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Toward Sustainable Materials: From Lignocellulosic Biomass to High-Performance Polymers

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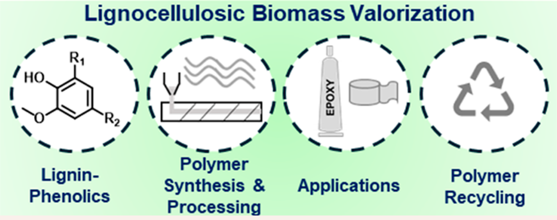

CONSPECTUS: Lignocellulosic biomass is an ideal feedstock for the next generation of sustainable, high-performance, polymeric materials. Although lignin is a highly available and low-cost source of natural aromatics, it is commonly burned for heat or disposed of as waste. The use of lignin for new materials introduces both challenges and opportunities with respect to incumbent petrochemical-based compounds. These considerations are derived from two fundamental aspects of lignin: its recalcitrant/heterogeneous nature and aromatic methoxy substituents. This Account highlights four key efforts from the Epps group and collaborators that established innovative methods/processes to synthesize polymers from lignin deconstruction products to unlock application potential, with a particular focus on the polymerization of biobased monomer mixtures, development of structure−property−processing relationships for diverse feedstocks, functional benefits of methoxy substituents, and scalability of lignin deconstruction.

First, lignin-derivable polymethacrylate systems were probed to investigate the polymerization behavior of methacrylate monomers and predict thermomechanical properties of polymers from monomer mixtures. Notably, the glass transition temperatures (T_gs) of lignin-derivable polymethacrylates (∼100−200 °C) were comparable to, or significantly above, those of petroleum-based analogues, such as polystyrene (∼100 °C), and the T_gs of the complex, biobased copolymers could be predicted by the Fox equation prior to biomass deconstruction.

Second, an understanding of structure−property relationships in polymethacrylates was applied to create performance-advantaged pressure-sensitive adhesives (PSAs) using phenolic-rich bio-oil obtained from the reductive catalytic fractionation of poplar wood. The use of actual lignin-derived monomers as the starting material was an important step because it underscored that nanostructure-forming, multiblock polymers could be readily made despite the complexity of real lignin deconstruction products. This work also highlighted that lignin-based phenolics could be used to make colorless/odorless PSAs, without complex separations/purifications, and still perform as well as commercial adhesives.

Third, an intensified reductive catalytic deconstruction (RCD) process was developed to deconstruct lignin at ambient conditions, and the deconstructed products were successfully employed in 3D printing. The reactive distillation-RCD process operated at ambient pressure using a low-volatility and biobased solvent (glycerin) as a hydrogen donor, which reduced capital/operating costs, energy use, and safety hazards associated with conventional RCD. Technoeconomic analysis showed that such optimization could lead to a 60% reduction in cost to make the PSAs described above.

Fourth, lignin-derivable bisguaiacols/bissyringols were explored as potential alternatives to petroleum-derived bisphenol A (BPA) in diamine-cured epoxy resins. A distinguishing feature of the lignin monomers (vs. BPA/bisphenol F [BPF]) was the presence of methoxy groups on the aromatic rings, and these methoxy moieties enabled tuning of application-specific properties, such as T_g, degradation temperature (T_d), and glassy storage modulus (E'), to achieve improved processing and performance. The lignin-derivable thermosets exhibited T_gs above 100 °C, T_ds above 300 °C, and E's above 2 GPa, all values that were comparable to those of BPA-/BPF-based analogues. Moreover, the methoxy groups on these lignin-derivable compounds sterically hindered hormone receptor binding and could mitigate many of the toxicity concerns associated with BPA/BPF.

This Account concludes with suggestions on future research needed to advance lignin-derived materials as sustainable and performance-advantaged alternatives by leveraging recycling/upcycling strategies and scaling-up/commercializing biomass waste.

■ INTRODUCTION

Polymeric materials are integral to many commercial products, and offer numerous benefits, such as low cost, durability, flexibility, and high strength-to-weight ratio.[1,2] Yet, there are several concerns associated with current materials and their monomeric precursors.[2−4] Polymers are primarily derived from

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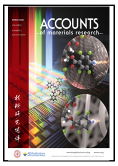

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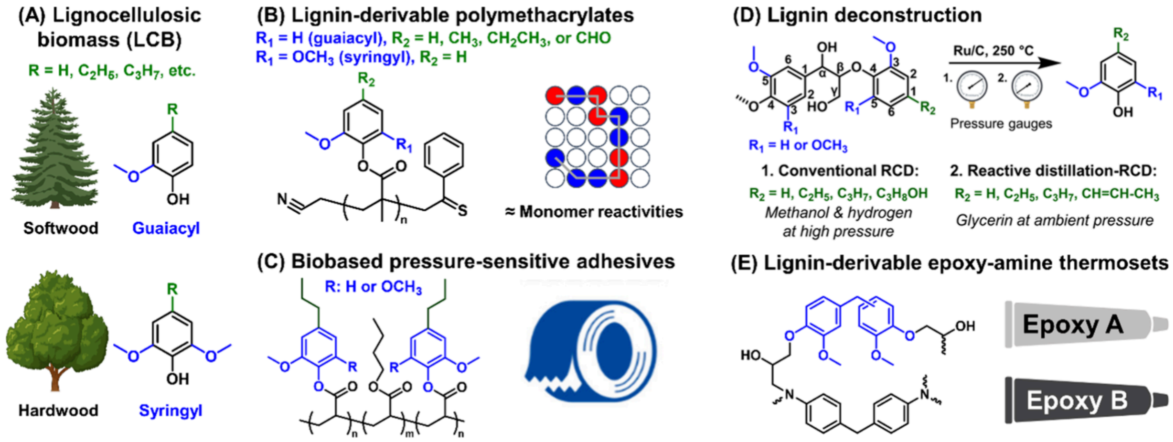


Figure 1. Overview of the LCB valorization to high-performance polymers. (A) LCB feedstocks (softwood and hardwood) and their major phenolic products. (B) Lignin-derivable polymethacrylates.[32] (C) Lignin-derived, pressure-sensitive adhesives.[34] (D) Lignin deconstruction methods: 1. conventional reductive catalytic deconstruction (RCD) (uses methanol as a solvent and hydrogen gas at high pressure) and 2. reactive distillation-RCD (uses glycerin as a combined solvent and hydrogen donor at ambient pressure).[35] (E) Lignin-derivable epoxy-amine thermosets.[33] Panels (A) and (E) were created in BioRender. Mahajan, J. (2025) https://BioRender.com/v21v441. Panel (C) was reproduced with permission from ref 34. Copyright 2018 American Chemical Society.

petroleum feedstocks, and their processing is a significant contributor to greenhouse gas emissions and volatile organic compound generation.[1,2] Many petroleum-based monomers are also toxic and associated with significant human health hazards. For example, styrene (used to make styrenic polymers)[2] and methylene diphenyl diisocyanate (commonly used in polyurethanes)[5] are both known carcinogens,[6] and bisphenol A (BPA) (widely used to make epoxy resins,[7] polycarbonates,[8] and polysulfones)[9] is a suspected endocrine disruptor.[10] These considerations, in addition to the non-renewable nature of petroleum resources and geopolitical considerations[1] (e.g., the uneven distribution of global resources),[1,11,12] suggest that sustainable and safer alternatives to petroleum-based monomers/polymers are necessary.

Lignocellulosic biomass (LCB) is the most abundant and accessible source of renewable aromatic precursors on the planet.[1,2] LCB is mainly comprised of cellulose (38−50 wt %), hemicellulose (23−32 wt %), and lignin (15−25 wt %).[13,14] Conventionally, pulp/paper mill and biorefinery approaches have been focused on the recovery of cellulose and hemicellulose for pulp, paper, and fuels.[1,2] During this process, lignin is separated as a byproduct (~100 Mt/year worldwide),[15] of which only ~1.7 Mt/year is isolated as technical lignin;[16] the remainder is generally landfilled or burned for energy.[2] Additional emerging sources of lignin are biofuel production and agricultural/food waste. ~62 Mt/year of lignin is generated during bioethanol production,[17] and shells from various nuts contain ~30−40 wt % lignin[18] with ~1 Mt/year of almond shells separated in California alone.[19]

Lignin is a low-cost and non-food-competing feedstock that is a viable option for renewable materials.[20−25] Currently, bulk lignin finds primary use in low-value applications, such as components in binders, dust suppressants, and cement additives, due to significant challenges that stem from lignin's chemical makeup.[15,26,27] The main components of lignin are *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) subunits, and the relative content of these three units varies with the source of biomass.[28−30] Softwoods contain a majority of G units; hardwoods include a mixture of G and S units; and grasses contain a mixture of H, G, and S units.[20−22] This chemical and structural heterogeneity is further amplified by interphenolic connections that can vary in type based on both the biomass source and processing history.[31] As a result, polymeric materials generated from bulk lignin tend to have inconsistent thermal/mechanical properties, as well as odor and dark color.[2] Many of these limitations can be overcome by breaking down lignin into mixtures of substituted mono-phenolics, and this outcome can be readily achieved via catalytic, pyrolytic, or enzymatic pathways.[20−22] Additionally, lignin deconstruction products generally contain functional handles, such as hydroxyl, methoxy, aldehyde, and carboxylic acid groups, that are useful for the development of new monomers and performance-advantaged polymers.[20−22]

The use of lignin-derived phenolics for new materials introduces both challenges and opportunities with respect to incumbent petrochemical-based compounds. These considerations are derived from two fundamental aspects of lignin: its recalcitrant/heterogeneous nature and aromatic methoxy substituents (Figure 1A). The compositional variability described above can lead to inconsistent material performance if not managed appropriately, and phenolics from deconstruction normally exist as mixtures that are expensive to separate into technical-grade, single-component streams; thus, they are more commonly available as a multicomponent bio-oil.[31] To overcome this limitation, reaction engineering approaches can enable the production of phenolic mixtures that can be cost-competitive with incumbent materials and lead to the generation of polymers with consistent/predictable properties.[32] Moreover, the functionality of lignin-aromatics (e.g., methoxy groups) can be leveraged to improve the thermal/mechanical properties of the polymers[33] and reduce the toxicity concerns associated with the monomers and possible leachates.[10]

This Account highlights innovative methods/processes to synthesize materials from lignin deconstruction products for higher-value applications, with a particular focus on understanding polymerization behavior of these phenolic mixtures, structure−property−processing relationships in biobased materials, the functional benefits of methoxy substituents, and scalable lignin deconstruction. To this end, four key efforts are highlighted. First, lignin-derivable polymethacrylates were explored to probe the polymerization of methacrylate

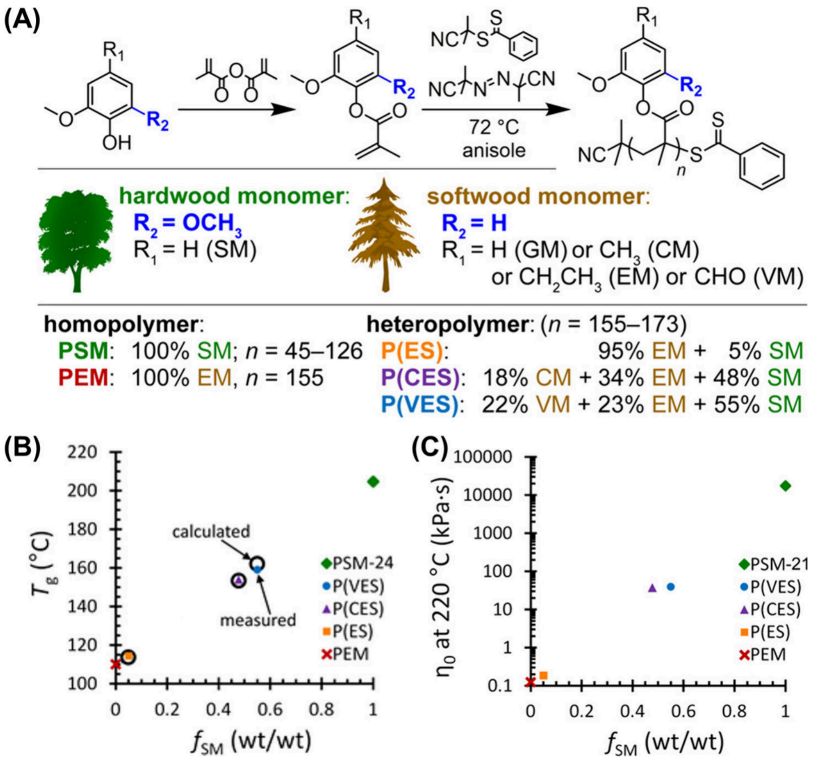


Figure 2. (A) The synthesis scheme for lignin-derivable methacrylate monomers and polymers. The abbreviations for lignin monomers were guaiacyl methacrylate (GM), syringyl methacrylate (SM), 4-ethylguaiacyl methacrylate (EM), vanillyl methacrylate (VM), and creosyl methacrylate (CM). The abbreviations for homopolymers were poly(syringyl methacrylate) (PSM) and poly(4-ethylguaiacyl methacrylate) (PEM). (B) Measured and calculated T_g as a function of SM content showed the wide-ranging and predictable T_gs available through hardwood and softwood lignin-based methacrylates. Differential scanning calorimetry data were shifted vertically and normalized to a slope of zero at $T > T_g$ for clarity. (C) η_0 (zero-shear viscosity) as a function of SM content. Reproduced with permission from ref 32. Copyright 2016 American Chemical Society.

monomers and predict thermal/mechanical properties of polymethacrylates from monomer mixtures (Figure 1B).[32] Second, this understanding of structure–property relationships in polymethacrylates was leveraged to create performance-advantaged, pressure-sensitive adhesives (PSAs) using substituted methoxyphenols generated via the reductive catalytic fractionation (RCF) of poplar wood (Figure 1C).[34] Third, an intensified reductive catalytic deconstruction (RCD) process was developed to deconstruct lignin at ambient conditions, and deconstruction products were successfully functionalized and employed in stereolithographic 3D printing (Figure 1D).[35] Fourth, lignin-derivable epoxy-amine thermosets were studied, wherein the methoxy moieties inherent in biomass aromatics enabled tuning of application-specific thermal/mechanical properties, such as glass transition temperature (T_g), degradation temperature, and storage modulus (Figure 1E).[33] Finally, this Account concludes by proposing several avenues to advance the development of lignin-based, high-performance polymers, with the goal of improving translation to commercial use and further reducing environmental impacts.

■ POLYMETHACRYLATES FROM LIGNIN-DERIVABLE PHENOLIC MIXTURES

A major challenge associated with producing cost-competitive materials from lignin monomers stems from lignin's heterogeneous composition. Typical lignin deconstruction reactions can produce a multitude of compounds, often with close boiling points, which makes separations to yield single-molecule product streams difficult or costly.[31] This constraint appears counter to most petrochemical monomer feedstocks that rely on specific compounds at relatively high purities, as opposed to mixtures, to generate polymeric products. Thus, it is critical to establish the predictable chemical and material behavior for materials derived from phenolic mixtures to enhance economic and processing competitiveness vs. incumbent systems.

Controlled polymerizations (e.g., atom transfer radical polymerization, reversible addition–fragmentation chain transfer [RAFT] polymerization) are promising because these methods allow the precise manipulation of polymer architecture, composition, and molecular weight.[32,36,37] RAFT polymerization is particularly attractive for the valorization of complex biomass feedstocks.[32,36] To generate useful materials from lignin-phenolics, homopolymers were synthesized from single softwood- and hardwood-derivable model molecules using RAFT polymerization to establish a baseline for evaluating the polymerization kinetics of monomer mixtures and assessing the thermal/mechanical characteristics of the resulting macromolecules.[32] Notably, the polymerization rates were nearly comparable across all model systems despite the additional methoxy groups on the hardwood-derivable compounds, and the hardwood-derivable polymethacrylates exhibited significantly higher T_gs than those of softwood-derivable versions, due to the additional methoxy moieties (Figure 2A).[32,36] For example, softwood-derivable poly(4-ethylguaiacyl methacrylate) (PEM) had a T_g of 110 °C, poly(guaiacyl methacrylate) (PGM) had a T_g of 120 °C, and poly(vanillyl methacrylate) (PVM) had a T_g of 130 °C, whereas hardwood-derivable poly(syringyl methacrylate) (PSM) had a T_g of 205 °C.[32] Thus, from a thermoforming

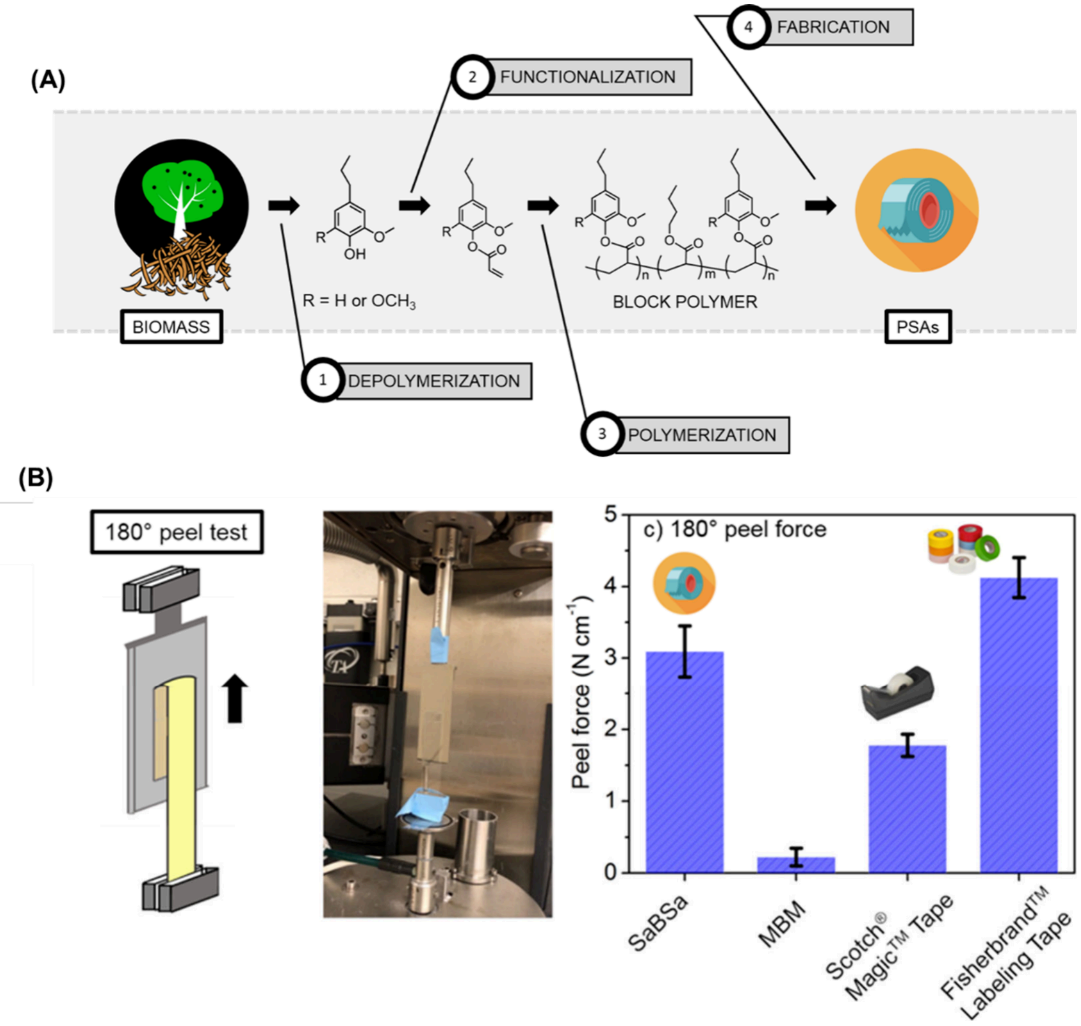
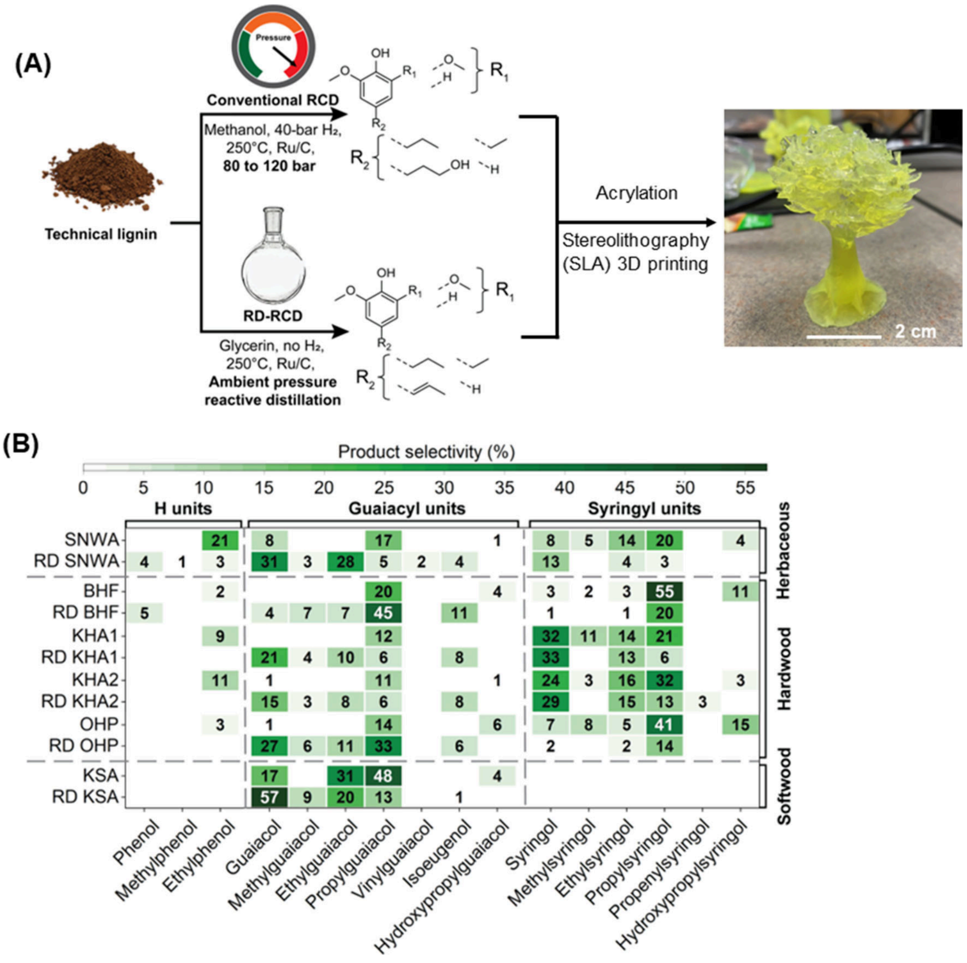


Figure 3. (A) Process from raw biomass to PSAs (4-propylsyringol, R = OCH$_3$; 4-propylguaiacol, R = H). (B) Illustration of ASTM-based 180° peel test and comparison of 180° peel force of lignin-derived SaBSa triblock polymer with commercial MBM, Scotch Magic tape, and Fisherbrand labeling tape. Reproduced with permission from ref 34. Copyright 2018 American Chemical Society.

standpoint, these lignin-derivable polymethacrylates could function as alternatives to polystyrene (T_g ∼ 100 °C) or similar macromolecules, while also offering environmental benefits with respect to the carcinogenicity and volatility of styrene in polystyrene production.[32]

The knowledge of the polymerization kinetics gained from the above homopolymerizations was used to study phenolic mixtures. To mimic the complexities of real-world bio-oils, hardwood-derivable syringyl methacrylate (SM) was mixed with softwood-derivable monomers (e.g., 4-ethylguaiacyl methacrylate (EM), vanillyl methacrylate (VM), creosyl methacrylate (CM)).[32] The corresponding heteropolymers (e.g., poly(EM-*co*-SM) [P(ES)], poly(CM-*co*-EM-*co*-SM) [P(CES)], poly(VM-*co*-EM-*co*-SM) [P(VES)]) with their respective weight compositions are shown in Figure 2A. The heteropolymers had compositions that represented possible fractions of monomer mixtures prepared from switchgrass organosolv lignin [weight fraction of SM (f_{SM}) = 0.48 for P(CES) and 0.55 for P(VES)].[32] As noted in the homopolymers, the polymerization rates and reactivity of SM were consistent with those of the softwood-derivable monomers.[32] This finding was crucial because it resulted in statistical polymers, and thus, the utilization of known monomer composition and T_gs of the respective homopolymers allowed estimations of the T_gs of these bioderivable copolymers using the Fox equation.[32] The predicted T_gs (using Fox equation) for P(CES) and P(VES) of 153 ± 3 and 162 ± 3 °C were consistent with the measured T_gs of 154 ± 1 and 159 ± 1 °C, respectively (Figure 2B).[32] These results suggested that the T_gs of lignin-based polymers can be predicted from knowledge of the feedstock and separation process.[32]

The Epps group also explored the processability of these bioderivable materials. A couple of the key attributes of polymer manufacturing include thermal degradation temperature, which guides the processing temperature window, and zero-shear viscosity (η_0), which describes how easily a material may deform at a given temperature.[32,36] The thermal degradation (in air) temperatures of the polymethacrylates were at least 100 °C greater than their T_gs, suggesting that these polymers are suitable for melt processing and thermoforming similar to polystyrene and other common, commercially relevant thermoplastic materials.[32,36] The lignin-derivable polymethacrylates also provided a wide space over which processability and deformation resistance can be optimized.[32] For instance, materials with η_0 of ∼0.1 kPa·s



	Phenol	Methylphenol	Ethylphenol	Guaiacol	Methylguaiacol	Ethylguaiacol	Propylguaiacol	Vinylguaiacol	Isoeugenol	Hydroxypropylguaiacol	Syringol	Methylsyringol	Ethylsyringol	Propylsyringol	Propenylsyringol	Hydroxypropylsyringol
SNWA			21	8			17			1	8	5	14	20		4
RD SNWA	4	1	3	31	3	28	5	2	4		13		4	3		
BHF			2				20			4	3	2	3	55		11
RD BHF	5			4	7	7	45		11		1		1	20		
KHA1			9				12				32	11	14	21		
RD KHA1				21	4	10	6		8		33		13	6		
KHA2			11	1			11			1	24	3	16	32		3
RD KHA2				15	3	8	6		8		29		15	13	3	
OHP			3	1			14			6	7	8	5	41		15
RD OHP				27	6	11	33		6		2		2	14		
KSA				17		31	48			4						
RD KSA				57	9	20	13		1							

Figure 4. (A) Overview of RCD processes and a 3D-printed tree using the SLA resin in a commercially available SLA printer. (B) Product selectivity for phenolic RCD and RD-RCD products. The nomenclature of lignin samples - KHA1: kraft hardwood CO_2 acidification 1, KHA2: kraft hardwood CO_2 acidification 2, OHP: organosolv hardwood solvent precipitation, BHF: biorefinery hardwood filtration, SNWA: soda non-wood mineral acidification. The sample name indicates conventional RCD (e.g., SNWA), and RD indicates reactive distillation (e.g., RD SNWA). Dashed lines separate feedstock type (horizontal lines) and lignin subunit type (vertical lines). Selectivities above 40% are shown in white text for clarity. Reproduced with permission from ref 35. Copyright 2022 American Association for the Advancement of Science.

(e.g., η_0 ∼ 0.2−40 kPa·s at 220 °C for SM-containing heteropolymers) are easily spread/shaped, and polymers with η_0 of ∼1,000−100,000 kPa·s (e.g., η_0 ∼ 17,000 kPa·s at 220 °C for homopolymer PSM) are highly deformation resistant.[32]

Altogether, the Epps group has demonstrated that high T_g (∼100−200 °C) and processable polymethacrylates can be synthesized from lignin-derivable phenolics that possessed complex and somewhat variable compositions to generate desirable polymers.[32] The findings revealed that the functionality (methoxy groups) on the lignin-derivable monomers impacted T_g but did not appreciably influence polymerization kinetics, and the T_g could be predicted from the composition of complex biomass feedstocks.[32]

■ PSAs FROM DECONSTRUCTED RAW LCB

Although model compounds provide an efficient starting point for understanding structure−property relationships in lignin-derivable materials, the ability to produce polymers from real lignin feedstocks is ultimately necessary to have a practical impact. The Epps group developed PSAs using real lignin-derived phenolics that demonstrated performance competitive to commercial products and highlighted the viability of lignin phenolics as a feedstock for next-generation materials.[34] It is also worth noting that these lignin-based PSAs lacked any dark colors or unpleasant odors typically found in lignin-derived products,[34] likely as a result of the target catalytic fractionation/deconstruction process.

One important class of commercial PSAs uses triblock polymers with glassy end blocks (e.g., poly(methyl methacrylate) [PMMA]) and a rubbery midblock (e.g., poly(*n*-butyl acrylate) [P*n*BA]). The Epps group employed lignin-aromatics to create biosourced PMMA mimics and bioderivable butanol to make the P*n*BA block (see Figure 3A for workflow).[34] The aromatics were generated from real poplar wood using RCF with minimal purification (i.e., cyclohexane-based extraction) to yield a mixture of 4-propylguaiacol and 4-propylsyringol (4pS) with relative mass fractions of 0.6 and 0.4, respectively, at a total yield of 10 wt % on the weight basis of dry poplar wood and purity of ∼91 wt %.[34] These phenolics were used to synthesize a high-molecular-weight, lignin-derived, triblock copolymer [poly(4pSA-*b*-*n*BA-*b*-4pSA) (SaBSa), which exhibited a number-average molecular weight (M_n) of 66.4 kg/mol, a dispersity ($Đ$) of 1.15, comparable to that of commercial poly(MMA-*b*-*n*BA-*b*-MMA) (MBM) [M_n ∼ 66.9 kg/mol, $Đ$ ∼ 1.12] and also reasonable for a RAFT polymerization.[34] More importantly, the impurities did not appear to be active during the polymerization and did not prevent the realization of higher-molecular-weight materials.[34] The resultant biosourced polymer (SaBSa) exhibited the nanoscale characteristics of the conventional, phase-separated, MBM system with an identical spherical morphology and similar domain spacing of ∼20 nm.[34] The bioderived PSA had peel/tack forces (∼2−4 N/cm as measured by ASTM protocols) that were comparable to those of commercial tapes such as Scotch Magic tape and Fisherbrand labeling tape (Figure 3B).[34] Importantly, this performance was achieved without any additional tackifiers, which could potentially simplify manufacturing and improve shelf life, while also indicating that the native functionality of lignin-aromatics could improve the surface properties of PSAs.[34]

LIGNIN DECONSTRUCTION INTENSIFICATION AND 3D PRINTING

Lignin or whole biomass can be deconstructed or fractionated via RCD or RCF, respectively. RCD/RCF processes typically use a metal catalyst (e.g., ruthenium on carbon (Ru/C)), hydrogen gas at high pressure (∼80−120 bar) at ∼200−250 °C, and an alcohol solvent (e.g., methanol, isopropanol) to concurrently dissolve/disperse and deconstruct the lignin.[35] A major challenge for scaleup is the safety hazards caused by the use of volatile, flammable solvents at high temperatures and pressures.[35] Additionally, high-pressure reactions are most amenable to batch processing and can have limited throughput due to the system size, which results in higher unit operation costs.[35] An intensified reactive distillation-reductive catalytic deconstruction (RD-RCD) process was developed by the Epps group to overcome such drawbacks.[35] RD-RCD employed biobased glycerin as both a low-volatility solvent and a hydrogen donor, which allowed RD-RCD to operate at ambient pressure (Figure 4A).[35] Thus, this new RD-RCD process had reduced safety hazards, capital requirements, and energy intensity relative to conventional RCD and was amenable to a continuous process.[35] Moreover, technoeconomic analysis (TEA) for PSA production demonstrated that RD-RCD provided a favorable minimum selling price (∼\$6000/ton−\$8000/ton) competitive with incumbent commercial PSAs.[35] Overall, intensified RCD reduced the cost of biobased PSA production from softwood Kraft lignin by up to 60% in comparison to the conventional, high-pressure RCD process.[35] A key driver of the improved unit economics was the process intensification as the operation combined the deconstruction of lignin and distillation/separation of phenolics in a single step.[35]

Phenolic product yields of RD-RCD were mostly comparable to those of conventional RCD for six technical lignin samples from various sources produced by different processes (e.g., Kraft, organosolv, thermomechanical pulping) and precipitation methods (e.g., CO_2 and mineral acidification, solvent precipitation, filtration).[35] As expected, softwood lignin samples yielded mostly G units, hardwood lignin samples created a mixture of G and S units, and herbaceous lignin samples formed a mixture of H, G, and S units using both RCD and RD-RCD processes (Figure 4B).[35] It was noted that the concurrent removal of phenolic products through distillation as they form can lead to differences in yields between RD-RCD and RCD.[35] The RCD technique produced higher phenolic product yields than RD-RCD for more deconstructable lignins like hardwood biorefinery lignin; on the contrary, RD-RCD resulted in greater phenolic yields than RCD for more recalcitrant lignins like softwood kraft lignin.[35] Additionally, RCD and RD-RCD techniques generated bio-oils with varying product distributions due to the volatility of the compounds.[35] As the S units are less volatile than H/G compounds and thus do not distill completely in the RD-RCD process, the RD-RCD products contained lower amounts of S compounds than RCD.[35] For example, the sum of the selectivities of S-type compounds from the same hardwood biorefinery lignin sample was 74 wt % after conventional RCD and 22 wt % after RD-RCD (Figure 4B).[35] Therefore, RD-RCD may be complementary to RCD depending on the products of interest, or more process optimization may be desirable to enable increased recovery of the S compounds in RD-RCD.[35]

We also showed feasibility by designing biorefinery using yard waste and conducted the “cradle-to-gate” life-cycle assessment (LCA) of a biorefinery that used yellow poplar forest residues (e.g., twigs, branchlets, leaves, bark) to produce phenolics and coproducts like *p*-xylene and furfural.[38] The LCA suggested that bark and twigs/branchlets as feedstock for the above chemical products had an advantage over traditional petroleum-based feedstocks, as greenhouse gas emissions were reduced by 849 and 1,110 kg CO_2-eq/metric ton of bark and twigs/branchlets, respectively.[38] Additionally, we demonstrated reduced environmental impacts of the biorefinery. Sensitivity analyses indicated that this biorefinery had better environmental performance (i.e., lower global warming potential) than conventional petrochemical production methods.[38]

To demonstrate the utility of the bio-oils obtained from RD-RCD, the group functionalized the products to make sustainable 3D-printing resins as potential alternatives to commercial petroleum-based materials.[35] The lignin-based resin, containing acrylated bio-oil (40 wt %), vanillyl alcohol diacrylate (40 wt %), photoinitiator (5 wt %), and commercially sourced 3D-printing resin (15 wt %), was 3D printed using stereolithography to produce cross-linked, well-defined objects (Figure 4A).[35] Although the biobased 3D-printing resin had a high content of potentially renewable components, recycling through mechanical or solvent-based reprocessing techniques would be challenging owing to the cross-linked structure. Thus, in a separate study using model compounds, the Epps and Boydston groups 3D-printed thermoplastic parts that were dissolvable in common organic solvents and enabled reprocessing of printed parts.[39] The thermoplastic parts used lignin-derivable monomers (e.g., 4-propylguaiacyl acrylate, SM) via vat photopolymerization, and these polymers displayed tunable mechanical properties (ranging from soft elastomers to rigid plastics).[39] As one example of the mechanical robustness of the biobased macromolecules, 4-propylguaiacyl acrylate-based 3D-printed materials had a breaking stress between 0.2 and 20 MPa and elongation-at-break (ε_b) between 5% and 1700%.[39]

Overall, 3D-printable biobased photoresins were prepared using products obtained from the catalytic deconstruction of technical lignin via a process intensification strategy that enabled ambient pressure reaction using a bioderived solvent with low volatility (i.e., glycerin).[35] The new RD-RCD process demonstrated economic advantages, scalability, and improved safety over conventional RCD/RCF approaches.[35]

BISPHENOL ALTERNATIVES FROM LIGNIN-DERIVABLE PHENOLICS

Numerous conventional polymers (e.g., polycarbonates,[8] polysulfones,[9] epoxy resins)[24] are derived from BPA, a

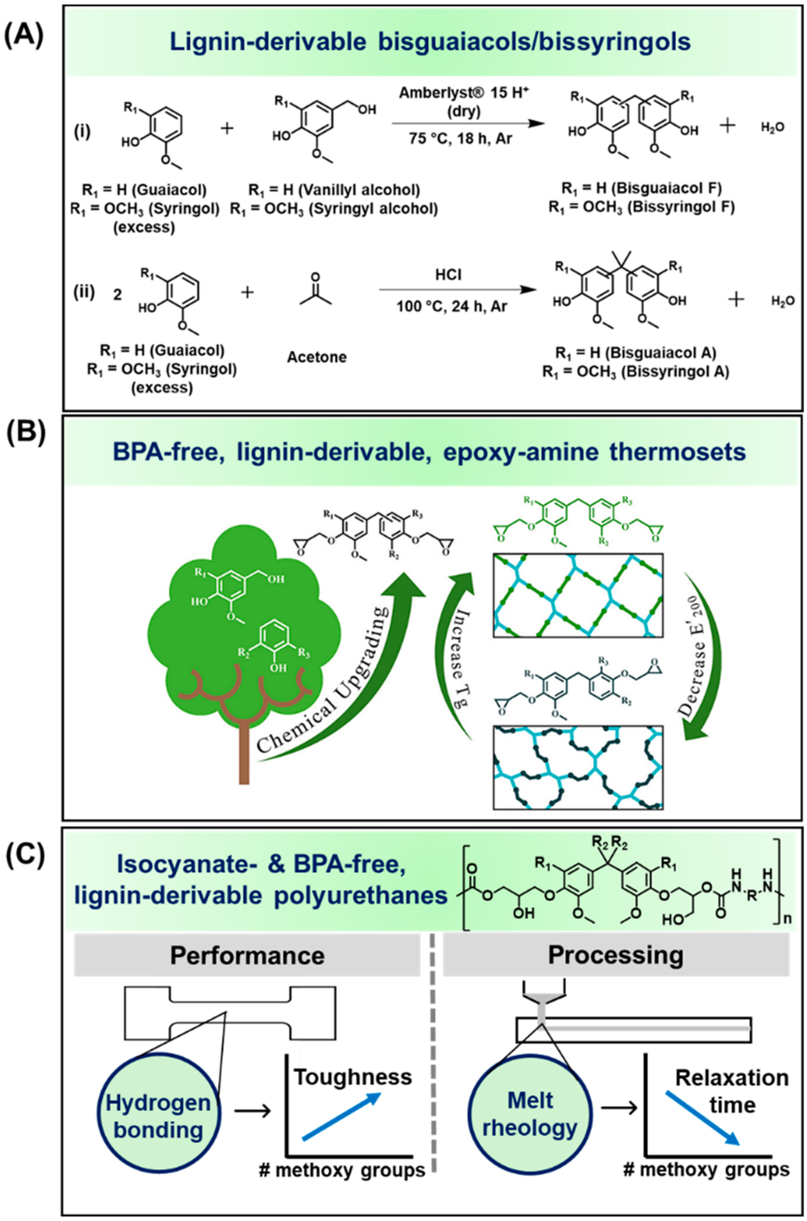


Figure 5. (A) Synthesis schemes of (i) unsubstituted bridging carbon-based bisguaiacols/bissyringols using guaiacol/syringol and vanillyl/syringyl alcohol and (ii) dimethyl-substituted bridging carbon-based bisguaiacols/bissyringols using guaiacol/syringol and acetone. (B) Lignin-derivable epoxy amine thermosets demonstrating tunable T_g and modulus by the relative number of methoxy moieties and the regioisomer content. (C) Lignin-derivable, thermoplastic, non-isocyanate polyurethanes with increased hydrogen bonding, toughness, and processability due to the methoxy functionality on lignin-aromatics. Panel (B) was reproduced with permission from ref 33. Copyright 2018 American Chemical Society. Panel (C) was reproduced with permission from ref 42. Copyright 2024 Royal Society of Chemistry.

suspected endocrine disruptor.[10,40] Although several other commercial bisphenols (e.g., BPF, bisphenol S, tetramethyl BPA) have been reported as alternatives to BPA, many of these bisphenols also have endocrine disruption potential.[10,40] Lignin-derivable bisguaiacols/bissyringols have emerged as viable alternatives to the above bisphenols, in which the functionality inherent in lignin-aromatics can improve the performance of the resultant polymers while also mitigating the toxicity concerns commonly associated with their petrochemical-derived counterparts.[33,41,42]

Lignin-derivable bisguaiacols/bissyringols were synthesized via acid-catalyzed direct aromatic substitution or aldehyde/ketone condensation reactions, with variability introduced in both methoxy-group content on the aromatic rings and substituents on the bridging carbons through synthetic choice (Figure 5A).[33,42,43] The former approach eliminated the use of hazardous bridging elements, such as formaldehyde, in favor of potentially biobased reagents.[33] These bisguaiacols/bissyringols were converted to diglycidyl ethers and then cured with 4,4′-methylenedianiline to make lignin-derivable epoxy-amine thermosets (Figure 5B).[33] Notably, the lignin-derivable thermosets displayed comparable thermal/mechanical properties to those of petroleum-based epoxy-amine thermosets, likely because of the structural similarities of the bisguaiacols/bissyringols to commercial bisphenols.[33] In particular, lignin-derivable thermosets exhibited T_gs ∼ 110−150 °C, temperatures of 5% weight loss (T_{d5})s ∼ 344−368 °C, storage moduli (E')s ∼ 2.0−3.2 GPa at 30 °C, and E's ∼ 15−46 MPa at 200

°C, while the BPF-based epoxy counterpart had $T_g \sim 138$ °C, $T_{d5} \sim 375$ °C, $E' \sim 2.4$ GPa at 30 °C, and $E' \sim 31$ MPa at 200 °C.[33] Interestingly, the uncured bisguaiacol/bissyringol diglycidyl ethers offered wide processing flexibility, as the precursors ranged from viscous liquids (with melting temperature [T_m] ~ 20 °C) ideal for composite applications to powders (with T_m ~ 110 °C) suitable for powder-coating applications.[33]

The methoxy motifs on lignin-aromatics were also leveraged to improve the performance and processing of non-isocyanate polyurethanes (NIPUs).[41,42] The methoxy groups in lignin-derivable NIPUs increased the hydrogen-bonding content (vs. BPA-/BPF-based counterparts), which led to enhanced toughness and ε_b.[41,42] These improvements in mechanical properties were obtained without detrimental effects on application-specific metrics, such as modulus, tensile strength, and thermal stability.[41,42] For example, bisguaiacol-based NIPU thermosets exhibited increased toughness and ε_b (toughness ~49−59 MJ/m^3 and ε_b ~ 195−280%) as compared to BPA-/BPF-based systems (toughness ~26−35 MJ/m^3 and ε_b ~ 85−165%).[41] Importantly, the processability of the lignin-derivable, thermoplastic NIPUs remained favorable, and the lignin-derivable NIPUs exhibited lower melt viscosities and had faster terminal relaxation times than the non-methoxy-containing (i.e., petroleum-based) NIPUs (Figure 5C).[42] Thus, these lignin-derivable materials possessed increased thermoforming potential in comparison to their petroleum-derived analogues while also offering improved thermomechanical stability.[42]

The methoxy substituents on bisguaiacols/bissyringols also played a crucial role in the reduction of toxicity by providing steric hindrance around the phenolic hydroxyl groups.[24,40] *In silico* (e.g., molecular docking simulations),[40] *in vitro* (e.g., MCF-7 assay - human breast cancer cell line),[44] and *in vivo* (e.g., chicken embryo assay)[44] studies suggested that hardwood-derivable aromatics created less-toxic bisphenols. Analysis of structure−activity relationships revealed that the bisphenols with two methoxy groups on each aromatic ring exhibited significantly reduced binding affinities toward estrogen receptor alpha in comparison to BPA.[24,40] Additionally, the bisguaiacols also showed lower genotoxicity and oxidative DNA damage than BPA due to the presence of these methoxy groups.[45] Together, these findings highlight the importance of functional handles (particularly methoxy groups) on lignin-aromatics, which can improve the thermal/mechanical properties of the polymers (like epoxy-amine thermosets/NIPUs), enhance or maintain processability, and reduce the toxicity concerns associated with many common bisphenol monomers.

CONCLUSIONS AND OUTLOOK

This Account highlights efforts from the Epps group and collaborators that established innovative methods/processes toward more sustainable polymeric materials from lignin deconstruction products. Major foci were to leverage the properties and functional handles of phenolic mixtures to control/tune polymer performance, develop structure−property−processing relationships, and improve process scalability. In one case, high T_g (~100−200 °C) polymethacrylates were synthesized via RAFT polymerization using monomers obtainable from lignin deconstruction products.[32] The methoxy groups on the lignin-derivable phenolics impacted T_g but did not appreciably influence polymerization kinetics.[32] Notably, T_g and η_0 could be predicted from the composition of the biomass feedstock, which can be readily determined prior to materials synthesis,[32] enhancing translation to commercial viability. This understanding of structure−property relationships in polymethacrylates also helped to create low-dispersity, nanostructured, renewable, triblock polymers from minimally purified poplar wood for PSA applications.[34] A fully biobased PSA displayed competitive performance with commercial tapes, which suggested the practical utility of lignin-based materials.[34] Additionally, an intensified RCD process was developed to deconstruct lignin at ambient conditions, and deconstruction products were successfully functionalized and employed in stereolithographic 3D printing.[35] The RD-RCD process demonstrated economic advantages, improved scalability, and increased safety over conventional RCD/RCF approaches.[35] The Epps group also explored lignin-derivable bisphenols (i.e., bisguaiacols, bissyringols) as potential alternatives to BPA/BPF.[33] The lignin-derivable epoxy-amine thermosets retained desirable thermomechanical properties versus those of BPA-/BPF-counterparts, likely due to the structural similarities of the bisguaiacols/bissyringols to BPA/BPF, while also reducing adverse health and safety considerations.[33] Altogether, the insights from this Account provide avenues for lignin valorization to obtain high-performance polymers.

There are numerous opportunities to further reduce the environmental impact of lignin-derived materials. Although biobased polymers improve sustainability, end-of-life management of lignin-derived polymers remains a major challenge. As such, future research should focus on the recycling/upcycling of biobased polymers. For instance, lignin-derivable polymethacrylates (e.g., PGM, PSM) were thermally depolymerized to their constituent monomers with high yields/purity.[46] The recovered monomers were then readily upcycled to phase-separated block polymers, which demonstrated a (solvent-free) strategy for upcycling lignin-derivable monomers over multiple life cycles.[46] Extension of such approaches to other thermoplastic lignin-derivable polymers will be crucial. It is also important to consider the recycling/reprocessing of cross-linked systems.[24,47,48] The incorporation of reversible chemistries (like imine/disulfide exchange)[24,47,48] is a promising approach to improve the sustainability of lignin-derivable thermosets. Furthermore, monomer/polymer synthesis and polymer recycling/upcycling should avoid volatile, toxic, and hazardous precursors/solvents. Ionic liquid-mediated polymer synthesis or deconstruction could be one potential option in this endeavor.[49] TEA/LCA should be incorporated to guide process decisions to balance the economic and environmental impacts of the products and technologies,[31,50,51] as "biobased" should not be considered a synonym for "sustainable" without supporting systems-level data/analysis.

The development of "processable" lignin-based materials for commercial applications is essential. One focus should be on synthesizing lignin-based thermoplastics with (entanglement) molecular weights comparable to their petroleum-based counterparts to achieve desirable performance[52] and to process such polymers using existing technologies (e.g., extrusion, molding). Lignin-derived materials can also be blended with other commercial (biobased) polymers, wherein the functional handles on lignin-derivable polymers can improve the processability/mechanical properties of both petroleum-derived and other biobased polymers.[42]

The future of lignin-based materials depends on the success of biorefineries in producing cost-competitive lignin-phenolics in bulk quantities.[20,22] The path forward should include innovations in biomass deconstruction, catalyst development, and lignin sourcing (e.g., food waste).[31] Variation in lignin sources comes with significant compositional differences between biomass inputs, necessitating reliable, rapid, and high-throughput characterization methods. For example, thermogravimetric analysis can efficiently determine the phenolic product yield obtained from whole biomass deconstruction and achieve accuracy/repeatability comparable to that of current approaches.[53] Additionally, to further increase the throughput and efficiency of lignin-deconstruction/separation, flow-reactor systems or other continuous configurations likely need to be employed.[31,54] Finally, separations is still a major challenge, and with the goal of avoiding distillation of high-boiling-point compounds, there are opportunities to develop advanced, low-energy separation techniques for lignin monomers, such as countercurrent chromatography and alternative membrane-based strategies.[31,55,56]

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ABBREVIATIONS AND SYMBOLS

BHF	biorefinery hardwood filtration
BPA	bisphenol A
BPF	bisphenol F
CM	creosyl methacrylate
$Đ$	dispersity
E'	storage modulus
ε_b	elongation-at-break
EM	4-ethylguaiacyl methacrylate
f_{SM}	weight fraction of syringyl methacrylate
η_0	zero-shear viscosity
FCM	food contact material
G	guaiacyl
GM	guaiacyl methacrylate
H	*p*-hydroxyphenyl
KHA1	kraft hardwood CO_2 acidification 1
KHA2	kraft hardwood CO_2 acidification 2
LCA	life-cycle assessment
LCB	lignocellulosic biomass
MBM	poly(MMA-*b*-*n*BA-*b*-MMA)
M_n	number-average molecular weight
NIPU	non-isocyanate polyurethane
OHP	organosolv hardwood solvent precipitation
P(CES)	poly(CM-*co*-EM-*co*-SM)
PCM	poly(creosyl methacrylate)
PEM	poly(4-ethylguaiacyl methacrylate)
P(ES)	poly(EM-*co*-SM)
PGM	poly(guaiacyl methacrylate)

P*n*BA	poly(*n*-butyl acrylate)
PSA	pressure-sensitive adhesive
PSM	poly(syringyl methacrylate)
P(VES)	poly(VM-*co*-EM-*co*-SM)
PVM	poly(vanillyl methacrylate)
RAFT	reversible addition−fragmentation chain transfer
RCD	reductive catalytic deconstruction
RCF	reductive catalytic fractionation
RD-RCD	reactive distillation-reductive catalytic deconstruction
S	syringyl
SaBSa	poly(4pSA-*b*-*n*BA-*b*-4pSA)
SLA	stereolithography
SM	syringyl methacrylate
SNWA	soda non-wood mineral acidification
T_{d5}	temperature of 5% weight loss
TEA	technoeconomic analysis
T_g	glass transition temperature
T_m	melting temperature
VM	vanillyl methacrylate
4pS	4-propylsyringol

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