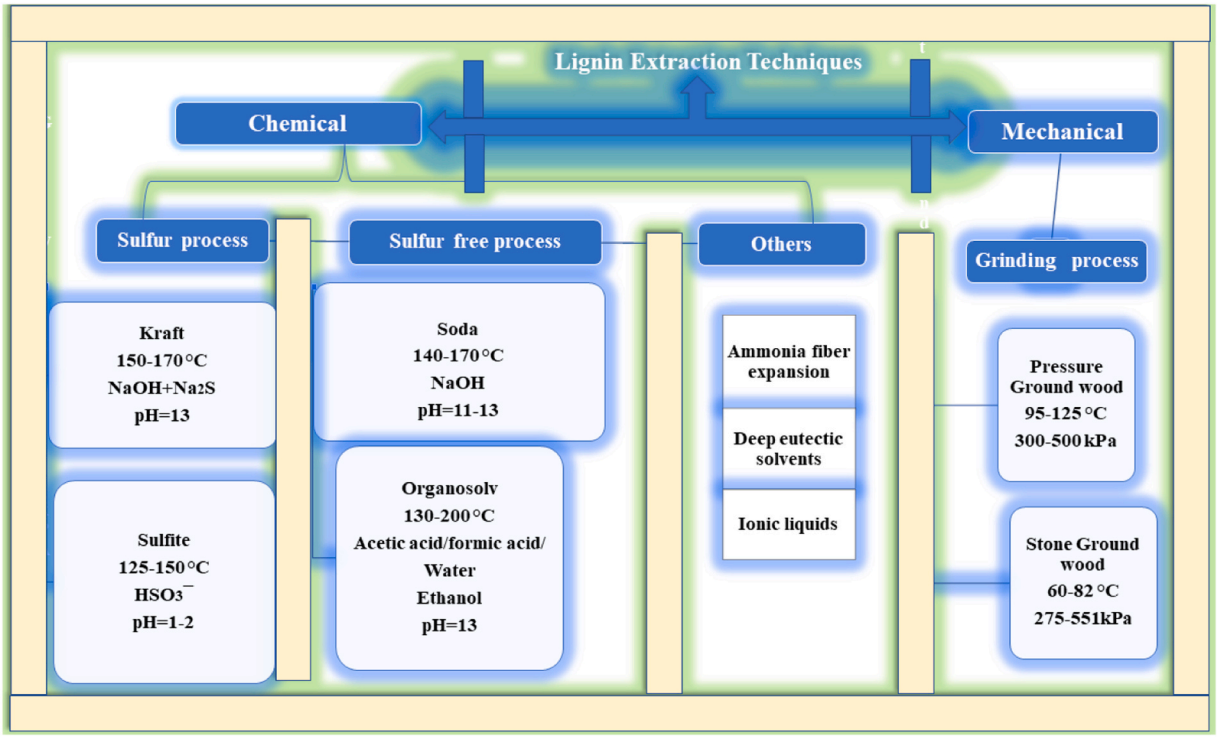

Fig. 3. Description of lignin extraction through several chemicals (Kraft, sulfite, soda pulping, organosolv process, ammonia fiber expansion, deep eutectic solvents, and ionic liquids) and mechanical (refiner mechanical, thermomechanical pulping, stone, and pressure groundwood) techniques[50–55].

and chemical techniques of lignin extraction are illustrated in Fig. 3, and their detailed description and their effects on the properties of lignin are presented in the following sections.

3.1. Lignin extraction via chemicals

3.1.1. Kraft pulping process

Kraft pulping is also recognized as a sulfate process, which is widely used in paper industries for lignin extraction because of its high performance in the extraction of lignin. The content of lignin is generally measured in kappa number, which is a measurement of the bleach solution required to bleach wood pulp to white. The primary goal of bleaching is to remove the residual lignin without degrading the pulp. The kappa number can be used to monitor the effectiveness of lignin extraction in the pulping process and it is determined by ISO 302:2004 standard. Usually, the kappa numbers range between 25 and 30 for softwoods and between 15 and 20 for hardwoods. Lignin obtained through this process contains 1–2% sulfur and has a reduced content of β-ether bonds. Compared to the lignin obtained through other processes, the sulfate/Kraft lignin is difficult to depolymerize [57].

3.1.2. Sulfite pulping process

Lignosulfonate is a by-product of sulfite pulping. Because of the presence of sulfonic acid, this type of lignin has a hydrophilic nature. Lignin is extracted via this method by a reaction that takes place between the metallic sulfite and sulfur dioxide. This type of lignin is mostly used in plasticizers, binders, glue, and industrial detergents [58]. However, its implementation in value-added products, such as vanillin, is needed to be further explored.

3.1.3. Soda pulping process

By Soda pulping process, lignin is extracted from bagasse of rice, wheat, sugarcane, and other crop-producing plants. The lignin obtained through this process is considered a by-product of the soda anthraquinone process/alkaline pulping. It is a method of lignin extraction by using chemicals, consisting of alkaline hydrolysis carried out at high temperatures (140–170 °C) for breaking the α and β aryl-ether bonds in lignin phenylpropane units, and is recognized as the first chemical extraction method. This type of lignin has the potential to produce phenolic resins, dispersants, and animal feeds [59].

3.1.4. Organosolv process

This method of lignin extraction uses organic solvents to separate lignin from the lignocellulosic biomass. Lignin extraction by this method can be achieved at a temperature of 140–170 °C. This type of lignin is highly pure because of the presence of β-O-4 linkage and contains a very low content of ash and without sulfur contaminants. Lignin extracted by this method is more suitable for use in varnish, adhesives, paints, and pharmacological products [60,61].

3.1.5. Other chemical-based delignification processes

Ammonia fiber expansion, deep eutectic solvents, and ionic liquids are some other chemical-based techniques used for lignin extraction.

Chemical methods used for lignin extraction involves the use of ammonia fiber expansion, where a physiochemical alkaline pretreatment process uses liquid ammonia at a temperature from 60 °C to 180 °C. This process generally requires a small amount of water, and about 95% ammonia can be recovered [62].

Deep eutectic solvents, a combination of several solvents containing Lewis and Bronsted acids with the configuration of anions/cations, reduce the melting point (50 °C approximately) [63,64]. This process has the potential to combine hydrogen bond acceptor and donner [65]. The use of ionic liquids, the green solvents used for improving the dissolution potential of carbohydrates and decreasing the rigidness of lignin [66], is another approach of lignin extraction. Table 1 presents different methods used for lignin isolation/extraction and the associated properties of the extracted lignin.

Table 1
Methods used for lignin isolation/extraction and the associated advantages, limitations, and properties of isolated lignin.

Isolation method and conditions	Sources	Advantages	Limitations	Average molecular weight and Properties of isolated lignin	Ref.
Kraft pulping (140–180 °C)	Kraft pulp and paper residues	Improve the quality of fertilizers, pesticides, activated carbon, energy storage materials, asphalt emulsifiers, and the production of vanillin, quinines, binders, and resins.	Sulfuric acid treatment increases the sulfur content of lignin, and hence, usage of such lignin should be avoided in sulfur-sensitive applications	1000–3000 M_n (g mol^{-1}), with high sulfur content, 80% of β-ether bonds are destroyed, difficult to depolymerize, insoluble in water and organic solvents, and condensation reaction to form C-C bonds	48, 57
Sulfite pulping (120–180 °C)	Residues from the sulfite process and papermaking	Lignosulphonates are mainly used in products such as binders, plasticizers, glue, and industrial detergents.	Its implementation is currently being sought in value-added products such as vanillin and the preparation of activated carbon for wastewater treatment	15,000–50,000 M_n (g mol^{-1}), water-soluble, high sulfur content 3–8%, containing sulfonic acid group, and reaction to form C-C bond	58
Organosolv process (130–200 °C)	Paper residues or alkaline preparation	Due to its low molecular weight and high chemical purity, low ash content, and no sulfur contaminant can widely use in the pharmaceutical industry, varnish, paints, and adhesives.	Due to low molecular weight, its utilization is limited in adhesives and binders. Poor solubility in water. Due to the reactive side chains, further reactions take place.	800–3000 M_n (g mol^{-1}), low ash content, No sulfur content easily soluble in alkaline solution	60
Soda ash pulping (160 °C)	Solvent extraction	Used in the production of phenolic resins, dispersants, animal feeds, low molecular weight substances, synthesis of polymers,	Recovery of non-wood soda lignin by filtration and centrifugation causes problems due to the high content of carboxylic groups, which make lignin highly hydrophilic.	500–5000 M_n (g mol^{-1}), soluble in alkaline solvents	59
Grinding process (105–125 °C)	Solvent and ball-mill extraction	Groundwood lignin can better maintain the natural structure of lignin	These methods are less efficient and offer a low yield.	Chemical structure representation of native lignin with about 25% reduction in β-O-4 bonds	71–73
Ammonia fiber expansion (60–180 °C), Deep eutectic solvents and ionic liquids	Cellulase hydrolysis extraction after removal of cellulose	Low energy consumption and costs, bioethanol production, and sugars valorization. 95% ammonia can be recovered. Low volatility, high thermal stability, and biodegradability.	High toxicity, pH, and cost parameters limit ionic liquids. It cannot be fully considered as technical lignin but can be considered as a promising option.	Narrow molecular weight distribution, high purity, maintain its originality to a certain context	62–66

3.2. Lignin extraction via physical/mechanical methods

3.2.1. Grinding process

Grinding/milling is a physical/mechanical method for lignin extraction from lignocellulosic biomass. However, it is not feasible from the economic point of view, due to high energy consumption, high cost of machinery steps, and the inability to completely remove lignin from lignocellulosic biomass. Therefore, an effective pretreatment, (such as dioxane solvents) is needed to remove the barrier effect of lignin and facilitate lignin utilization. The lignin preparations, milled wood lignin, obtained by this method have been considered as basic standard material to perform most chemical and biological studies. The extracted lignin with dioxane as the main solvent was found highly pure with low ash and negligible carbohydrate content. The solubility of extracted lignin by various organic solvents including dioxane makes lignin advantageous over other processes. In this method, stone and pressure groundwood techniques (ball, rod, roll, hammer, colloid, wet disk, and vibratory milling) are used for lignin extraction [67–73]. Groundwood lignin can better maintain the natural structure of lignin; however, these methods are less efficient and offer a low yield.

3.3. Biological extraction of lignin

Biological extraction of lignin residual from kraft pulp mainly includes enzymatic hydrolysis [74]. In this process, commercially, available cellulolytic enzyme was used for the dissolution and hydrolysis of carbohydrates (cellulose and hemicellulose) in the pulp. Due to enzymatic hydrolysis, lignin is left as an insoluble residue. Enzymes, cellulase, and β-glucosidase were used to extract residual lignin from kraft pulps [75,76]. These enzymes were found good enough to hydrolyze all pulp polysaccharides in a single step of enzyme treatment. Unfortunately, some drawbacks such as carbohydrates were found in the isolated lignin residual during enzymatic hydrolysis. Additionally, residual lignin samples obtained by this method contain protein impurities originating from the enzymes used in the hydrolysis stage. Thus, the samples need to be purified to remove most of these protein impurities [77]. Besides, enzymatic hydrolysis much more time spending procedures than chemical extractions. However, the residual lignin obtained from this isolation technique is considered to be chemically unchanged and the yield is quite good.

The pristine structure of lignin is mostly altered during its extraction because of its complex architecture. Currently, researchers are focusing on developing eco-friendly methods for the isolation of lignin with a more preserved pristine structure. The structure and properties of lignin obtained by different extraction methods vary and thus can be used for different applications. For instance, lignin can be used as a component in bio-composites and a coupling agent with natural fiber bio-composites for different applications, including thermal and mechanical behavior. A study reported that kraft lignin and acetylated lignin were used as fillers for the elaboration of composites with PLA. The addition of both types of lignin content increased the thermal stability of PLA [78]. Thus, based on the advantageous usage of lignin for different purposes, their applications for getting 3D printed materials are also different. For example, organosolv lignin and PLA hybrid thermoplastics can show good results by Fused deposition modeling (FDM) printing without adding additives. However, using sulfite lignin in 3D printing technology under the same conditions does not provide good quality 3D printed structures because of PLA degradation, as sulfite lignin has alkaline residuals. Therefore, as a 3D printable material, lignin could be blended with other materials/polymers according to the characteristics of different lignin and modified further if required to achieve the desired effect of 3D printing.

4. Advantages and current challenges of using lignin in 3D printing

Recently, 3D printing or additive manufacturing has been receiving great attention. This latest technology supports the production of unique, complex, and customized structured products through digitized and computer-assisted processes, and at the same time minimizes the time and manufacturing cost of the products [79]. Additionally, this technology minimizes the loss of raw materials during production as well as decreases the consumption of required materials as compared to traditional manufacturing processes [80]. Several techniques, such as FDM, Fused Filament Fabrication (FFF), direct ink writing (DIW), stereolithography (SLA), powder bed fusion, binder jetting, vat photopolymerization, sheet limitation, and selective laser sintering (SLS) have been applied in the 3D printing process [81,82]. Over the last decade, 3D printing has been employed to handle a broad range of materials, including polymers, ceramics, metals, and semiconductors, for electronics, robotics, energy, organs, satellites, etc [83–86]. Due to the non-toxicity, abundance, and renewable biopolymer, the use of 3D printing techniques to print lignin into composite materials with desired mechanical and functional properties would make it an extremely promising alternative to fossil-based polymers such as acrylonitrile butadiene styrene (ABS), polyamide, polycarbonate, and epoxy resins. The macro and micro-structures, and the resulting properties of 3D-printed lignin composites can be tuned to meet the requirements of optics, energy, drug delivery, and personalized medicine. Although, polymers including lignin are supposed to be suitable for almost all types of 3D printing techniques. However, progress in recent years demonstrated that lignin is only successful for techniques of material extrusion (FFF and DIW), SLA, and SLS because of its complex and unique structure [87].

FFF, a popular 3D printing technique, also known as melt-extrusion 3D printing. It can be used for polymer and polymer-based composites [88–90]. It is a low-cost and simple method with a wide range of printing rates [83]. Melting lignin to a low but sufficient viscous fluid is a critical process for FFF, where the thermo-stability of lignin plays an important role in the continuous printing of filaments. At low temperatures, the hard-molecular weight of lignin is hard to melt, while at high temperatures, the low molar mass lignin degrades to form a rigid char, both cases leading to increased resistance to flow and deformation. Besides, the oligomeric lignins with abundant aliphatic ether, oxygenated aromatic bonds, and β-O-4 linkages offer good flow characteristics and printability. However, only good flow characteristics are not enough to make oligomeric lignins a better choice for 3D printing. Because the filaments of only these phenolic oligomers a very brittle and cannot form a self-supporting structure alone. Therefore, the oligomeric lignins don't necessarily assure good printability in FFF, and the direct use of pristine lignin in 3D printing is limited [91]. Mostly, lignin is blended with polymer or copolymerized with a soft segment to enhance its toughness. The polymer matrix or soft segment for FFF mainly includes PLA [92], ABS [93], graphene [94], nylon12 [95], polyhydroxy butyrate [96], methacrylate [97], polyethylene oxide [98]. These polymers or soft segments can be used alone or as a mixture to improve rheology and toughness. For example, with good FFF compatibility, mechanical performance, and melt properties, ABS is a commonly used polymer for blending with lignin to improve printability. Compared with neat ABS, the viscosity of lignin/ABS generally decreases with lignin loading at low shear rates regions (1–500 s^{-1}) and tends to be similar at high shear rate regions (500–1000 s^{-1}), exhibiting a law shear thinning behavior [93].

DIW shows distinct advantages of excellent material compatibility, high spatial resolution, and low cost, which constructs arbitrary 3D structures through a layer-by-layer ink filaments deposition subsequence. DIW is well-suited for the printing of polymers because of its feasible processing of polymer ink at room temperature by using shearing force to rapidly fabricate several 3D patterns. There is no need

to heat the lignin or lignin/polymer blends above a melting or softening point for DIW. However, the main challenge for DIW is to design a viscoelastic ink that can easily flow via the nozzle and is capable of forming a free-standing structure. Therefore, good shear-thinning behavior and low zero shear rates of colloidal gels or organic ink are needed for the DIW technique [99]. Unlike the main constituents of cellulose of lignocellulose, lignin shows unfavorable rheological properties by directly mixing with water or organic solvents which disturb the smooth printing process of lignin and clog the nozzle [91]. With unfavorable rheological behavior lignin during the DIW process relies on other polymers for the formation of pastes and colloidal gels, such as cellulose nanofibers and their derivatives, carbon-based polymers, and viscoelastic polymers [100–102]. For example, a study reported the formation of organosolv lignin/hydroxypropyl cellulose inks. In these developed bio-based inks, lignin provides solid-like properties and stability for hydroxypropyl cellulose and confers the needed shear-thinning to the blends, resulting in a desirable viscoelastic behavior for DIW [103].

A few reports focused on SLA and SLS techniques for lignin 3D-printing. This technique is commonly used in enriching resin photo-properties, rheology, and chemistry to provide crosslinked thermoset objects [82,104–106]. A study reported that lignin is a suitable component for SLS of polyamide (PA12) to reduce cost and maintain/improve performance and processability [107]. According to Rubina Ajdary, SLS is shown as a developmental step towards lignin valorization in composites while allowing reduced cost, scalability, and facial processing [82]. The morphological, wetting, mechanical, and thermal characteristics of lignin/polyamide composite with 3D printed structures showed less degradation (30%), higher porosity (~10%) with a simultaneous increase in stiffness (~16%), and reduced tensile strength (~7%) as compared to pure polyamide during SLS technique. The partial replacement of polyamide with lignin demonstrates the contribution of the polyaromatic molecule, possible incorporation of new properties, and maintenance of thermomechanical properties [82]. Recently a 3D printing process based on thermoset biocomposites "Delayed Extrusion of Cold Mastedbatch" was developed for the printing of biobased resin (bioepoxy), sawdust, and lignin. This method was developed for the betterment of printing biobased resin ink because of the viscous nature of lignin and sawdust, not printable using direct printing approaches. The incorporation of lignin enhances the viscosity of biobased resin ink and provides a shear-thinning behavior without affecting curing kinetics. Furthermore, this approach is cost-effective, with shear-thinning dopes with high biobased contents (58–71%), and their demandable solidification during additive manufacturing [107].

The first research on constructing lignin-based 3D printed materials was reported in the 2010 s [98]. Since then, 3D printing of lignin has greatly broadened the application area of lignin-based materials. Besides, some insurmountable challenges, such as the unclear structural-rheological relationship, and the depolymerization and repolymerization of lignin structure during the extraction process. Furthermore, the interactions, such as the formation of inter and intramolecular non-covalent bonds (hydrogen bonding, CH-π bonding, π-π stacking), hinder the compatibility and solubility of lignin with various solvents and polymers, strong and unpleasant odor (especially sulfate lignin and sulfite lignin) and dark brown color need to be tackled for the board adoption of lignin 3D printed composites [87]. Therefore, the use of lignin in developing 3D printing materials requires targeted structural modification and functionalization to promote the fusion of lignin and materials. This structural modification and functionalization can be achieved via methylation, phenolation, demethylation, ring-opening, condensation polymerization, and solvolysis [108–115]. A linear polymer of caffeyl-alcohol, present in the exotic plant species seed coats, known as C-lignin, has the potential to produce high-value chemicals and carbon fibers because of benzo dioxane linkages [116,117]. In this novel benzo dioxane linkage, the radicals first recombine to a quinone methide intermediate prior to a re-aromatization. The benzo dioxane linkage proceeds as an entirely intermolecular process, providing a sufficient amount of the 5-OH group to act as the nucleophile [118]. Exogenous, a typical C-lignin, has been successfully obtained from Arabidopsis or Alfalfa hairy root cultures through metabolic engineering, which provides a new approach for future industrial-scale production of C-lignin that can be potentially used for developing 3D printed materials [60].

5. Applications of lignin-based 3D printed materials

5.1. Lignin-based bioactive materials application

Bioactive materials are extremely beneficial for healthcare applications such as wound dressing and tissue engineering. Lignin has antioxidant, antibacterial, anti-UV, antitumor, and antivirus properties, making it a promising bioactive material [119,120]. Recently, lignin composites have been used in drug and gene deliveries for disease therapy. With adaptability for biomedical applications, the 3D printing of lignin allows the construction of customizable and personalized objects that can be used as biomaterials [121]. Crosslinking of lignin with hydrophilic polyether-based polyurethane composite was printed by DIW and demonstrated to be biocompatible with human dermal fibroblasts. This composite is also capable of supporting cell growth and has no obvious effect on cell viability and shows great potential in biomedicine [122]. The lignin composites fabricated by FFF can also be used for wound dressings, as the lignin/PLA meshes containing drugs were printed by FFF, and the drug can easily diffuse through the mesh pores to the wound. Interestingly, the presence of lignin provided a slower curcumin release than the control one, and the incorporation with PVA further delayed curcumin release. With antioxidant properties, lignin contributes to reducing the concentration of the reactive oxygen species that are strongly linked to the pathogenesis of chronic wounds, which makes lignin/PLA a green and low-cost 3D printable biomaterial [123].

Fig. 4 demonstrates the development of lignin/PLA composite and the development of different 3D printed products, such as scaffolds for wound healing and plasters for fracture healing.

The antibacterial and antioxidant properties of lignin not only make it appropriate for polymerization with PLA to produce scaffolds but also to prepare materials for other potential medical materials such as coatings, nanoparticles, and hydrogels. Lignin-based nano-micelle, developed via a self-grafting method, are pH-sensitive and well-suited for oral administration [124].

5.2. Lignin-based hydrogels

Physical and chemical crosslinking of natural and synthetic polymers with hydrophilic properties are known as hydrogels. Hydrogels have a 3D architecture [125,126]. These are made up of renewable and bio-degradable polymers which have attracted great interest in biomedical and other fields [127], because of their versatile applications in pharmaceutical, biomedical, food, agricultural, personal care products, drug delivery systems, wound healing, tissue engineering, and wastewater treatment [128].

Hydrogels with biodegradability, biocompatibility, and stimuli-responsive characteristics are prepared from natural hydrophilic polymers [129]. Chemical diversity and versatility make lignin a viable alternative to renewable raw materials for the synthesis of new and sustainable biomaterials, including hydrogels. Lignin used in hydrogel preparation is mainly because of its biodegradability, low toxicity, environmental friendliness, cost-effectiveness, and suitability for enzymatic degradation [130]. Lignin-based hydrogels are considered biomaterials because of the promising characteristics, including antimicrobial activity, of this biomacromolecule [131–133]. The synthesis of lignin-based hydrogels usually employs polymerization methods, including interpenetration [134], semi-interpenetration

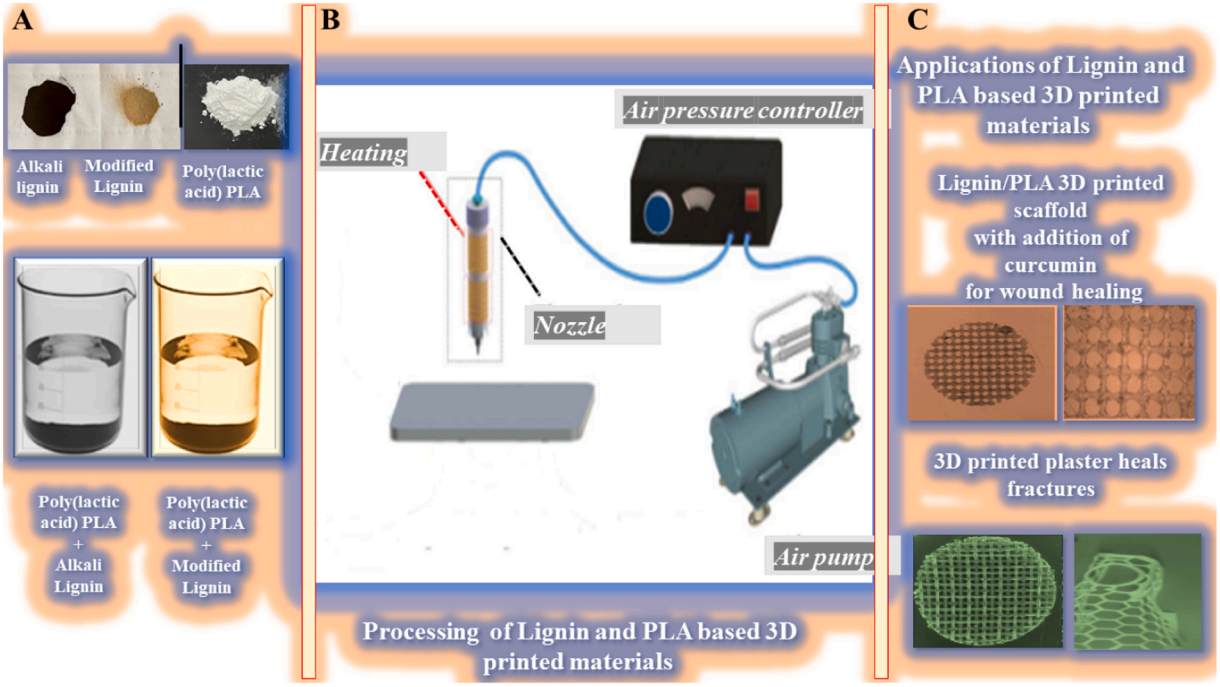

Fig. 4. Description of lignin, laccase modified lignin, and lignin/PLA composite and their use in 3D printing technology for fabrication of different products. (A) Alkali lignin and laccase-modified lignin combined with PLA and a mixture of alkali lignin with PLA, and laccase-modified lignin mixed with PLA used in 3D printing technology, (B) A typical 3D printer, (C) a scaffold of lignin/PLA with the addition of curcumin for wound healing and a scaffold of PLAplaster for fracture healing.

[135], polymerization [136], atom transfer radical polymerization [137], reversible addition-fragmentation chain transfer polymerization [138,139], crosslinking copolymerization [140], and open-loop polymerization [141].

There are several hydrogels utilized in the past, but the major drawbacks of these traditional hydrogels are their low tensile strength, mechanical instability, low durability, large pore size, and synthetic nature. Therefore, to meet biomedical needs, it is essential to advance the hydrogel properties and structure to revolutionize the way biomaterials are applied effectively. The lignin-based hydrogels meet the requirements of biomedical materials, because of their biocompatibility and biodegradability. Furthermore, lignin-based hydrogels, compared with other biopolymeric hydrogels, have super properties, including higher water-retention capacity, tensile strength, and compressive resistance [142–144]. Water uptake and retention capacity were inherent traits of lignin-based hydrogels. The presence of lignin not only increased the magnitude of active binding sites (free hydroxyl groups) but also led to a more porous structure, to encapsulate more drugs and more hydrophobic functional groups in the hydrogels [145]. A study reported that lignin-containing hydrogels showed better tensile strength than those without lignin. This is because lignin molecules could associate with each other to form “nanoparticle analogues”, enabling lignin to participate in and form rigid phases in the hydrogel network [146]. Lignin-based hydrogels are widely used in burn-wound therapeutics [147], targeted drug delivery systems [148], removal of heavy metals and dye super absorbents [149], and in food packaging [150]. A study reported the development of Ag-lignin NPs-PAA pectin hydrogels with outstanding mechanical, antibacterial, and burn-wound therapeutic properties, which can meaningfully accelerate the healing property of burn wounds. The lignin-grafted polyoxyethylene azoline hydrogel prepared via ring-opening polymerization exhibited remarkable anti-inflammatory, burn-wound therapeutic, antibacterial, and anti-biofilm activities after coupling with amphotericin B, indicating its suitability for use as the controlled drug release system [151]. Lignin/polyethylene glycol/polymethyl vinyl ether-maleic acid hydrogels and epichlorohydrin crosslinked lignin/xanthan hydrogels all have good drug-carrying potential [152].

The rapidly growing additive manufacturing/3D printing technology is an emerging approach for hydrogel formation that combine renewable and natural fibers with synthetic materials to modify the properties of polymers. Additionally, renewable materials can possess inherent properties, particularly at the molecular or nano-level, where their use can introduce 4D/3D attributes to products [153]. Due to the inherent properties of phenolic lignin, it can be used in smart design/3D printing [95,154]. Furthermore, the hydrophobic potentials’ lignin can be incorporated into 3D printed hydrogels to tune the hydrophilicity of the resulting matrix because a balance between the hydrophobicity and hydrophilicity of resulted/printed matrix/scaffold is important for cell adhesion [95,155,156]. A previous study reported the involvement of lignin-containing arabinoxylan and cellulose nanofibers in the preparation of 3D-printed hydrogel and aerogels [157]. PVA and PLA combined with lignin have been used for developing 3D-printed scaffolds. Herein, the first layer contained PLA/lignin while the second layer contained lignin/PVA following a solution by casting a drug using fused filament fabrication 3D printing methodology [158]. DIW technique is a 3D printing technology that is well suited for lignin systems (lignin-based hydrogel) because this technique allows the processing of materials at room temperature, well below the degradation of lignin temperature 200 °C [159]. In addition, due to the tunable rheological behavior of lignin-based hydrogel, it not only allows the alignment of composite materials but also enables vertical 3D printing. Fig. 5 presents the schematic illustration for the formation of a lignin-based 3D-printed hydrogel.

In nature, lignocellulosic biomass contains all three widely abundant biopolymers, i.e., cellulose, hemicellulose, and lignin, in the form of agricultural waste and agro-industrial by-products in addition to hard and softwood. The research of these biopolymers in the material application is quite limited, which gets even more restricted when their utilization is considered for 3D printing [160]. The above-mentioned studies show that lignin-based 2D and 3D hydrogels have broad application potential in the medical field. However, the commercialization of lignin-based hydrogels still faces many challenges, such as achieving

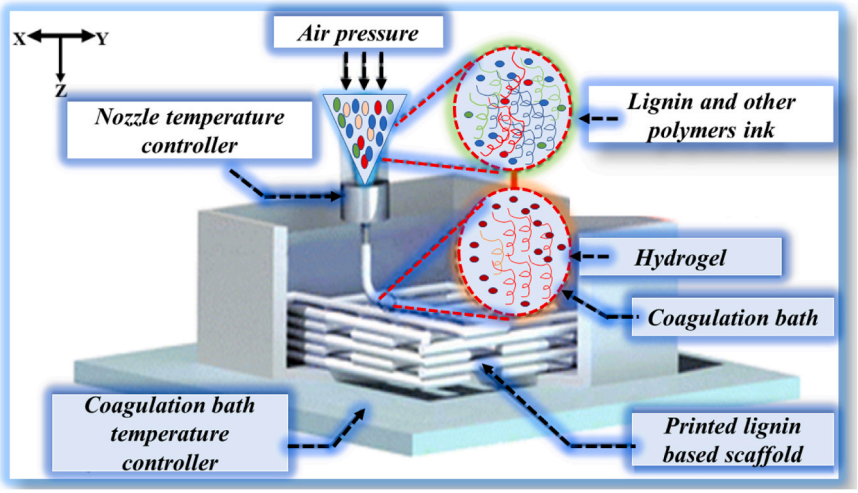

Fig. 5. The 3D printing technology for the development of lignin-based hydrogels, the operating system, control, injection, and printing nozzle system, nozzle printing scaffold, and image of a scaffold.

lignin of uniform molecular weight and minimizing the variation in lignin structure and molecular weight in batch-to-batch operation.

5.3. Lignin-based 3D printed engineered, environmental remediators, and photoelectrochemical hydrogen evolution materials for sustainable production of clean energy

Lignin, as the main/structural component of wood, can strengthen and rigid the cell wall and has the potential to protect carbohydrates from phytopathogens and other environmental stresses and regulate water transport and solutes [161,162]. Therefore, wood also acts as a lignin-based material that can be used to make different engineered products by 3D printing techniques, such as interlocking products, crates, napkin rings, and fully-functional treasure chests with the addition of additives [163]. In addition, the wood flour can also be blended with other polymers to improve the performance of the printed objects, and lignin in the materials will play a role similar to that in natural wood [164–166]. For example, the wood-PLA/polyhydroxyalkanoates filament shows comparable stiffness with polyethylene terephthalate, and nylon [167].

Lignin contains a high content of carbon (>60%) and is considered the prime precursor for the preparation of carbon-based materials. Recently, lignin has been widely used to produce activated carbon [168,169]. Generally, active carbon materials are widely used for the adsorption of dyes, organics, toxic gases, and metals. With the incorporation of 3D printing techniques lignin-based active carbon materials possess a higher adsorption efficiency than commercial carbon materials [170]. First, during the carbonization and activation process, the dense structure of printed lignin filaments becomes porous, and the micropores in the printed filaments are important for improving the mass transfer efficiency. Second, the space between the adjacent filaments is also tunable, which results in a hierarchical porous structure in the product. Third, the active carbon with 3D scaffolds also enables multiple recycling, which is desirable for the practical treatment of industrial pollutants.

DIW as a 3D printing technique for the alignment of 2D planar nanomaterials, such as the semiconductors of graphitic carbon nitride and MX-enes, offering significantly improved performance to these materials. However, the application of such printed materials is limited in liquid reactions due to the weak interaction between the 2D planar structures. A study reported shows that vertically 3D printed forest-like lignin/graphitic carbon nitride/carbon nanotube arrays with enhanced photoelectrochemical hydrogen evolution performance [171,172]. The multiple scattering of the arrays elongates the incident light path, meanwhile, the carbon nanotubes further promote photoelectron-hole pair effective separation, thus improving the utilization of light and the transfer efficiency of photoelectrons. The inherent hydrophobicity and good adhesiveness of lignin endow the printed arrays have high durability and enable it to continuously produce hydrogen. More importantly, lignin is an aromatic biopolymer and adonor–acceptor conjugated structure is considered to be formed due to the intermolecular π–π interaction between lignin and graphitic carbon nitride (gC_3N_3), resulting in an enhanced photoelectrochemical hydrogen evolution performance. The authors also demonstrated that lignin as a natural binder is much superior to other binders of PVA and poly (ethylene glycol), which may be because their non-conductive and long-chain molecular structures impede the generation and separation of photoelectrons. With the world's over-consumption of fossil fuels, such materials using green and renewable biomass as composition will open a new avenue for sustainable production of clean energy [173].

5.4. 3D printed applications of lignin materials as bio-feedstocks

To date, only a few studies have been reported on lignin and its derivatives for usage in 3D printed bio-feedstocks such as lignin and poly ethylene oxide filament preparation with uniform diameter, adequate surface, mechanical strength, and thermal stability. This filament can be used in the manufacturing of 3D carbon-based nano-structure electrodes via an FDM technology and also exhibits high electrochemical performance [174]. Another study reported the development of lignin-based 3D printed bio-feedstock made from hardwood lignin by modifying nylon 12 composites. This kind of lignin has a rich amount of sinapyl and melt-stable properties. Formulated 3D printed bio-feedstock from lignin exhibited enhanced stiffness and tensile strength at room temperature and a reduced viscous behavior at melting temperature [95,175,176].

Recently, many researchers have been focusing on lignin introduced to 3D printed bio-feedstocks as a reinforcing or nucleating agent, antioxidant, or filler to improve the applications of 3D printed objects [177–179]. Besides, lignin has been used as an additive material in 3D printing technology. However, the utilization of lignin as a major component compared to other polymers for 3D printed bio-feedstock still faces some challenges.

6. Challenges

Coined as one of the key drivers of the 4th industrial revolution, 3D printing technology is now empowering inventions in the consumption of biomass, initiated with the expansion of lignin-based materials.

However, lignin-based 3D printing technologies currently face some challenges, especially when designing thermosetting/thermoplastic by modification and/or polymer blending [180,181].

Extensive research has revealed that the rheological structural relationship of lignin does an important effect on lignin/polymer blend inks and the performance of the resulting composites (printability, mechanical strength, biocompatibility, tissue biomimicry, kinetic, and safe degradation). Although the 3D printing of lignin is compatible with FFF, SLS, SLA, and DIW techniques, good printability doesn't mean that lignin can be directly printed into 3D structures with high stability, desired properties, and performance. The direct use of lignin in the preparation of inks for 3D printing is limited by their low mechanical strength and stability and thus needs to be tuned with the addition of additives, especially macromolecules with linear structures. For example, FDM technology needs heat-induced flowability, for which native hardwood lignin is suitable with low molecular weight. FFF printing of lignin is highly controlled by its molecular structure and molecular weight, organosolv hardwood lignin and oligomeric kraft softwood lignin are common feedstocks for FFF that have flexible segments and low molecular weights. As an aerometric biopolymer with abundant active sites, lignin can be used for SLA technology with photoinitiators. The photopolymer in the printable blends plays a key role in SLA printing. With powder morphology and transition temperature, lignin is also compatible with the SLS technique but still presents a limitation in understanding a rheological structural relationship. DIW is suitable for lignin 3D printing because of tunable rheological behavior and allows vertical 3D printing. DIW is either extrusion-based or meniscus-guided and enables to the construction of diverse functional 3D structures in micro and nanometer scales [87,182–185].

Traditionally, the utilization of lignin is mainly based on direct use (including antioxidant, antibacterial, stabilizer, binders, and food additives), modification or depolymerization for chemicals or materials (including thermoplastics, gels, nanomaterials, fuels, etc), and carbon-based materials (including active carbon, carbon fiber, carbon quantum dots, etc). the immiscible brittle natures of lignins (original and technical) impede their wide applications. Although, modification and depolymerization is an effective ways to improve its interfacial compatibility with other polymers, excluding its specific properties, such as the redox and nutritional regulation characteristics. In addition, modification and depolymerization of lignin face great challenges in focusing on clear-cut methods using green chemistry and low-cost techniques. Traditionally, made carbon bases microporous materials form lignin, have a decisive influence on the charge (electron/ions) transport capacity. Unfortunately, these microporous structures prepared from lignin via conventional solution processing result in the formation of tortuous charge transport paths, which deteriorates the performance in energy storage and conversion.

Combined with 3D printing techniques, lignin is expected to produce value-added products. Although, 3D printing has given new insight and opportunities for the use of lignin, challenges and limitations still need to be focused on and overcome. For example, 3D printing of lignin mostly relies on the addition of petroleum-based polymers due to the improved rheological behavior. Materials for tissue engineering and robotic application need multiple functional compositions. To address these issues, it is necessary to replace petroleum-based feedstocks with other green polymers to construct fully biodegradable materials, and hybrid additive manufacturing will be tuned to meet the requirements for various applications. Due to the complex structure and morphology of lignin, flaws inside the printed materials generated lead to deteriorated mechanical properties. Such as the unsatisfied bonding between layers, the shape of lignin powder easily creates voids in printed products. Additionally, lignin-based filaments printed by FFF and DIW are usually tough and thick, resulting in a low-quality product.

Additive manufacturing faces many fundamental challenges for further research. For example, additives are capable of crosslinking with lignin or forming a network via in situ polymerization. Such chemically active additives affect the rheology, morphology, viscoelasticity, and a high 3D printing resolution [186]. Additives may also improve the chemical and physical properties of lignin (hydrophobic and hydrophilic), thus enhancing the interfacial compatibility and adhesion between adjacent printed layers. Stimulation or catalyzation of such in situ polymerization might be needed some external inputs (laser or active gasses) to eliminate residual voids and inhomogeneity during post-printing treatment (inks or pastes formation for printing), and to promote the microstructure evolution. The incorporation of inorganic components in additive manufacturing of lignin-based materials remains unexplored. In situ as well as post inspection are essential for lignin-based 3D printed materials. Additive manufacturing/3D printing techniques continuously moving toward the developments and directions of the diversification of materials, structures, and methods, and compatible with lignin. Further development in lignin structure properties and functions is needed to meet specific goals (biomedicine, aerospace, and automobile applications). We anticipate that the development of additive manufacturing/3D printing will broaden the utilization of lignin in value-added products.

7. Conclusions and future prospective

Recent developments and advancements in 3D printing technologies have a key role in the reduction of waste production and consumption of energy, also constructing extensive and multifaceted structures in the manufacturing area. In particular, lignin-based 3D printed materials have been found to overwhelm the existing challenges faced by petroleum-based materials, such as deficiency of resources and adverse effects on the environment, because of their widespread accessibility and environment-friendly nature. Diverse research in printing methodology, printing feed-stocks, printing features, and applications have led to expanding the properties of lignin-derived 3D printed materials and extending their applications. Lignin derivatives have been utilized in FDM, DIW, SLA, and binder jetting 3D printing technologies. Such techniques permit the use of lignin-derived materials in the fabrication of composites for use in biomedical (wound dressings, drug delivery systems, and drug removal materials) and pharmaceutical sectors, as well as battery capacitor materials, toys, and daily necessities. But many studies in the field of medicine are still in the proof-of-concept stage, and further clinical trials are still a long-term process.

In this emergent research area, the structure-processing-property association is yet-tailed because lignin is not easily stabilized, and its morphology is difficult to control. The finished 3D printed products with added lignin still have a performance gap compared with the plastic materials. Thus, the development of lignin-based high-performance materials remains challenging. Consequently, it is important to understand the structure of lignin, such as the crystallinity, material anisotropy, and interfacial interaction, that need to be studied further to reach the target 3D printed lignin-derived materials. For this purpose, it is necessary to undergo further engineering in numerous parameters, such as printing resolution and the port-production rate for making 3D printing competitive with conventional materials and construction machinery. In the future, the modification in lignin structural chemistry and use of bio-compatibilizers may improve the bonding and dispersal of lignin-derived fillers with plastics, which could meaningfully expand the concentration of fillers with modest strength to alleviate the reduction, at least partially, of the petroleum-based materials. Furthermore, the classified methods that are personalized to the final commercial applications can be appreciated to measure the strengths and weaknesses of lignin-derived 3D printed materials. An on-site characterization is also a possible approach that has been applied to metal 3D printing materials to improve and promote the quality of the printed materials.

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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