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PAPER

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Turning renewable resources into value-added polymer: development of lignin-based thermoplastic†

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Productive uses of lignin, the third most abundant natural polymer, have been sought for decades. One especially attractive possibility is that of developing value-added products including thermoplastics based on lignin. This possibility warrants special attention due to growth of the modern biofuel industries. However, the polydisperse molecular weight and hyper-branched structure of lignin has hindered the creation of high-performance biopolymers. Here, we report the preparation and characterization of novel lignin-based, partially carbon-neutral thermoplastics. We first altered the molecular weight of lignin, either by fractionation with methanol, or by formaldehyde crosslinking. Crosslinking of lignin increases the molecular weight, exhibiting M_n = 31 000 g mol^{-1}, whereas that of as-received lignin is 1840 g mol^{-1}. Tuning the molecular weight of lignin enabled successful preparation of novel lignin-derived thermoplastics, when coupled with telechelic polybutadiene soft-segments at proper feed ratios. Characteristic to thermoplastic rubbers, free-standing films of the resulting copolymers exhibit two-phase morphology and associated relaxations in the dynamic mechanical loss spectrum. To the best of our knowledge this article is the first report to demonstrate phase immiscibility, melt-processibility, and biphasic morphology of soft and hard segments in a lignin-based copolymer for all feed ratios of two macromolecular components. The use of higher molecular weight lignin enhanced the resulting shear modulus due to efficient network formation of telechelic polybutadiene bridges. The storage modulus in the rubbery plateau region increased with increasing lignin content. The successful synthesis of novel lignin-based thermoplastics will open a new pathway to biomass utilization and will help conserve petrochemicals.

1. Introduction

Lignin, a complex substituted polyphenol found in plant biomass, is the most abundant natural aromatic polymer that accounts for up to 18–35% by weight of wood.[1] Lignin is generated by plants *via* photosynthesis using carbon dioxide from the atmosphere followed by aromatization and polymerization of carbohydrates[2] (Fig. 1), thus making lignin a renewable resource. Additionally, certain wood-rotting fungi can efficiently depolymerize and mineralize lignin to make it essentially biodegradable.[3] It has been estimated that the annual production of lignin on earth ranges from 5–36 × 10^8 tons.[4] Lignin is a valuable by-product of the paper and pulp industry produced in quantities exceeding 50 million tons annually,[5] but the majority of this by-product is currently disposed as low-cost fuel to meet the energy needs of the mill. In addition to the conventional paper and pulp industry, ethanol biorefineries also produce lignin as a by-product[6] and this vast quantity of lignin will be available from biorefineries in the near future. The lignin from biorefineries is currently used as a low-cost fuel, also. Therefore, significant attention has been given to a wide-scale use of lignin by-products in various applications.

Over 1 million tons of lignin products are currently produced annually for commercial applications including concrete additives, dyestuff dispersants, binders or surfactants for animal feed, dust control, and pesticides.[7,8] However, all of these lignin uses are relatively low-value applications and their market demand represents a negligible fraction of current lignin production rates. Lignin possesses significant potential for being a component of value-added products; however, there has been little success in creating lignin-derived high performance materials.

Various researchers have synthesized and characterized lignin-containing polymers. Rigid lignin molecules were blended with flexible polymers[9–15] and subsequently crosslinked,[16–21] or

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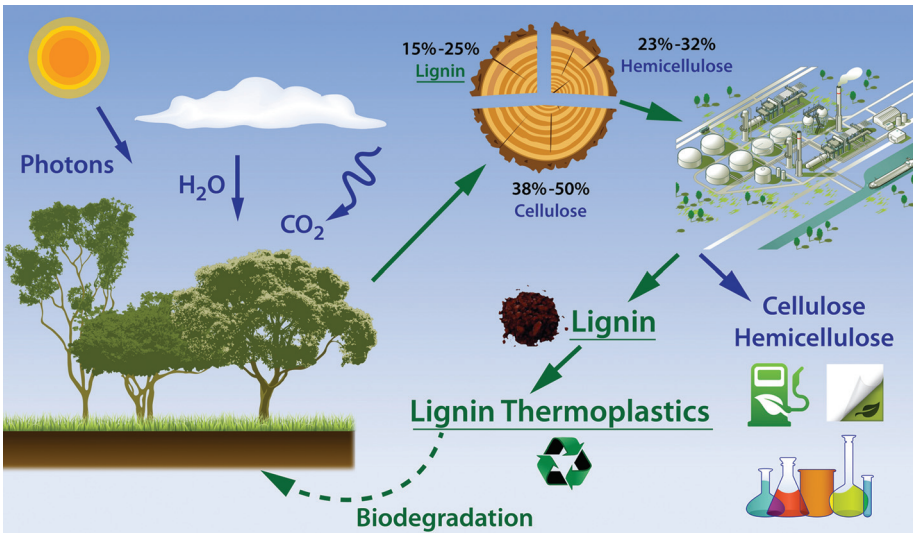

Fig. 1 Production of natural lignin and lignin-derived polymers and their recycling.

copolymerized to form polyurethane,[9,16–18,22–41] polyesters,[40,41] and other copolymers[42–51] of different morphologies including interpenetrating polymer networks. However, most of these reported lignin-derived polymers were thermosets and brittle materials, *i.e.* barely recyclable. The brittleness of these materials is related to the high crosslink density due to the low molecular weight of the lignin segments. The highly polydisperse molecular weight of lignin molecules was likely the primary hindrance to synthesizing recyclable high-performance lignin copolymers. Lignin-containing recyclable thermoplastics have not been developed, while such products will have a significant impact on lignin usage as new advanced bio-derived polymers.

The thermoplasticity of a polymer is governed by its structure and composition. A thermoplastic elastomer, polystyrene(PS)-*b*-poly(ethylene-*co*-butylene)(PEB)-*b*-polystyrene(PS) triblock copolymer commercialized by Kraton polymers and others is a good example of the polymer architecture engendering these unique thermoplastic and elastomeric properties. The PS hard segment, which possesses a high glass transition temperature (T_g), is typically microphase-separated *via* the PEB soft segment, a covalently-bonded low T_g segment. The hard PS block serves as thermally reversible crosslinks and the PEB soft phase gives rise to high elasticity.[52] The thermally reversible crosslinks make thermoplastic copolymers re-processable, thus, reusable and recyclable. Lignin thermoplastics should be composed of a lignin hard segment bridged with a low T_g soft segment. The lignin hard segment would possess mechanically robust properties similar to PS, while the soft segment would provide rubbery flow characteristics. Lignin thermoplastics can be designed as recyclable and completely biodegradable with the proper choice of soft segment copolymer composition. Proper utilization of renewable lignin to create lignin-based thermoplastics will be one of the great strategies to contribute to a sustainable society (Fig. 1). Ideally, a carbon-neutral copolymer system can be developed by this methodology, where nature-based soft rubbery segments such as microbe-grown soft molecules or *Hevea brasiliensis* latex-derived polyisoprene can be utilized with lignin-based hard segments and the product would be recyclable, perhaps, biodegradable as well.

Therefore, we pursued synthesis and characterization of novel lignin-based copolymers. Lignin was first modified *via* fractionation using solvent and crosslinking reaction with formaldehyde. The relationships of the lignin molecular weight and molecular weight distribution to the thermal response and the dynamic mechanical properties of the lignin copolymer were investigated. Lignin served as the hard segment of the copolymer, while dicarboxy-terminated polybutadiene was used as the soft segment. Dicarboxylic acid functional groups were chosen as reacting sites with hydroxyl groups on lignin since carboxylic acid is a common functional group in nature. As a next step, readily available bio-based soft segments such as polyhydroxy alkanoates and polypeptides could be used to make lignin-based thermoplastics as a completely bio-based renewable material. In addition, diene rubbers can be produced from renewable sources[53,54] and lignin-polybutadiene or -polyisoprene thermoplastics can potentially be completely renewable. The effect of lignin content in the copolymer as well as the synthetic route to the properties of the lignin thermoplastic copolymers was investigated.

2. Results and discussion

2.1 Lignin properties

Lignin hard segments provide rigidity to the rubbery thermoplastic copolymers and altering the properties of lignin is expected to have a significant impact on the resulting copolymer's properties. An experimental-grade solvent-extracted lignin from hardwood biomass[22,55–62] was used as-received (A-Lignin) in addition to the insoluble fraction after washing with methanol (W-Lignin) and its derivative form after reaction with formaldehyde (F-Lignin). A-Lignin showed a significant low molecular weight fraction from size exclusion chromatography (SEC) (Fig. 2), which resulted in M_n = 1840 g mol^{-1} with

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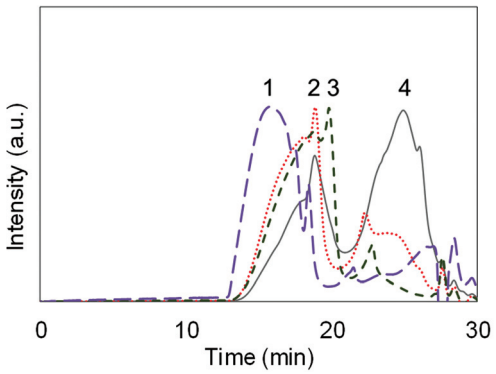

Fig. 2 SEC curves of 38 wt% F-Lignin-PBD(COOH)$_2$ copolymer (— —) (1), W-Lignin (·····) (2), F-Lignin (- - - ·) (3), and A-Lignin (———) (4).

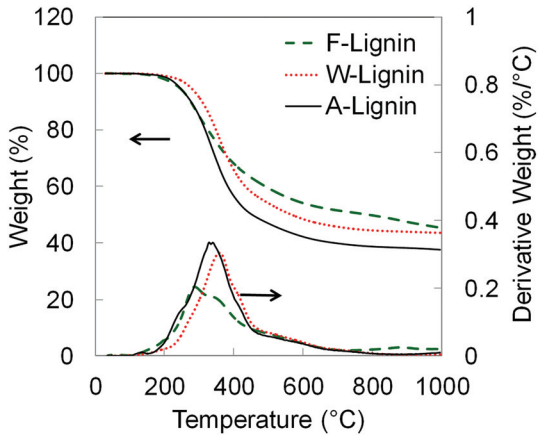

Fig. 3 TGA analysis of F-Lignin (dashed line), W-Lignin (dotted line), and A-Lignin (solid line) at 10 °C min^{-1} under N_2.

Table 1 Properties of modified lignins

	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI	T_g (°C)	Char yield at 600 °C (wt%)	Char yield at 1000 °C (wt%)
A-Lignin	1840	225 000	122	108	42	38
W-Lignin	8960	664 000	74.2	178	48	44
F-Lignin	31 000	641 000	20.7	—	54	45

polydispersity index (PDI) of 122 (Table 1). Washing with methanol removed a significant portion of the low molecular weight fraction (Fig. 2) and resulted in a M_n = 8960 g mol^{-1} with a PDI of 74.2, while the yield of W-Lignin after washing with methanol 5 times was 17%. The fractionation using methanol or some other solvents is known to remove low molecular weight fractions and increase the average molecular weight.[22,56–65] Formaldehyde is known to crosslink phenolic groups[66–68] and lignin[69–71] in acid or base catalyst. The formaldehyde crosslinking reaction increased the molecular weight of F-Lignin to M_n = 31 000 g mol^{-1} with a PDI of 20.7. This reaction with formaldehyde increased the high molecular weight fraction and decreased the low molecular weight fraction as compared to W-Lignin as shown in the SEC curve (Fig. 2). The initial isolated yield after precipitation, washing with methanol and drying at a reduced pressure was 54%, while further sequential washing with methanol a few more times reduced the yield to 28%. In spite of multiple dissolution and precipitation steps involved in the process, the higher isolated yield of F-Lignin than W-Lignin supports the effect of increasing molecular weight *via* reaction with formaldehyde. The overall measured molecular weight ranges are consistent with previously reported values.[22,60–62]

The increased high molecular weight fraction in W-Lignin and F-Lignin altered the thermal transition temperatures. The glass transition temperature (T_g) of W-Lignin increased to 178 °C compared to that of A-Lignin, 108 °C (Table 1), which are consistent with other reported T_g values of lignin.[72] The T_g of F-Lignin was not detected probably due to its higher molecular rigidity; it is possible the T_g of F-Lignin is greater than the onset of decomposition temperature, ~220 °C. The much lower T_g of A-Lignin than that of W-Lignin suggests that the free ends of low molecular weight species caused increasing free volume and decreased the resulting T_g. Increasing the molecular weight of lignin also altered the thermal stability (Table 1 and Fig. 3). The amount of char residue during thermogravimetric analysis (TGA) under nitrogen increased with an increase in lignin molecular weight. For example, at 600 °C, F-Lignin residue was 54 wt%, while W-Lignin and A-Lignin had 48 wt% and 42 wt% residue, respectively. The increasing amount of residue during TGA with the increasing molecular weight of lignin was also reported in the work of Thring *et al.*[65] The improved thermal stability suggests that these three lignin samples possess altered functionality and degree of crosslinking in addition to their molecular weight.

The chemical structures of A-Lignin, W-Lignin and F-Lignin were investigated using ^{13}C NMR analysis. Lignin ^{13}C NMR spectra (Fig. S2 in ESI†) were quantified by integration. The integral of the 162–102 ppm region was set as the reference, equal to 6.12 carbons, assuming that it includes six aromatic carbons and 0.12 vinylic carbons.[73,74] The chemical structures are reported as equivalences per aromatic ring (equiv./Ar) in Table 2 and the chemical shift assignments followed assignments from a few reported studies.[73–76] It should be noted that these lignins did not show signals between 90 and 102 ppm (Fig. S2†), indicative of the absence of sugars.[74] The majority of assigned carbon contents in Table 2 were similar to or within the error range for A-Lignin, W-Lignin, and F-Lignin. Since the starting lignin (A-Lignin) is the same material, solvent fractionation or formaldehyde modification may not give significantly different integral measurements. If the formaldehyde crosslinking follows the same mechanism as phenol crosslinking to synthesize resole resin (uses base catalyst),[68] it should form hydroxymethyl groups on the *ortho* or *para* position which would condense to a methylene bridge. As the *para* position of phenolic rings in lignin is occupied, the reaction can likely occur at the available *ortho* position of coniferyl or guaiacyl alcohol (cartoon 'g' in Table 2) and *p*-coumaryl alcohol (that is likely absent in the present sample and mostly exists in softwood and annual fiber lignins). Thus, the differences in the NMR signals are expected to be marginal. The integration of F-Lignin did not show an increase of $C_{Ar–C}$ at 140–123 ppm; rather, it showed an

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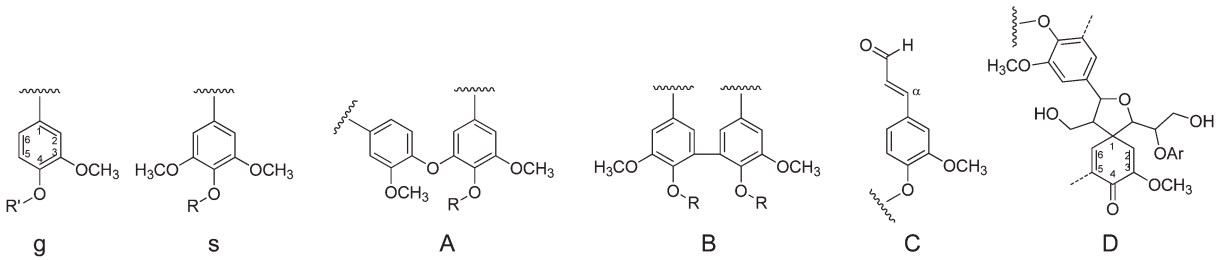
Table 2 Integration of ^{13}C NMR spectra

		Number of carbons/aromatic ring		
δ (ppm)	Assignment	A-Lignin	W-Lignin	F-Lignin
175–168	Aliphatic COOR	0.1	0.0	0.0
162–140	$C_{Ar–O}$	2.1	2.2	2.6
140–123	$C_{Ar–C}$	2.0	2.2	1.9
123–102	$C_{Ar–H}$	2.0	1.8	1.7
98–58	Aliphatic C–O	1.2	1.2	1.3
58–54	Methoxy OCH_3	1.6	1.5	1.5
49–0	Aliphatic C–C	0.6	0.5	0.3
157–151	g-4, s-3,5, A-3,5, B-3, C-α, D_g-3,6, D_s-3,5	0.5	0.5	0.9



increase of $C_{Ar–O}$ at 157–151 ppm. Since the methoxy peak integral of A-Lignin and F-Lignin at 58–54 ppm were essentially unchanged, the increase at 157–151 ppm may be caused by the increase of other segments such as g-4, C-α, D_g-6. Therefore, it is very likely that partial etherification of phenolic –OH groups has occurred. Lignin possesses various functional groups in comparison to phenol. It is possible that reactions other than those which occur during resole synthesis could occur from the condensation of hydroxymethyl groups in F-Lignin. F-Lignin also exhibited a reduction in $C_{Ar–H}$ and aliphatic C–C. The decreased $C_{Ar–H}$ indicates that more substitution occurred on the aromatic ring and the decreased aliphatic C–C also indicates a possible occurrence of dehydration. (Namely, a decrease in aliphatic C–C can only be explained by conversion of structures in cartoon 'D' (Table 2) to its equivalent form similar to cartoon 'C' (Table 2) with olefinic linkages.) Reduced aliphatic C–C links in F-Lignin decreases the loss of aliphatic segments during pyrolysis and increases the char yield in TGA experiments. Further detailed study of lignin-formaldehyde crosslinking mechanisms is not a focus of this study; however, it is worth investigating in the future due to the capability of tuning properties such as molecular weight and T_g *via* formaldehyde crosslinking.

2.2 Lignin-polybutadiene copolymers

Lignin-polybutadiene copolymers were synthesized and the impact of the synthetic methodology on their thermal response and mechanical properties were investigated. Lignin (A-Lignin, W-Lignin, F-Lignin, 22 wt%) was reacted with carboxytelechelic polybutadiene (PBD(COOH)$_2$, M_n 4200 g mol^{-1}). F-Lignin-PBD(COOH)$_2$ resulted in a solid derivative at room temperature and a free standing film could be fabricated (Fig. 4), while W-Lignin-PBD(COOH)$_2$ formed a highly viscous liquid and

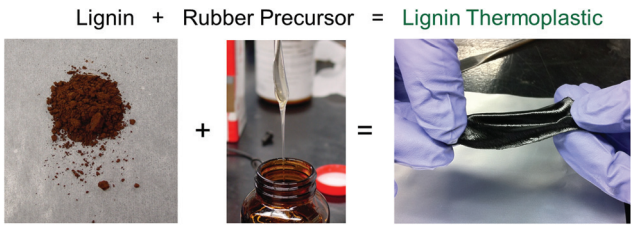


Fig. 4 Pictures of Lignin, PBD(COOH)$_2$, and F-Lignin-PBD(COOH)$_2$.

A-Lignin-PBD(COOH)$_2$ formed a viscous liquid at room temperature. Melt rheology was performed to study the effect of lignin molecular weight on the network formation in the resulting lignin-PBD interpolymer. As expected, a solid free standing film *versus* a liquid polymer at room temperature, F-Lignin-PBD(COOH)$_2$ adduct had significantly higher storage shear modulus (G′) and corresponding loss modulus (G″), which was approximately an order of magnitude higher than W-Lignin-PBD(COOH)$_2$ adduct and approximately four orders of magnitude higher than A-Lignin-PBD(COOH)$_2$ derivative (Fig. 5). F-Lignin-PBD(COOH)$_2$ showed a gel point (determined as G′ and G″ cross-over point) at lower angular frequency than that of W-Lignin-PBD(COOH)$_2$, while A-Lignin-PBD(COOH)$_2$ did not show any sign of a gel point in the measured frequency range, which is expected based on the form of these materials at room temperature (solid *versus* viscous liquid). The presence of a gel point at lower angular frequency for F-Lignin-PBD(COOH)$_2$ compared to A-Lignin-PBD(COOH)$_2$ indicates a significant degree of entanglement in the former copolymer formulation. Since the same reaction conditions and the same weight percentage of lignin were used, the modulus trend in this melt rheology data demonstrates the use of higher molecular weight lignin to enhance the resulting mechanical properties. The presence of a significant quantity of high molecular weight fraction in

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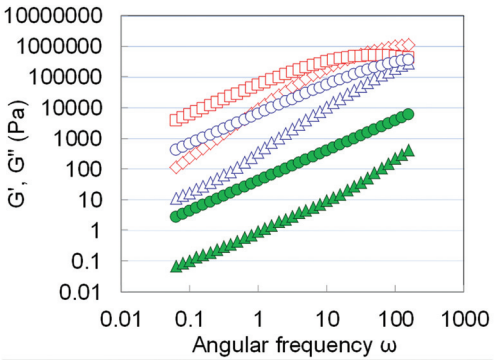

Fig. 5 Storage modulus (G′) and loss modulus (G″) of F-Lignin-PBD(COOH)$_2$ (◇, □), W-Lignin-PBD(COOH)$_2$ (△, ○), and A-Lignin-PBD(COOH)$_2$ (▲, ●) from melt rheology.

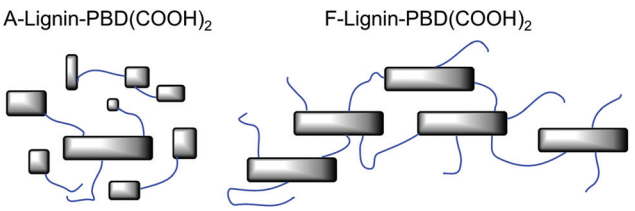

Fig. 6 Schematic representatives of F-Lignin-PBD(COOH)$_2$ and A-Lignin-PBD(COOH)$_2$.

F-Lignin facilitated formation of a more continuous network with telechelic polybutadiene bridges, whereas the very broad molecular weight distribution of A-Lignin resulted in a poorly networked structure (Fig. 6).

The effect of telechelic carboxylic acid end groups in the PBD segment was investigated using the same amount of F-Lignin under identical reaction conditions with a similar molecular weight of unfunctionalized polybutadiene (PBD, M_n 5000 g mol^{-1}) to obtain a product designated as F-Lignin-PBD. The product (F-Lignin-PBD) resulted in a viscous liquid form, while F-Lignin-PBD(COOH)$_2$ formed a solid material at room temperature (Fig. 4). F-Lignin-PBD showed no improvement in the storage modulus (Fig. 7), which suggests that no reaction occurred between F-Lignin and PBD. The physical blend of F-Lignin with PBD(COOH)$_2$ (no reaction performed, and designated as F-Lignin/PBD(COOH)$_2$-blend) also showed similar rheological values (*i.e.* G′, G″) to that of PBD(COOH)$_2$, which indicates that the reaction or interaction between bifunctional telechelic PBD and lignin is the reason behind enhanced shear modulus of the product. The reactive functionality of PBD soft segment in addition to the use of high molecular weight lignin was the key to form a reusable rubbery thermoplastic material with appreciable mechanical properties.

2.3 Effect of lignin contents in lignin-polybutadiene copolymers

F-Lignin-PBD(COOH)$_2$ gave the most promising material in this series; thus, the effect of lignin content in F-Lignin-PBD(COOH)$_2$ was further investigated. Synthesis of F-Lignin-PBD(COOH)$_2$ with varied F-Lignin content as 12, 22, 30, and 38 wt%

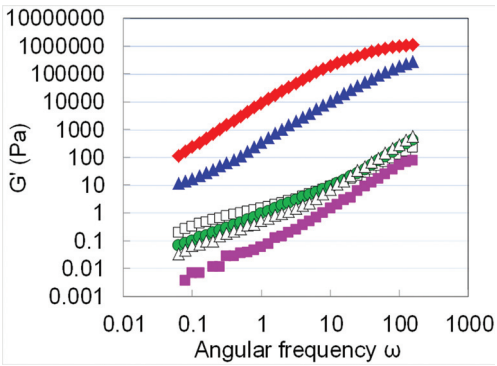

Fig. 7 Storage modulus (G′) of F-Lignin-PBD(COOH)$_2$ (◆), W-Lignin-PBD(COOH)$_2$ (▲), A-Lignin-PBD(COOH)$_2$ (●), F-Lignin-PBD (■), F-Lignin/PBD(COOH)$_2$ blend (□), and PBD(COOH)$_2$ (△), obtained from melt rheology.

with the same reaction conditions was performed to determine the effect of lignin content on the properties and thermal transition characteristics. All F-Lignin-PBD(COOH)$_2$ adducts with 12, 22, 30, and 38 wt% F-Lignin formed a free standing solid film at room temperature (Fig. 4). From TGA data, the F-Lignin content in F-Lignin-PBD(COOH)$_2$ adduct was determined using char yield at 600 °C. It was found that the products from 12, 22, 30, and 38 wt% F-Lignin feed ratios contained 18, 24, 28, and 37 wt% F-lignin, respectively. Considering some lignin loss during isolation and error in TGA data, F-Lignin content was confirmed to be reasonably close to the feed ratio (12, 22, 30, and 38 wt%); therefore, the feed ratio will be used as composition nomenclature for F-Lignin-PBD(COOH)$_2$ formulations in the remainder of this manuscript. Films of these F-Lignin-PBD(COOH)$_2$ copolymers were prepared *via* compression molding. The resulting films were characterized using a dynamic mechanical analyzer (DMA).

Two phase transitions were observed for all of these F-Lignin-PBD(COOH)$_2$ films in modulus-temperature response *via* DMA (Fig. 8). Through an extensive literature survey it has been concluded that, to date, there is no report of a lignin-based copolymer exhibiting two-phase thermoplastic dynamic mechanical behavior at varied lignin contents. Earlier reports by Glasser *et al.* showed two-phase dynamic mechanical response only at certain lignin-copolymer ratios for interpenetrating polymer networks from lignin-containing polyurethane and poly(methyl methacrylate)[16] or poly(butadiene glycol)-containing lignin polyurethane.[35] The storage modulus (E') of the rubbery plateau in the range of −60 to 20 °C increased as F-Lignin content increased in the copolymer composition, while E' showed similar values in the glassy region below −80 °C. The approximate midpoint of the rubbery plateau range, −30 °C, was chosen to represent the increased E' upon increased F-Lignin content (Table 3). For example, 38 wt% F-Lignin-PBD(COOH)$_2$ showed $E' = 8.2 \times 10^7$ Pa, while 12 wt% F-Lignin-PBD(COOH)$_2$ resulted in $E' = 2.5 \times 10^7$ Pa at −30 °C. The first transition between a glassy to a rubbery state should correspond to the T_g of polybutadiene segments. The first transition temperature for all of the F-Lignin-PBD(COOH)$_2$ samples determined by the first peak in E'' and tan δ ranged from −74 °C to −72 °C and −69 °C to −67 °C, respectively (Table 3). As measured by

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differential scanning calorimetry (DSC), the T_g of the PBD segment for all of the F-Lignin-PBD(COOH)$_2$ copolymers was in the range of −81 °C to −78 °C, which is in close agreement with the first transition temperature from DMA. A second transition in E'' was observed in the DMA data (Fig. 8 and Table 3), which corresponds to the flow or softening temperature, rather than the T_g of F-Lignin. As F-Lignin itself did not show a T_g value below the decomposition temperature, no other glass transition from these F-Lignin-PBD(COOH)$_2$ copolymers was observed in DSC. The flow temperature was much lower than the T_g of the hard segment probably due to the internal plasticization of F-Lignin by polybutadiene segments and imperfect network formation.

The SEC curve for 38 wt% F-Lignin-PBD(COOH)$_2$ shifted toward shorter retention times than for F-Lignin (Fig. 2), which confirms the network formation of F-Lignin with PBD(COOH)$_2$. The broad distribution in the high molecular weight range prevented the software from calculating the molecular weight. SEC could not be performed for the other F-Lignin-PBD(COOH)$_2$ samples with different F-Lignin content due to poor solubility in DMF or other common SEC solvents. Considering polybutadiene is almost insoluble in DMF, 38 wt% F-Lignin-PBD-(COOH)$_2$ being soluble in DMF also indicates the formation of F-Lignin-PBD(COOH)$_2$ copolymer network rather than being a simple blend. The lignin segment in 38 wt% F-Lignin-PBD-(COOH)$_2$ aided dissolution in DMF. 38 wt% F-Lignin-PBD-(COOH)$_2$ also showed a low molecular weight fraction in SEC curve. The low molecular weight fraction probably corresponds to unreacted or partially reacted PBD(COOH)$_2$ because the peak in the long retention time did not correspond to the peak of F-Lignin. The existence of the low molecular weight PBD (COOH)$_2$ fraction explains the imperfect connectivity of F-Lignin-polybutadiene network, which resulted in a flow temperature lower than the presumed T_g of the lignin hard segments.

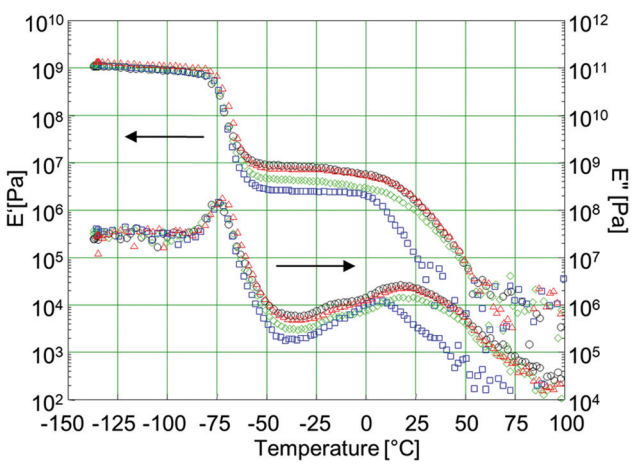

Fig. 8 DMA of F-Lignin-PBD(COOH)$_2$ with varied F-Lignin content (38 wt% ○, 30 wt% △, 22 wt% ◇, 12 wt% □).

2.4 Lignin-polybutadiene network

Spectroscopic characterization of Lignin-PBD(COOH)$_2$ chemistry with A-Lignin, W-Lignin, F-Lignin and PBD(COOH)$_2$ could not be confirmed by ^{1}H NMR, ^{13}C NMR, and FTIR due to very poor resolution in the spectra, likely caused by poor solubility in NMR solvent and hydrogen-bonding interactions. FTIR spectra showed potassium carboxylate peak (~1590 cm^{-1}) or carboxylic acid peak (~1710 cm^{-1}) in Lignin-PBD(COOH)$_2$ (Fig. S3 in ESI†), indicative of a significant fraction of uncrosslinked PBD(COOH)$_2$ or PBD(COOK)$_2$ present in the copolymer. The presence of dicarboxy-polybutadiene reinforces the imperfect connectivity of F-Lignin-PBD(COOH)$_2$ and the low flow temperature in DMA. A poor leaving group (–OH) of carboxylic acid, no applied vacuum to remove water to shift the reaction equilibrium, and relatively low reaction temperature hinders the condensation reaction and probably prevented completion of lignin and PBD(COOH)$_2$ condensation reactions.

Potassium salt (K^+), that comes from the catalyst used in the reaction, could be another factor to aid bridging PBD(COOH)$_2$ and F-Lignin. When PBD(COOH)$_2$ was treated with excess potassium hydroxide (KOH), PBD(COOH)$_2$ transformed from a viscous liquid to a solid gel due to ionic bonding of K^+ carboxylate. Since KOH was used as a base catalyst in the reaction of lignin with PBD(COOH)$_2$, the remaining K^+ in the copolymer might help to bridge PBD(COOK)$_2$ and lignin. To understand the effect of K^+, 22 wt% F-Lignin-PBD(COOH)$_2$ was dissolved in tetrahydrofuran (THF) and sulfuric acid was added to the solution to exchange K^+ to proton. The solution was washed with water several times to remove extra salts or acid. Melt rheology of the resulting copolymer showed that G', G'', and viscosity were lower than that of original 22 wt% F-Lignin-PBD(COOH)$_2$ but higher than that of F-Lignin/PBD(COOH)$_2$ blend (Fig. 9). The decrease in rheological properties suggests that the presence of K^+ salt might have contributed to the enhancement of the properties of the copolymer probably by forming K^+ linkages between carboxylates on polybutadiene and phenolic salts on lignin (Fig. 10(B) and (C)). Although much care was taken to prevent an ester hydrolysis upon addition of sulfuric acid, it is possible that such a reaction occurred to a small extent. Irrespective of the possible side reactions, FTIR and rheology data suggests that lignin bridged with telechelic polybutadiene *via* both covalent (Fig. 10(A)) and ionic bonding (Fig. 10(B)) as well as potential formation of an interpenetrating network (Fig. 10(C)) due to the presence of K^+. Since all of the reactions in this manuscript used the exact same amount of base in the

Table 3 Storage modulus at rubbery plateau and transition temperatures from DMA

	E' (Pa) at −30 °C	1st transition from E'' (°C)	1st transition from tan δ (°C)	2nd transition from E'' (°C)
12 wt% F-Lignin-PBD(COOH)$_2$	2.5×10^7	−74	−67	8
22 wt% F-Lignin-PBD(COOH)$_2$	4.2×10^7	−73	−67	24
30 wt% F-Lignin-PBD(COOH)$_2$	7.2×10^7	−72	−67	22
38 wt% F-Lignin-PBD(COOH)$_2$	8.2×10^7	−74	−69	22

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exact same scale, all of the observed trends are valid despite the relative contributions from ester and ionic linkages. The effect of salt concentration and type was not further investigated in this work but the concept of ionic linkages between lignin and polybutadiene could prove advantageous in stimuli-responsive polymer systems, especially those containing altered lignin functionality. We plan to further investigate the effect of salts for blending F-Lignin and PBD(COOH)$_2$ in the future.

3 Experimental

3.1 Modification of lignin

Experimental-grade solvent extracted lignin from Kraft-processed hardwood biomass (Oak variants) was obtained from lignin-based carbon fiber research group at Oak Ridge National Laboratory and used as-received (A-Lignin), washed with methanol (W-Lignin), and reacted with formaldehyde (F-Lignin). In methanol washing, the insoluble fraction of lignin in methanol (Mallinckrodt Chemicals) was collected *via* filtration on a fritted funnel using an aspirator and subsequent drying in a reduced pressure at 60 °C for 18 h (W-Lignin). An example of lignin-formaldehyde crosslinking reaction is described as follows: A-Lignin (100 g) is dissolved in THF (700 mL, BDH Chemicals) along with 4 wt% formaldehyde solution (120 mL, 0.16 mol of formaldehyde, Aldrich) and potassium hydroxide (KOH, 4.5 g, 0.08 mol, Alfa Aesar) in 1 L round-bottomed flask equipped with a magnetic stirrer and a condenser. The reaction was performed at 70 °C for 4 h. The resulting reaction solution was filtered using filter papers (Whatman #2) to remove insoluble chunks and precipitated into isopropanol (Mallinckrodt Chemicals). The precipitated lignin was collected *via* filtration and subsequent washing with methanol on a fritted funnel using an aspirator. The produced F-Lignin was dried in a reduced pressure at 60 °C for 18 h. The longer reaction time of lignin with formaldehyde was also attempted; however, insoluble particles increased as reaction time increased. Thus, F-Lignin reaction time was chosen as 4 h.

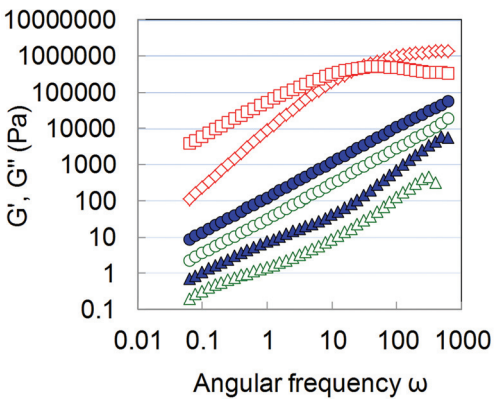

Fig. 9 Storage modulus (G′) and loss modulus (G″) of F-Lignin-PBD(COOH)$_2$ (◇, □), acid treated F-Lignin-PBD(COOH)$_2$ ▲, ●), and F-Lignin/PBD(COOH)$_2$ blend (△, ○) from melt rheology.

3.2 Synthesis of lignin-polybutadiene copolymers

Lignin (A-Lignin, W-Lignin, F-Lignin, 22 wt%, 1.40 g) was reacted with dicarboxy-terminated polybutadiene (PBD-(COOH)$_2$, M_n 4200 g mol^{-1}, Aldrich, 5 g) with KOH (0.133 g, 2.4 mmol) in 1,4-dioxane (~40 mL, Alfa Aesar) for 24 h at 100 °C. Different amount of F-Lignin (12 wt%, 0.68 g; 30 wt%, 2.14 g; 38 wt%, 3.06 g) with the same reaction condition was also investigated, and F-Lignin (22 wt%, 1.40 g) was reacted

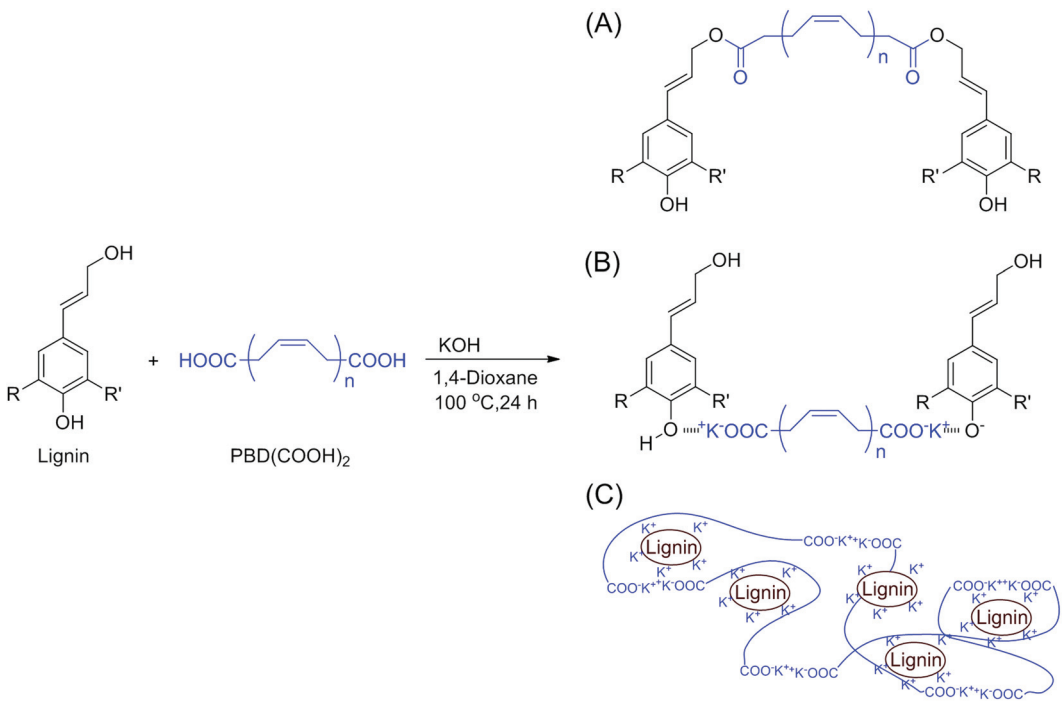

Fig. 10 Lignin-polybutadiene linkage: ester linkage (A), ionic linkage (B), and interpenetrating network (C).

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with unfunctionalized polybutadiene (PBD, M_n 5000 g mol^{-1}, Aldrich, 5 g) in the same condition as a control. All of the resulting lignin-polybutadiene copolymers were isolated *via* precipitation into methanol and dried under reduced pressure at 50 °C for 18 h.

3.3 Polymer characterization

Films of F-Lignin-PBD(COOH)$_2$ copolymers were prepared using a hot press at 120 °C. High-temperature size exclusion chromatography (HTSEC) was performed on a Waters GPCV2000 equipped with three Polymer Labs PLgel Mixed C columns in series, a differential refractometer (λ = 880 nm), a Precision Detectors two-angle light scattering detector (λ = 682 nm), and Waters viscometer operating at 60 °C. Waters Alliance GPC 2000 software was used to collect data, which was subsequently analyzed using Waters Empower software in which a conventional calibration curve based on low-PDI poly(2-vinylpyridine) standards (1620–256 000 g mol^{-1}) was used to evaluate molecular weight characteristics. DMF was used as the eluent at a flow rate of 1.0 mL min^{-1}. TGA measurements were performed on Q-500 thermogravimetric analyzer (TA Instruments) under nitrogen at a heating rate of 10 °C min^{-1}. DSC (Q-2000 TA Instruments) determined glass transition temperatures at a heating rate of 10 °C min^{-1} under nitrogen. Glass transition temperatures are reported as the transition midpoints of the heat capacity change during the third heating cycle. Viscosities of the lignin-polybutadiene copolymers were measured using TA Instruments AR G2 rheometer. A 25 mm parallel plate geometry was used, and rheological analysis was performed at a 5% strain amplitude at 100–0.01 Hz with a 1000 μm gap. Dynamic mechanical analysis (DMA) was performed with a TA Instruments RSA 3 dynamic mechanical analyzer in dynamic temperature ramp mode from −135 to 200 °C at 0.1% strain and a frequency of 1 Hz with a heating rate of 10 °C min^{-1}. Portions of 22 wt% F-Lignin-PBD(COOH)$_2$ were dissolved in THF and sulfuric acid (2 equivalents to carboxylate functional groups in 22 wt% F-Lignin-PBD(COOH)$_2$) aqueous solution was added. The resulting solution was dried and rinsed with DI water several times to remove unbound salts or acid. ^{1}H and ^{13}C NMR were performed *via* Varian 500 MHz using DMSO-d$_6$ as NMR solvent. For the quantitative ^{13}C NMR of A-Lignin, W-Lignin, and F-Lignin, 200 mg of lignin in 0.5 mL DMSO-d$_6$ with 2.5 mg of chromium(III) acetylacetonate (0.01 M) was placed in a NMR tube and a total of 20 000 scans were collected with a 90° pulse width, a 1.4 s acquisition time, and 1.7 s relaxation delay.[75] FTIR was performed in ATR mode with 32 scans using OPUS FTIR instrument.

4. Conclusions

Higher molecular weight lignins were successfully prepared *via* reaction with formaldehyde (F-Lignin) or washing with methanol (W-Lignin). The use of high molecular weight lignin facilitated preparation of free standing films of lignin-based thermoplastic. The properties of higher molecular weight lignin systems were enhanced as evidenced by the melt rheology. The presence of a significant portion of high molecular weight fraction in F-Lignin enabled formation of a more continuous network with telechelic polybutadiene bridges, whereas the very broad molecular weight distribution of A-Lignin formed a poorly networked structure. Two-phase viscoelastic behavior was observed for films of F-Lignin-PBD(COOH)$_2$ with varied F-Lignin content. As F-Lignin content increased, the storage modulus at rubbery plateau increased. The flow temperature of those films of F-Lignin-PBD(COOH)$_2$ was much lower than the presumed F-Lignin T_g, probably due to the presence of ionic linkages rather than all covalent linkages and nonbridging PBD (COOH)$_2$, which plasticizes the copolymer and reduces the flow temperature. Considering future use of bio-polymers as a soft segment, we chose carboxylic acid terminated polybutadiene, where carboxylic acid is a common functional group in nature. The alternation of the functional groups such as acyl chlorides or isocyanates would provide robust mechanical strength *via* the efficient formation of covalent bonding, which would increase the flow temperature to as high as the T_g of lignin. Further investigation of lignin-thermoplastics with different types of soft segments either using different functional groups or other sustainable polymers are currently underway. These types of lignin thermoplastics could be used in applications similar to styrenic thermoplastic elastomers such as (i) replacement for vulcanized rubber, (ii) adhesives, sealants and coatings, (iii) polymer blends, (iv) bitumen modification, and (v) modifiers for thermosets.[77] This success of synthesizing thermoplastics from lignin opens up new avenues to incorporate lignin as a component of value-added polymers while utilizing renewable resources.

Author contributions

F.S.B., J.M.P., M.K., and A.K.N. designed research; T.S., R.H.B., M.A.H., D.L.P., and J.M.M. performed research; T.S., R.H.B., M.A.H., D.L.P., J.M.M., J.M.P., and A.K.N. analyzed data; T.S., M.A.H. and A.K.N. wrote the paper.

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