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REVIEW

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3D printing of lignin: Challenges, opportunities and roads onward

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Abstract

As the second most abundant biopolymer on earth, and as a resource recently becoming more available in separated and purified form on an industrial scale due to the development of new isolation technologies, lignin has a key role to play in transitioning our material industry towards sustainability. Additive manufacturing (AM), the most efficient-material processing technology to date, has likewise made great strides to promote sustainable industrial solutions to our needs in engineered products. Bringing lignin research to AM has prompted the emergence of the nascent "lignin 3D printing" field. This review presents the recent state of art of this promising field and highlights its challenges and opportunities. Following a review of the industrial availability, molecular attributes, and associated properties of technical lignins, we review R&D efforts at implementing lignin systems in extrusion-based and stereolithography (SLA) printing technologies. Doing so underlines the adage of lignin research that "all lignins are not created equal," and stresses the opportunity nested in this chemical diversity created mostly by differences in isolation conditions to molecularly select and tune the attributes of technical lignin systems towards desirable properties, be it by modification or polymer blending. Considering the AM design process in its entirety, we finally propose onward routes to bring the full potential to this emerging field. We hope that this review can help promote the unique value and overdue industrial role of lignin in sustainable engineered materials and products.

KEYWORDS
3D printing, additive manufacturing, extrusion-based printing, lignin, stereolithography

Abbreviations: ABS, acrylonitrile butadiene styrene; AM, additive manufacturing; CNF, cellulose nanofibers; DIW, direct ink writing; DLP, digital light processing; DOD, drop on demand; FDM, fused deposition modeling; G, guiaiacyl; H, hydroxy-phenyl; HPC, hydroxypropyl cellulose; HW, hardwood; Mn, number average molecular weight; OSL, organosolv lignin; PC, polycarbonate; PDI, polydispersity index; PEEK, polyether ether ketone; PET, polyethylene terephthalate; PLA, polylactic acid; PP, polypropylene; S, syringyl; SLA, stereolithography; SLS, selective laser sintering; SW, softwood; Tg, glass transition temperature; UA, urethane acrylate.

1 | INTRODUCTION

While additive manufacturing (AM) emerged in the late 1970s to 1980s with the pioneering work of Charles Hull for stereolithography (SLA), Scott Crump for extrusion-based 3D printing and Ross Householder for powder bed fusion, the last two decades have seen exponential research and development in the technology and its implementation in various application fields such as rapid prototyping, aerospace, tooling, spare parts, customized medical tooling and some mass production.[1] Ceramics, metals, inorganic glasses, polymers and composites are all suitable AM feedstocks and several technologies are amenable to multimaterial printing.[2] With the pressing need to transition our society's consumption behaviors towards sustainability, some of the most recent efforts have turned towards combining this material-efficient manufacturing process with environmentally friendly materials such as bio-based and biodegradable polymers.[3] Among the bio-based polymers considered, lignocellulosic polymers have attracted particular attention for AM over the past 5 years.[4–6] This stems in part from their large natural abundance—cellulose and lignin are the two most abundant biopolymers on earth—but also from their recent availability in purified and/ or nanoparticulate colloidal form from traditional pulp and paper processing and from biorefineries.[6] While most efforts in this arena have concentrated on AM of complete lignocellulose as fillers[5] or cellulosics, in particular nanocellulose and cellulose derivatives,[6] attempts at implementing lignin in AM remain scarce. Yet, AM is a promising avenue to add value to lignin in its polymeric form and could significantly contribute to "making lignin great again".[7] In this review the focus will be on using lignin in its oligomeric or polymeric form as a feedstock for AM. The aim is to present research, which uses lignin as an additive (more than 30% of total volume), rather than a filler (up to 5% of total volume).[8] After briefly presenting the commercial availability and structural features of technical lignins, this review attempts to highlight the recent advances in AM of lignin-based feedstocks. While seven AM technologies exist,[9] lignin has only been implemented to date on extrusion-based technologies and VAT-photopolymerization. The advances in implementing lignin systems in each of these processing technologies is thus examined, with a special focus on the desirable properties of lignin for each technology. This enables the delineation of challenges and opportunities to further add value to technical lignin's through AM, as discussed

TABLE 1 Overview of the structural parameters of isolated technical lignins that are currently commercially available for AM

	Sulfur-containing lignin		Sulfur-free lignin	
Lignin type	Kraft	Lignosulfonate	Soda	Organosolv
Raw materials	Softwood, hardwood[13]	Softwood, hardwood[13]	Annual plants[13]	Softwood, hardwood, annual plants[13]
Sulfur content (%)	1.8[14]	3.5-8[15]	0[15]	0[15]
Solubility	Alkali[13]	Water[13]	Alkali[13]	Wide range of organic solvents[13]
Mn (g/mol)	1000-3000[13]	15 000-50 000[13]	800-3000[13]	500-5000[13]
PDI	2.5-3.5[13]	6-8[13]	2.5-3.5[13]	1.5-2.5[13]
Tg (°C)	140-150[13]	130[13]	140[13]	90-110[13]
Aliphatic OH (mmol OH/g)	1.5[16]	5.7[16]	1.3[16]	2.9[17]
Phenolic OH (mmol OH/g)	1.3[16]	0.6[16]	1.6[16]	2.8[17]
Carboxylic acid (mmol/g)	0.6[16]	0.3[16]	0.7[16]	0.48[18]
Volume (ton/year)	10 000 (West Fraser pulp mill, Alberta, Canada)[19] 8000 (Nordic Paper Bäckhammer, Sweden) 27 300 (Domtar Plymouth Mill, US) 50 000 (Stora Enso, Finland)[20] 60 000 (MeadWestvaco Corporation, US)[21]	120 000 (Domsjö Fabriker, SE)[22] 500 000 (Borregaard LignoTech, Norway)[15] 570 000 (Tembec, Canada) Other suppliers: Nippon Paper Chemicals (Japan), La Rochette Venizel (France)[23]	500 (Northway Lignin Chemicals) 10 000 (GreenValue SA, Switzerland)[23]	500 (CIMV, France) 500-3000 (Lignol Innovations Corp., Canada) Other suppliers: CLARIANT (sunliquid site in Romania), DECHEMA/Fraunhofer (Germany), Dedini (Brasil),[23] Renmatix (US), TennEra (US)[24]
Price (US $/ton)	260-500[23]	180-500[23]	200-300[23]	280-520[23]

subsequently. Finally, we formulate some recommendations for routes onward to make 3D printing of lignin an industrial reality.

1.1 | Overview of lignin resources

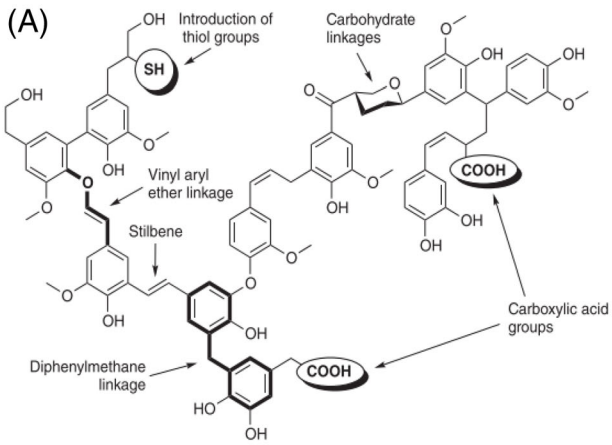
With a worldwide generation of 100 million dry tons/ year as by-product of pulp and paper-making and a price ranging from 200 to 500 USD/dry ton (Table 1),[10] well below that of polyethylene (1000 USD/dry ton), lignin represents a vast and inexpensive feedstock that could substitute synthetic polymers currently processed with AM, such as ABS, PET, PC, PEEK, PP, and Nylon. Additionally, the inherent properties of lignin, viz. antioxidant and antibacterial properties, but also its propensity to return to humus upon biodegradation, can be expected to be retained in lignin-based parts. Two principal categories of lignin are derived from wood pulping, viz. lignosulfonates (~88%) and kraft lignins (~9%).[10] A new category, organosolv or biorefinery lignin (~2%) is further gaining popularity and is expected to experience the highest growth over the coming years.[10] Along the development of these biorefinery technologies, the recent industrial transfer of isolation technologies, such as Lignoboost for kraft lignins, as in the case of the Domtar plant (Plymouth, NC), further enables a significant supply of isolated, purified and even "designer" technical lignins for the first time in lignin research history. An overview of their structural and physico-chemical properties is presented in Table 1, alongside their main producers. Extracting lignin from lignocellulosic biomass invariantly results in structural specificities, as inherited traits from the raw lignocellulosic source, or as acquired traits from the extraction process. For example, despite a rather low molecular weight, kraft lignin is not soluble in water or common solvents, in contrast to lignosulfonates and organosolv lignin, which through their specific extraction processes acquire ionic sulfonic groups and a low molecular weight distribution, respectively. Equally well established, hardwood lignins differ from softwood and grass lignins in their native states already and are categorized as GS, G or GHS lignins respectively, in relation to their proportion in syringyl (S), guiaiacyl (G) and para hydroxy-phenyl (H) units. S, G and H contents are one of the prime factors governing lignin topology and viscoelastic properties. Namely, with their higher syringyl content (G:S ~ 50:50) hardwood lignins typically adopt a more linear and less branched topology than softwood lignins (G:S ~ 90:10), thus exhibiting a lower softening temperature[11] and facilitated thermal viscous flow upon heating. This can be advantageous for thermally activated AM technologies, where thermal energy is needed to induce flow while thermal degradation, typically starting at 150 to 170 °C for lignins, must be avoided.

Additionally, as a natural polymer not "designed" for mankind manufacturing, technical lignins lack the essential processability of engineered polymers. Although viscous flow can be achieved upon heating especially for the less branched hardwood lignins, their amorphous morphology precludes the possibility of melting and crystallization. Therefore, polymer blending and/or derivatization is needed to endow melt-processability or solubility to technical lignins.[7] In this endeavor, the specific structural features of the technical lignins influence their amenability to a particular AM technology (Table 1 and Figure 1). In addition, this inherent processing challenge necessitates that one designs a lignin system, in which lignin is either blended with another polymer or reactive monomer, or derivatized, rather than utilizing pure lignin. Alternatively, and while not yet commercially transferred, progresses in producing lignin colloids, in the form of aqueous dispersions of lignin micro- and nano-particles, open new prospects for AM of lignin systems.[12]

2 | OVERVIEW OF AM TECHNOLOGIES FOR POLYMERIC SYSTEMS

3D-printing generates three-dimensional parts by stacking up layers on top of each other. In comparison to conventional manufacturing techniques, little waste material is generated and the production of molds is not necessary, as the geometric data is retrieved from a computer aided design (CAD) file.[28] Furthermore, the scale and raw material used can be adjusted to a certain extent by modulating the computer file.[29] The freedom of modeling data enlarges the design space, enabling the manufacture of a wide range of structures and complex geometries.[1] On the other hand, postprocessing is often required to improve part quality and mechanical properties are often below those obtained by traditional polymer processing technologies such as injection molding.[30] For polymeric feedstocks, different types of 3D-printing technologies are available including material extrusion, vat-photopolymerization, powder bed fusion and material jetting[9] (Figure 2).

The extrusion-based techniques viz. fused deposition modeling (FDM) and direct ink writing (DIW) are layer additive manufacturing processes, in which the printer head rises. In FDM a continuous, thermoplastic filament, is heated in the nozzle to a semi-liquid state and extruded to the build platform on the previously printed layer. The thermoplastics are typically heated slightly above their melting temperature, so that solidification is reached directly after extrusion.[28] FDM enables large scale fabrication; windmill blades have for example been printed in the Oak Ridge National Lab Big Area Additive Manufacturing (BAAM). In contrast, it is limited in details with the smallest layer thickness in the order of ~0.1 mm and invariantly delivers anisotropic parts. At the smaller scale, DIW or robocasting is a microscale extrusion AM, which can process thermoplastic materials as well as solution-based hydrogels and pastes. For both FDM and DIW, the rheology of feedstock plays a crucial role and its engineering to concomitantly display strong shear-thinning for nozzle extrusion and form dimensionally stable self-supporting features upon printing is a major challenge.[31,32] As an extrusion-based method, DIW also generates anisotropic parts and alike FDM is amenable to multi-material printing. As processing can occur at room temperature, DIW is ideal for tissue-engineering, whereby living cells can be incorporated in the feedstock a priori. Also, a layer-wise method, vat-photopolymerization, including SLA and DLP, relies on the light-induced polymerization of a photoactive and low viscosity resin, typically comprising acrylic- or epoxy- based monomers. A rapid free radical or



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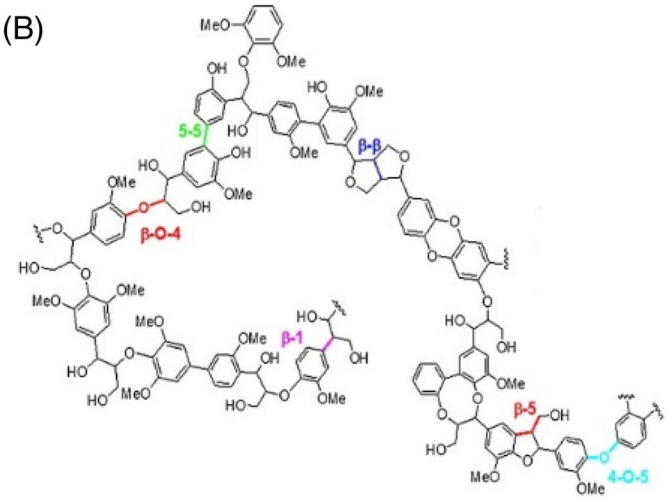

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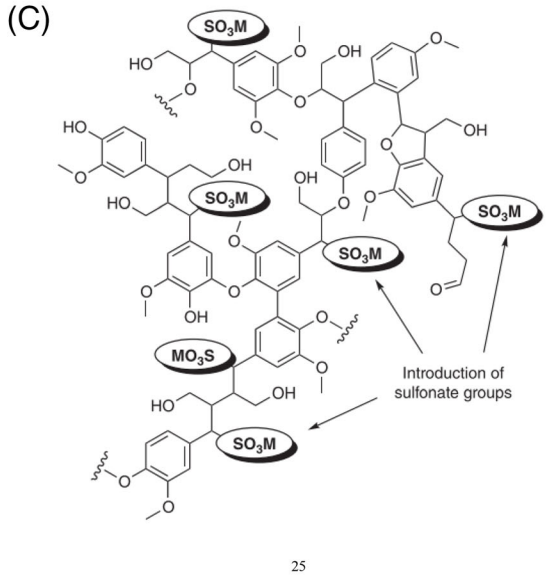

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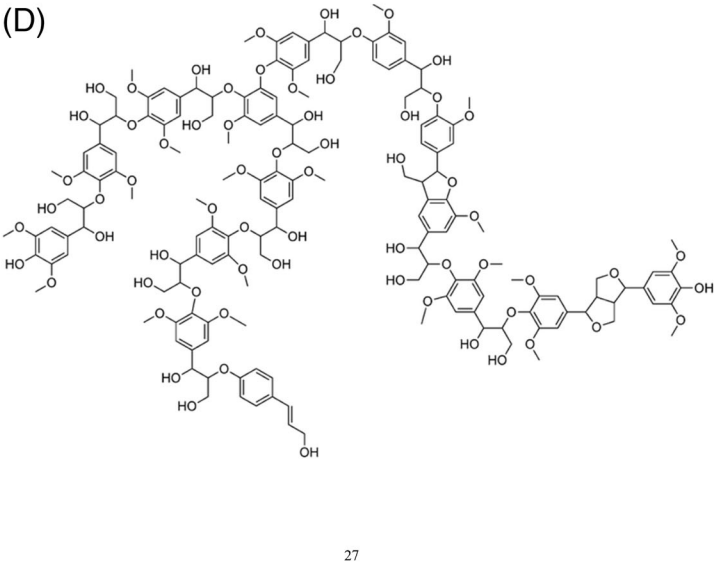

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FIGURE 1 Overview of the chemical structure of isolated technical lignins (A: kraft[25], B: soda[26], C: lignosulfonate[25], D: organosolv lignin[27]) that are currently commercially available for AM

cationic photopolymerization is initiated by application of light (UV light, electron beam, light emitting diodes in combination with projectors, or two photon) onto a layer of resin or monomer solution. Once the 3D model is generated, the unreacted resin is removed.[1] Vat-photopolymerization delivers much finer features, better surface quality and enables a broader range of length scales (from the micrometer to the meter scale) than extrusion-based AM, while producing isotropic parts. However, it is restricted to date to a small range of photosensitive liquids.[33] In powder bed fusion of polymers, or selective laser sintering (SLS), a focused energy source such as a laser is scanned over a bed of powder feedstock, causing local sintering or melting of the polymer powder.[34] In SLS, the build area is preheated to just below the polymer melting point, enabling a much higher throughput than extrusion and vat-photopolymerization at the same resolution. SLS is ideally suited for semicrystalline thermoplastics although amorphous polymers can also be utilized. It can produce beautiful complex shapes and is ideally suited for fine lattice structures. Material jetting follows the principle of inkjet printing, in which droplets (as small as 10 μm in diameter) of feedstocks are deposited from an inkjet printhead with spatial control and subsequently light-cured. Because feedstock placement and composition can be controlled one droplet at a time, multimaterial complex shapes can be

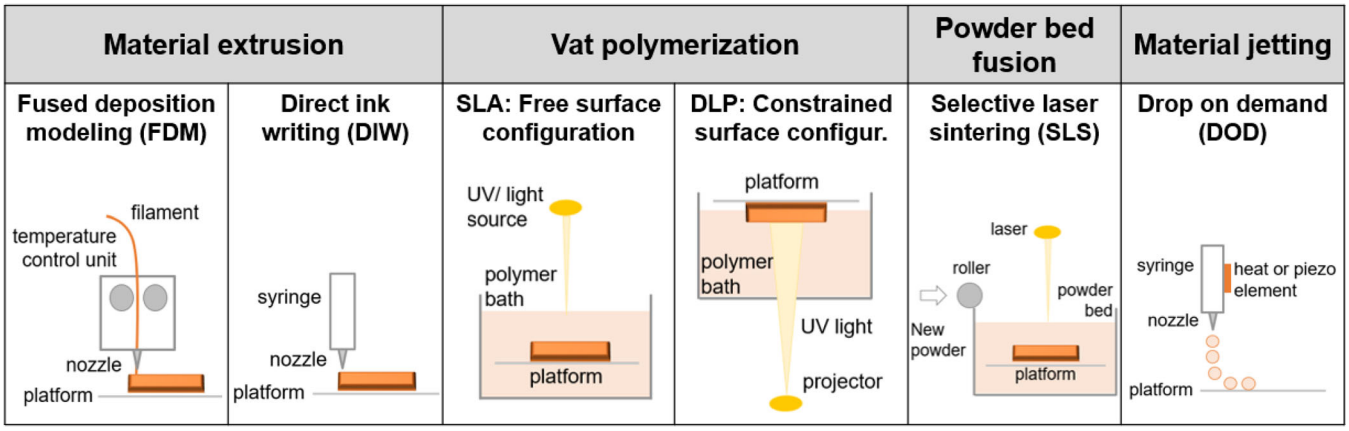

FIGURE 2 Overview of 3D printing techniques available for polymeric feedstocks. DLP, digital light processing; SLA, stereolithography

printed at high speed, with fine surface finish and spanning small length scales from ~0.1 mm to meter length scales, while producing zero waste.

3 | FDM WITH TECHNICAL LIGNINS

Not every polymeric material can undergo FDM and deliver a 3D printed part. For example, low T_g rubbery materials do not form good printable pellets or extruded strands that can undergo FDM. Some semi-crystalline polymers such as polylactic acid (PLA) and polyether ether ketone (PEEK) are commonly printed using FDM, yet it is difficult to print polypropylene without using an additive. One reason for this is that in FDM the solid strand material must meet sufficient rigidity (high enough Young's modulus) to avoid buckling at the entrance of the temperature-controlled melting chamber (see Figure 2). Pellets of polymer feedstock can be used for FDM to overcome this buckling obstacle; however, it requires a special screw-type feeding device for melting, extrusion, and deposition on a build plate. In addition to the filament's high Young's modulus, the melt must have low enough viscosity to facilitate extrusion, which depends on the solid filament to seal the melt from escaping through the top and act as a piston exerting force on the melt.[35] Furthermore, the deposited layer must have high enough zero shear viscosity to avoid any flow or dimensional change. To meet these requirements for FDM printability, lignin systems must form a rigid fiber as well as a stable melt.[36] To further complicate this task, not all lignins are created equal as highlighted in section 1 and Table 1; their source and method of isolation from biomass dictate structure and the rheological properties. Sinapyl alcohol-rich woody biomass-derived lignin is inherently melt-processable. In contrast, coniferyl alcohol-rich softwood lignin and lignin from perennial plants do not flow well unless oligomers of very low molar mass (~1000 Da) fractions are used. Conventional polymers can exhibit reduced viscosity with increased temperature; however, a similar strategy cannot be adopted for lignin because of its susceptibility to undergo thermal degradation. Nonetheless, various lignin fractions with <1000 Pa.s viscosities are available and those can be consistently extruded to a fiber or large diameter filament form.[36,37] Yet, filament extrudability does not necessarily assure 3D printability of the lignin. Oligomeric filaments or deposited layers of lignin are very brittle and difficult to handle. Therefore, in most cases, lignin is either blended with a printable plastic matrix or copolymerized with a soft segment that induces toughness to the composition, but the interaction between the different lignins and the matrix must be taken into consideration. For example, thermally stable lignin blended with ABS renders the matrix more brittle, primarily due to inadequate compatibility between the phases. However, use of nitrile rubber[38] or polyoxyethylene[39] in lignin loaded blends of ABS makes the composition tough and strong through superior dispersion of lignin. These compositions exhibit excellent printability via FDM. A relatively soft and tough polymer, nylon12, exhibits plasticization of the melt caused by blending with a melt-stable lignin. Such a composition does not require additional compatibilizer. Furthermore, 4 to 12 wt% discontinuous carbon fibers (3-4 mm long) can be added to the nylon/lignin blend to not only enhance the stiffness and strength of the composition but also to render it amenable to be fed through a tight heating chamber without buckling of the filament. Presence of fibers also helps to improve weldability of the deposited layers of lignin-based plastics and improve the inter-layer adhesion.[38] The rheological data of a few of the mentioned lignin samples and polymer-modified lignin compositions are displayed in Figure 3.

An equal mass alloy of lignin with nitrile rubber shows excellent toughness and yield stress and a high tensile strength.[40] This soft composition is, however, very difficult to 3D print. The factors that hinder printability include high viscosity of the composition caused by the high molecular weight rubber component and its crosslinking with lignin. To mitigate this issue, the composition was further modified by blending with a rigid plastic such as high impact polystyrene, and the composition showed excellent 3D printability. Traditional use of polymer extenders or impact modifiers to enhance processability can also be applied to induce printability of various bio-based plastics including lignin.[41,42] Ongoing research suggests modification of these lignin-based compositions with natural fibers produces printed composites that can find application as wood substituents.[43]

A few lignin modified thermoplastic matrices, on the other hand, exhibit excellent 3D printability without needing additives. For example,

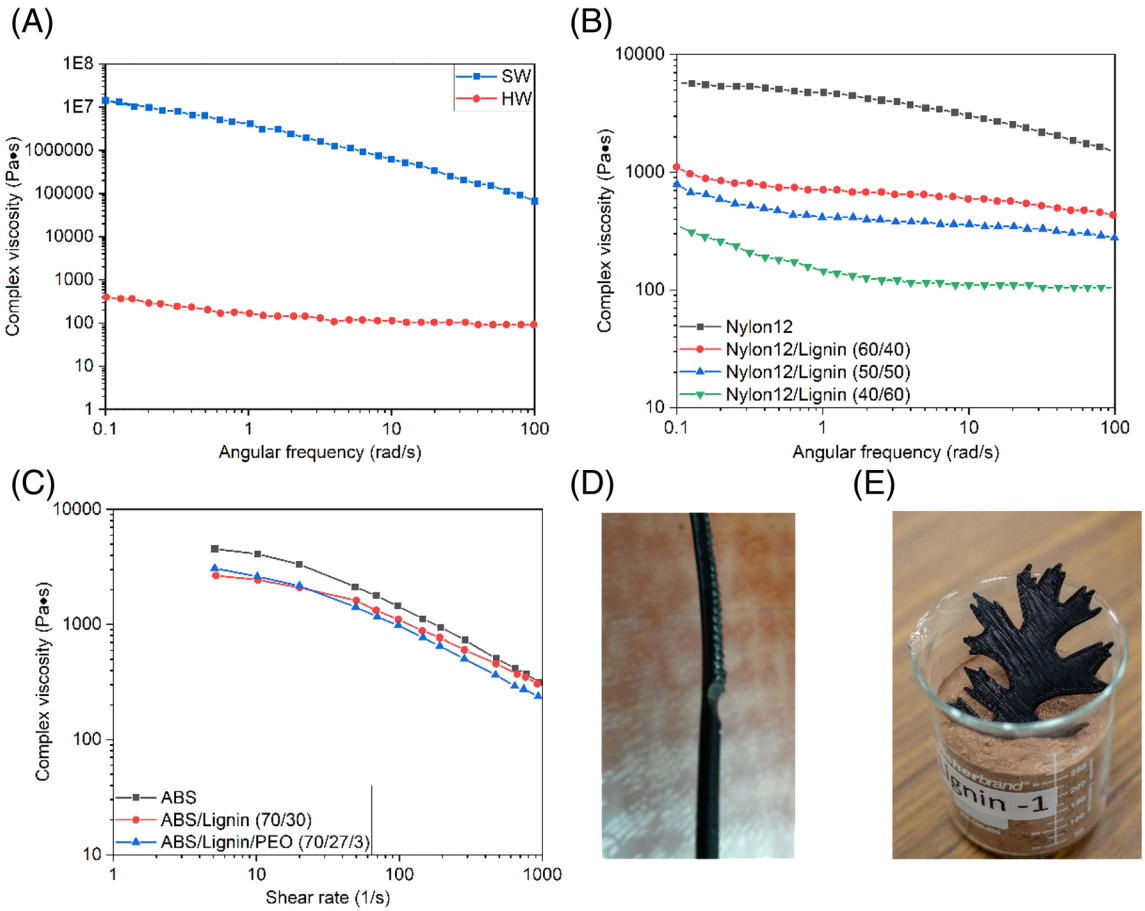

FIGURE 3 Rheological data and 3D printability (by FDM) of lignin derivatives, through layer-by-layer deposition of melt, based on zero shear viscosity, shear thinning behavior, and room-temperature stiffness and toughness of the extrudable material. (A) Sinapyl alcohol-based organosolv hardwood (HW) lignin shows significantly lower viscosity than that of a Kraft coniferyl alcohol-rich softwood (SW) pine lignin at 190 °C; (B) Reduced viscosity of the HW lignin lowered the viscosity of the nylon12 matrix at 210 °C. An increasing lignin content decreased the melt viscosity of the nylon12-lignin compositions. Adapted from.[36] © The Authors, some rights reserved; exclusive licensee AAAS. Distributed under a CC BY-NC 4.0 License (http://creativecommons.org/licenses/by-nc/4.0/) (C) ABS matrix does not show such a significant lowering in viscosity after inclusion of 30 wt.% HW lignin. Adapted with permission from.[39] Copyright 2015 American Chemical Society; (D) Buckling-induced mechanical damage in the filament during FDM of a soft rubbery composition that inhibits 3D printability; and (E) 3D printed oak leaf

organosolv hardwood lignin shows excellent compatibility with PLA matrix, and its 15 wt% lignin loaded composition shows very good printability by FDM. Contrastingly, an equivalent composition with a softwood kraft lignin shows worse printability, primarily due to the degradation of PLA caused by residual alkali in the lignin.[44] Because of the inherent antioxidant nature of the lignin, its slight loading in PLA along with a wound healing compound delivered a printed mesh with significant use as wound dressing material.[45] Other work suggests significantly loaded lignin (40 wt%) in PLA exhibiting very good printability and high free radical scavenging capacity.[46]

4 | DIW OF LIGNIN SYSTEMS

With DIW, a multitude of inks can be printed, as long as these are in the form of pellets or paste, strongly shear thinning, and able to form self-supporting parts at rest.[31] Ink prescreening protocols have been recently proposed, enabling a fast optimization of ink formulations.[47] DIW is well-suited for lignin systems as it allows processing at room temperature, well below the degradation temperature of lignin around 200 °C.[48] Yet, implementation of DIW on technical lignins remains scarce (Table 2) to date and invariably relies on polymer blending to form gels or pastes, that can be ultimately crosslinked for final shape retention. For example, cellulose nanofibers (CNF), alginate and colloidal lignin particles, produced from softwood kraft lignin powder and crosslinked with Ca^{2+} ions, have been recently printed for soft tissue engineering and demonstrated to be biocompatible with HepG2 cells.[49] In this work, lignin nanoparticles were found to increase shape fidelity and bestow antioxidant properties to the printed parts, even in concentrations as low as 0.5 wt%.[49] While such use of colloidal lignin is promising, its marginal fraction in the ink and the niche application considered restrict its potential to low volume handling of lignin.

TABLE 2 Overview of lignin-based inks for Direct Ink Writing

3D printed object	Type of lignin	Lignin content	Polymer blend	Cross-linking	Reference
 0.5 cm Copyright 2020, American Chemical Society	Colloidal lignin particles	0.5 wt% in final ink	CNF and alginate	Chemical crosslinking using Ca^{2+} ions	[49]
 Copyright 2020. Reproduced with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim	Alkali lignin	38-56 wt%	Pluronic F127	Chemical crosslinking using Pluronic F127	[50]
 2 mm Copyright 2020, American Chemical Society	Organosolv lignin	25 wt%	Hydroxy-propyl cellulose	Esterification with dimerized fatty acid	[51]
 Copyright 2020, American Chemical Society	Organosolv lignin	50 wt%	Hydroxy-propyl cellulose	Chemical crosslinking with citric acid and borate ions	[54]

Soda lignin has also been combined for DIW with an acrylate-containing soft triblock copolymer, Pluronic F127, which acts as crosslinking agent.[50] After printing, parts were freeze-dried and subsequently oven-cured at 120 °C to yield crosslinked, water-insoluble objects. The parts, comprising up to 83 wt% lignin content, exhibited high Young's modulus (5 GPa) and UV-blocking properties,[50] paving the way to promising applications and high-volume usage of soda lignin. Yet, its combination with a petroleum-derived photopolymer limits the environmental-friendliness of this lignin-based ink.

Blending the lyotropic gel-forming hydroxypropyl cellulose (HPC) with up to 25 wt % beech organosolv lignin (OSL) in an acetic acid aqueous solution delivered liquid crystalline shear thinning inks, which could be successfully direct ink written.[51] Thermal postcuring of ink formulations with polycarboxylic acid crosslinkers such as citric acid and a dimerized fatty acid, endowed parts with water insolubility and anisotropic swelling. While both HPC and lignin alone were found not to be amenable to DIW, blending these two bio-based polymers bestowed the ink with both the required shear thinning for extrusion by virtue of the HPC liquid crystalline formation, and the needed shape retention at rest by virtue of lignin stabilizing effect. Lignin stabilizing effect in this blend was further found to stem from its phenolic-OH groups and low molecular weight fraction, which enhanced lignin miscibility with HPC.[52,53] The anisotropic swelling imparted by molecular orientation and the resulting band texture formation endowed parts with morphing properties upon exposure to humidity, paving the way to the manufacture of sensing and soft robotic devices from fully bio-based lignin systems. However, dragging of the outer layers to the center during printing limited dimensional stability and restricted the design space to continuously-printed structures such as rings.[51] In the aim to improve solidification, shape freedom and shape retention, ethanol was further used as cosolvent of the aqueous acetic acid solution for this lignin/HPC system.[54] Prescreening of ink formulations according to Paxton *et al*. 2017, followed by assessment of mechanical properties and part quality, revealed an optimum ink solid content of 49% and a OSL content of 50 wt%. With such inks, simple cylinders and lattice structures could be printed containing exclusively bio-based polymers and large amounts of lignin. Yet, an instantaneous crosslinking and solidification mechanism remains desirable in such lyotropic lignin-based inks to enlarge shape freedom and printing throughput.[54

5 | SLA WITH LIGNIN-CONTAINING RESINS

At its core, SLA is a photopolymerization process that requires a photoinitiator and a reactive monomer suitable for chain-growth

polymerization reactions. However, it is a complex process that entails simultaneous control of resin photoproperties, rheology, and chemistry to provide crosslinked thermoset objects. This control is imparted by multicomponent resins, which are precisely engineered mixtures that provide photo-, rheological, and mechanical properties required to ensure a successful print. For commercially available SLA printers, there are two general configurations as shown in Figure 2.[55] In a free-surface configuration, the light source is above the resin bath and the layers are printed on top of each other as the build platform moves down into the bath. The size of the object is limited by the vertical height of the resin bath, and more resin must be used to ensure the object is always coated.[56] Many commercial printers employ the constrained-surface configuration, where the light source is below the resin bath. The object is created in subsequent layers between the bottom surface of the bath and the build platform. As the build platform moves upward, a peeling step is required that removes the cured object from the bottom of the vat. Meanwhile, resin must have a sufficiently low viscosity that it is able to flow into the space vacated by moving the build platform upward. These complex steps highlight the necessity of precisely engineering several properties of each resin simultaneously to ensure a successful print. As with other AM technologies, attempts to enrich resin systems for SLA with lignin have considered both unmodified and modified technical lignins. These efforts are successively reviewed next.

Ragauskas and coworkers reported on incorporation of small amounts of solvent-fractionated Kraft lignin into commercially available 3D printer resin from Formlabs Inc.[57] Those researchers purified and mixed the Kraft lignin with a commercial methacrylate resin in 0.2-1 wt% using a solution blending procedure. Kraft lignin and commercial resin were separately suspended in acetone and then those individual mixtures were combined and concentrated to afford a lignin-resin blend. Using UV-Vis spectroscopy, the researchers showed that the measured lignin concentration in each sample was higher than expected. They attributed this to inefficient dispersion of the unmodified lignin, which tended to settle to the bottom of the printer reservoir during printing (see Figure 1). Moreover, they discovered that the addition of unmodified lignin hinders the curing process during printing. They found that the addition of 1 wt% lignin to the resin leads to less than half of the material to be cured by printing, with 54% of the noncrosslinked, uncured resin removed from partially printed parts by washing with acetone. Unsurprisingly, this leads to a substantial decrease (up to 85% decrease) in the ultimate tensile strength and elastic modulus of the printed objects. To fully crosslink the nongel fraction of the printed objects, the researchers developed a postcure scheme where printed parts were cured in a UV chamber for 4 hours. This methodology led to a modest increase in tensile strength (on the order of 50%) and elastic modulus (on the order of 30%) of the printed and postcured objects when compared to the unadulterated commercial resin.

Sajab and coworkers also studied the effects of adding small amounts of lignin to SLA resins.[58] After isolating organosolv lignin from oil palm empty fruit bunches using a formic acid-catalyzed solvolytic extraction, they incorporated it without modification into a commercially available resin whose primary component was a urethane acrylate (UA) oligomer. Having no modification of the lignin to enhance its dispersion in the resin material, the researchers reported only a modest increase in ultimate tensile strength (on the order of 15%) and a decrease in ductility corresponding to an increase in elastic modulus that in the lignin-UA composite parts. These embrittled composites contained up to 1 wt% lignin, with higher concentrations (up to 3 wt%) causing a drastic reduction in performance properties of the printed objects.

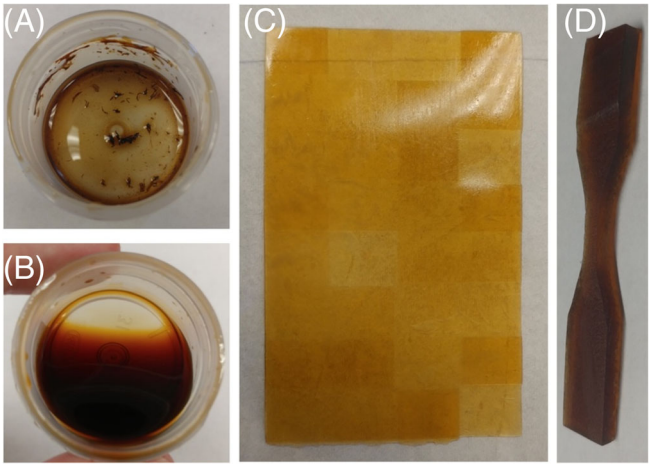

FIGURE 4 Images of lignin-containing samples printed by SLA. Unmodified lignin dispersed in resin components affords a heterogenous mixture (A), whereas acetylation with methacrylic anhydride affords a homogenous solution (B). A working curve "windowpane" consisting of 32 squares of varying thicknesses of 5 to 20 layers (C) can be used to generate resin working curves that interrogate photoproperties of lignin-containing resins. ASTM D638 Type V tensile testing specimens (D) can be 3D printed to test performance properties of lignin-containing resins. Adapted with permission from.[59] Copyright 2018 American Chemical Society

In contrast to incorporation of unmodified lignin into SLA resins, major enhancements in performance properties can be realized by judicious chemical modification of lignin before incorporation into new resins (Figure 4). The Chmely group demonstrated that acylation of organosolv lignin using methacrylic anhydride allowed up to 15 wt % lignin to be incorporated into an open-source SLA resin.[59] This is an increased order of magnitude of lignin than examples where no chemical transformations of the lignin are used, which highlights the importance of chemical transformations on dispersibility of the lignin in the resin matrix. Moreover, modified lignin substantially enhanced the performance properties of the printed objects, with 10 wt% lignin affording two times the ultimate tensile strength and a 3-fold increase in strain at break.

In addition, the group constructed working curves for each of the resins to compare critical energy dosage to cure each resin (Figure 4C). Since the myriad aromatic groups in lignin impart a high photon cross section, the light dose (405 nm) required to cure lignin-containing samples was lower than the unadulterated resin using diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) as the

photoinitiator. In fact, lignin has been recently reported to be useful as a photoinitiator itself.[60,61] This is an exciting development regarding SLA with lignin, whereby potentially the oligomers and the photopackage could consist entirely of properly modified lignin.

Another important consideration regarding lignin modification is related to the ability of lignin to react with radical species to form stable quinone methide structures. Kim and coworkers demonstrated that methylation of the phenolic hydroxyl group in lignin prevents the formation of quinone methides.[62] The blocking action imparted by chemical modification of these hydroxyl groups by acetylation with methacrylate moieties perhaps prevents competitive radical quenching reactions during photopolymerization, leading to cured objects with superior mechanical properties. Additional research regarding the differences in curing kinetics imparted by lignin modification could elucidate these structure-function relationships.

In addition to biorefinery lignin, researchers have demonstrated the utility of chemical modifications of lignin-based phenolics to create new photoactive resins for 3D printing. For example, Reineke and coworkers created a slate of mono- and di-functional photoactive monomers from guaiacol and vanillyl alcohol, respectively.[63] The group was able to show that these monomers, when suitably modified with methacrylate moieties, could be used to generate photoactive SLA resins, and that changing the concentration of these multifunctional monomers allowed for precise control of resin photoproperties and rheology, and subsequent performance properties of printed objects. Likewise, Stanzione and coworkers showed that photocurable resins based on vanillin could be used for SLA.[64] These resins have low viscosity, are derived from acetylation of vanillin using methacrylic anhydride, and the objects printed with them have thermal and mechanical properties that support their use as high-strength and high-Tg resins. Although these examples do not use lignin as a resin component, these results support the conclusion that chemical modification of lignin through acetylation of hydroxyl groups is one methodology that successfully enhances dispersion and performance properties of the resulting resins and printed objects.

6 | CHALLENGES AND OPPORTUNITIES OF AM FOR LIGNIN

Coined as the fourth industrial revolution, AM is now also fueling innovations in the biomass utilization field, starting with the development of lignin-based feedstocks for these processing technologies. While implemented to date only on two of the four AM technologies suitable for polymer feedstocks, the feedstock solutions brought to life to date underline the same challenges as those identified early on in lignin research, when designing thermosetting or thermoplastic systems by modification and/or polymer blending.[7] First, all technical lignins are not created equal; to the diversity of available AM technologies and their corresponding feedstock requirements responds a diversity of available technical lignins and associated structural features, physicochemical and viscoelastic properties. Therefore, each AM technology and application requires a thoughtful selection of the desirable lignin features. For example, heat-induced flowability is desirable for FDM, favoring native hardwood lignins of low molecular weight and low Tg, lignin modification for solubility and reactivity with organic monomers is critical for SLA. Second, a subtle engineering of rheological properties is needed to implement lignin-based feedstocks in AM; this involves an informed selection of the desirable characteristics of the technical lignins and modification/ blending strategies. Finally, thermodynamic miscibility, be it in the form of polymer blend compatibility in feedstocks to extrusion-based 3D printing, or solubility within a liquid reactive monomer in resin feedstocks to vat-photopolymerization, underlies processability, material final morphology and thus part performance. Feedstocks for vat-photopolymerization can for example develop phase separation in the initial low molecular weight resin but also during network formation, alike that described in traditional heat curing lignin-based epoxy thermosets.[65] Likewise, phase separation during extrusion-based 3D printing of lignin-based polymer blends can reduce lignin contribution to that of a glassy reinforcement phase, instead of its superior role as a structuring polymer for supramolecular systems. During such morphological development, it is likely that neither full phase separation nor molecular miscibility maximize performance. Rather, light must be shed on structure/processing/morphology/performance relationships for every lignin and technology pair considering the desirable part application. In this realm, the studies examined in this review are only touching a new domain of knowledge and understanding that remains to be developed.

Most importantly, while these studies have rightfully set an initial focus on feedstock design, they have not yet considered the entire complexity of designing and manufacturing for AM. Aside part printing itself, AM requires multiple preparation and post-processing steps, such as the optimization of support structures for parts and overhangs, the optimum use of build volume for manufacturing productivity, the removal of support structures and the part finishing. In this endeavor, using relevant artifacts such as the NIST artifact,[66] lignin-based feedstocks need to be benchmarked against established feedstocks to assess feature resolution in pores, steps, columns etc. and shape-forming flexibility for an AM process. Thus, further development of lignin-based feedstock remains necessary to alleviate some of the listed challenges and expand precision, shape forming flexibility and parts performance. In this endeavor, it appears worth to the authors to continue exploring lignin in its polymeric form while capitalizing on the unexpected compatibility between a compression-modulus building aromatic lignin and Young s modulus building carbohydrates.[7] Certainly, current industrial advances in wood-based nanotechnology, with the industrial availability of cellulosic nanoparticles and the laboratory scale preparation of lignin but also tannin colloids, also invite opportunities for the design of fully bio-based feedstock from such colloidal assemblies.

Feedstock development goes hand in hand with the selected AM technology. No doubt, that the presented studies are just premises of significant AM development with lignin-based systems. Indeed, with the AM technologies currently implemented for lignin, there is ample room for further development. FDM and DIW both afford

multimaterial printing and would expand the versatility of lignin-based printed parts, especially if various lignin-based feedstocks with distinct properties could be printed together. Other AM technologies such as DLP, but also SLS and material jetting remain vastly open for lignin-based feedstocks. Furthermore, to advance the field of lignin 3D printing, a holistic approach towards the specific goal and application is most recommended. Asking oneself questions such as: what is the problem and application one is trying to solve in implementing lignin in 3D printing? Are we merely wanting to replace petroleum-based feedstocks with renewable feedstocks? Are we looking for new design opportunities and functionalities by printing lignin-based parts such as lignin inherent antioxidant properties? Finally, while the science and engineering of lignin 3D printing is valuable new knowledge as itself, it will be in as much valuable as it paves the way to commercial utilization of lignin. Thus, routes for upscaling and for technology transfer to real life implementation and application must be pursued. Here, collaborations along the product life cycle, from its conception with chemists, physicists, engineers and designers, to its manufacturing and finally its commercialization with entrepreneurs, industrial partners are economists will be critical. This review has thus the ambition to spark interest in this field from a wide range of actors and stakeholders along the chain supply and product life cycle of the lignin AM products with a view to finally "making lignin great again".[7]

7 | CONCLUSIONS

R&D to implement lignin-based systems in AM is in its infancy but has already shown outstanding promise to add-value to a vastly available and underutilized bio-based polymer while fostering sustainability. Extrusion-based and VAT-photopolymerization technologies have already been successfully demonstrated with lignin-based systems, enabling the production of 3D parts with moderate to high lignin content (from a few % to 50%), with partial to total biobased carbon content, and with at times drastically improved mechanical performance. Yet, much R&D remains to be done to unleash the full potential and synergies of lignin and AM, as a sustainable bioresource and as a material-efficient processing technology and bring new bio-based innovations into the real world with applications in construction materials, lightweight structures, sensing and biomedical materials among others.

With the recent scientific and industrial advances in biorefining, the forest product industry is ripe to empower the chemical and material industry to produce lignin-based products on the industrial scale. Leveraging 5 decades of fundamental research and development on lignin-based polymers and lessons from the past[7] with this disruptive technology, opens vast opportunities. Wood scientists, chemists, engineers, designers and entrepreneurs need to come together and seize these opportunities towards a more efficient use of mother earth resources and a more sustainable society. This entails a thorough knowledge and molecular manipulation of the highly tunable resource that lignin truly is, as a well as close collaborations along the chain supply and life cycle of the 3D printed lignin parts, from suppliers of the raw resource to parts end users. With this review, we hope we can contribute some excitement for this nascent field, and motivate the various stakeholders to further advance the science, technology and industry of AM for lignin-based systems in the near future so that, together, we can finally find commercial value of lignin and bring it to reality in industry and in our consumption habits.

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CONFLICT OF INTEREST

The authors declare no competing interests.

DATA AVAILABILITY STATEMENT

Data sharing not applicable to this article as no datasets were generated or analysed during the current study.

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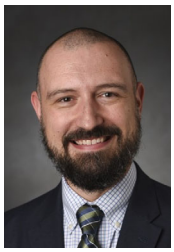

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