An Approach towards Tailoring Interfacial Structures and Properties of Multiphase Renewable Thermoplastics from Lignin–Nitrile Rubber

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Abstract

Lignin-derived thermoplastics and elastomers with both versatile performance and commercialization potential have been an elusive pursuit for the past several decades. Lignin content has been limited to about 30 wt. %, often requiring chemical modification, solvent fractionation of lignin, or prohibitively expensive additives. Each of these factors is a deterrent to industrial adoption of lignin-based polymers, limiting the potential of this renewable resource. Herein we describe high-performance multiphase thermoplastics made with a blend of 41 wt. % unmodified industrial lignin and low-cost additives in a matrix of general-purpose acrylonitrilebutadiene rubber (NBR). Hardwood soda lignin (HSL) and softwood Kraft lignin (SKL) were blended under high shear conditions with NBR, carbon black (CB), polyethylene oxide (PEO), boric acid (BA), and dicumyl peroxide (DCP). This combination with SKL lignin in the proper proportions resulted in a thermoplastic with a tensile strength and failure strain of 25.2 MPa and 9%, respectively; it exhibited an unexpected tensile yield, similar to that of ABS, a commodity thermoplastic. The analogous HSL lignin compositions are tough materials with tensile strengths of 7.3-16.7 MPa and failure strain of 80-140 %. The contrasting ductility and yield stress behavior were analyzed based on the compositions' morphology and interfacial structure arising from the chemical nature of each lignin studied. The roles of CB as a reinforcement in the rubbery phase, DCP and BA as cross-linkers to create multiphase networks, and PEO to promote the adhesion and compatibility of lignin in commercial-grade NBR are also discussed in detail.

1. Introduction

Increasing marketplace volatility, resource scarcity, and global climate change have created an immediate need to replace carbon-polluting, petroleum-derived products with nonfood, biorenewable alternatives. Lignin, a major component of biomass and the least valued coproduct of the paper and biorefining industries, is a promising feedstock to address this issue (1, 2). Significant interest has been shown in creating pharmaceuticals, fuels, and plastics from lignin. In the recent past, researchers have demonstrated that lignin can be used directly to create a number of plastic resins, but most have had lignin content below one-third of the total composition weight, have required additional chemical modification steps to induce compatibility with blend polymers, or have exhibited reduced final mechanical properties (3, 4). In many cases, lignin has been used as low-cost diluent filler in polymer matrices with an emphasis on reducing the negative impacts of lignin addition, rather than on using it to improve performance.

The coarse morphology of lignin-filled polymer systems can be described as a combination of spaghetti-like polymer chains or strands and meatball-shaped lignin aggregates (Fig. 1). Flexible polymers do not adhere to lignin without some sort of dipole, ionic, or covalent bonding interaction; without it, composites easily fall apart under thermal, shear, or mechanical strain. When properly bound, however, lignin can impart significant rigidity to the softer polymer, improving mechanical properties. In the past, we reported two thermoplastics that used the inherent functionality of lignin to create covalently bound networks with a suitable copolymer. These plastics, a polyester (5) and a polyurethane (6), represented a significant step forward into using unmodified technical lignins, but the produced materials had poor mechanical properties, leading us to seek alternative approaches to make use of lignin as a feedstock for next-generation bioplastics.



Fig. 1. Spaghetti and meatball morphology of lignin–polymer blends, very similar to the morphology of thermoplastic elastomers like Styrene-Butadiene-Styrene (SBS) block copolymer in which the hard polystyrene segment (meatball) is covalently bound to the flexible polybutadiene segment (spaghetti).

Previous methods to produce lignin-based polymers have required a number of chemical modification steps using in-solution reactions. This approach introduces solvent waste, requires energy- and time-intensive separations and solvent removal, and renders most formulas cost-prohibitive to industry (Fig. 2*A*). Our new method exploits the inherent reactivity and large interfacial volume of nanodispersed lignin molecules to react with a variety of host polymers and additives in the melt phase, using a suitable blend polymer as both a viscous solvent and a matrix for the final composite material. The reactive processing method we have developed allows for combining all components in a single reactor vessel (melt-mixer or extruder, in this case), saving time and energy, and eliminating unnecessary and wasteful chemical pretreatments and separations (Fig. 2*B*).

In much of the previous work, lignin has been used as a catch-all term. We presume this mindset to be detrimental to the advancement of lignin-based polymers and other value-added products. Individual technical lignins vary greatly, and characterization based on their as-received state is very important. Variation of lignin extraction methods (7, 8) all produce different characteristics, the chemistry of each dictating the ability of these lignins to interact favorably or unfavorably in polymer blends. In addition, different plant species each also produce lignins with a high variability in functional groups, with phenols being some of the most abundant and most useful (Fig. 3).(9)

In the past, researchers used chemical modification to overcome the incompatibilities of lignins used in some polymer work, often because their detailed characterization and understanding of their self-assembly were not considered. In other attempts, lignin–polymer blends were well characterized but lignin loading was very low (1 %), materials were cast from solvent, and the lignin was simply described as "Kraft" with no indication of biomass source (10). This is not representative of material that could be produced using commercial processes, as there is no accounting for miscibility changes due to temperature or high shear. Indeed, in most of the work lignin is treated as a material accessible only through dissolution in solvents, when in reality a number of lignins are melt processable (11). Understanding this has guided us toward more energy-efficient methods of incorporating lignin into polymers at significant loadings via melt-compounding and reactive processing for enhanced compatibility. For this processing method, it is important to understand how the type and source of lignin affect strength and toughness of the compounded material.



Fig. 2. (A) Conventional methods to create lignin–polymer blends or multiphase lignin copolymers required batch chemical modification of lignin in organic solvents, creating waste, followed by reaction with other organic polymer substrates in solution or melt. (B) Our method involves the proper selection of host polymer and/or additives in the molten state to form unique polymer morphologies having superior performance in a semi-continuous operation without the use of solvents.



Fig. 3. The three primary phenylpropanoid lignin subunit precursors. The subunits have the designations H, G, and S to represent their condensed structures; H: p-hydroxyphenyl (paracoumaryl alcohol), G: guiacyl (coniferyl alcohol), S: syringyl (sinapyl alcohol). Other groups, including proton, vinyl, hydroxyl, carboxyl, carbonyl, and additional methylene-bridged subunits connected via β -O-4, β -5, β - β and other linkages may occur at the α , β , and γ sites.(1) The unoccupied 5 position prevalent in G-type subunits – the dominant subunit in softwood lignins, is significant in this work.

The toughening of brittle thermoplastics by combination with elastomeric fillers is a wellknown art, as well as filling elastomeric materials with rigid thermoplastics to improve modulus and tensile strength (12). Some recent work in the reinforcement of epoxidized natural rubber with bio-based PLA was shown to increase tensile strength and modulus at the cost of reduced elongation (13). In particular, this rigid reinforcement also resulted in nearly a 10-fold improvement in impact strength of blends over that of neat PLA. The aromatic structure of lignin makes it an inherently rigid and often brittle material, but melt-processable fractions are a promising feedstock for dispersing as a reinforcing filler in otherwise soft rubber materials. Experimental data has shown this to produce poor performance materials unless either the lignin is surface modified or an adhesion promoter is used (14, 15). Our recent work showed that the combination of a melt-stable fraction of lignin and a nitrile rubber (NBR) of high acrylonitrile content (40-50 %) resulted in a thermoplastic elastomeric product with significant yield stress and strain hardening at large deformation. (16) This high acrylonitrile content resulted in excellent compatibility with multiple lignins without the need for surface modification or adhesion promoters. The requirements of both specialty NBR with high acrylonitrile content and solvent-fractionated, melt-stable lignin oligomer prohibit the direct use of lower-cost technical lignins and low acrylonitrile, commodity NBR to produce these molecularly engineered products. Other recent efforts to use lignin as a significant component in polymer blends or graft copolymers have resulted in a number of elastomeric compositions, including shape-memory materials.(17) Some of the compositions show great promise for the production of complex materials due to their ability to be handled as a viscous liquid prior to curing. These materials demonstrate that it is possible to incorporate lignin at greater than 40 wt. %, however they are thermoset materials and are not yet demonstrated as recyclable. This motivated us to study alternative compositions with as-received lignin (i.e., without fractionation) and general-purpose NBR (i.e., not needing the use of high acrylonitrile content rubber). An example of commodity NBR is one that contains 33 mol % acrylonitrile (NBR-33).

Our method to increase the mechanical properties of NBR matrix uses either hardwood or softwood lignin as a reactive thermoplastic hard segment instead of treating it as a diluting filler material. Since our aim is to use commodity NBR, interfacial adhesion promoters for the lignin and rubber phases are desirable. We also attempted to increase rigidity in the rubber and induce elasticity in the lignin by introducing intermolecular cross-linking agents. In summary, our approach involves (i) cross-linking chemistry of both rubber and lignin phases by use of an organic peroxide (13, 18) and boric acid (19) respectively; (ii) reinforcement of rubber by the addition of carbon-based reinforcing filler (N330 grade equivalent carbon black) (20); and (iii) use of an interfacial adhesion promoter for acrylonitrile-containing polymers and lignin in the form of a high molecular weight polyether (21, 22). Use of these additives was studied to achieve our goals of producing high lignin content modified NBR compositions that are simultaneously stiff and tough. We also sought to understand if the generic type of biomass from which the lignins are isolated affects interaction with the NBR matrix, the additives proposed here, and the properties of the resulting multiphase polymers. Ultimately, our results demonstrate that the biobased nature of lignin and the lack of any need for organic solvents opens new doors into research for high lignin content, green polymer blends with exceptional mechanical properties by adhering to the 12 Principles of Green Chemistry and Engineering (23).

2. Experimental

Materials & Reagents. NBR (Krynac[®] 3330F, 33 % acrylonitrile content) was obtained from Lanxess Buna LLC (Pittsburgh, PA). Carbon black (CB, VULCAN[®] M, N330 grade) was obtained from Cabot Corporation (Alpharetta, GA). Dimethylformamide (DMF), and tetrahydrofuran (THF) were ACS grade and purchased from Fisher Scientific. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Trioxane, 2-chloro-4,4,5,5tetramethyl-1,3,2-dioxaphospholane, endo-N-hydroxy-5-norbornene-2,3-dicarboximide, chromium (III) acetylacetonate, polyethylene oxide (PEO, M_n ~ 5,000,000), dicumyl peroxide (DCP), and boric acid (BA) were purchased from Sigma Aldrich. Hardwood soda lignin (HSL) was provided by Domtar, Inc. (Kingsport, TN). Softwood Kraft lignin (SKL) was provided by Domtar, Inc. (Plymouth, NC). Lignins were dried under vacuum at 80 °C for 24 hours prior to use. All other materials were used as received.

Lignin Characterization. Lignin functional groups were characterized and quantified by ¹³C and ³¹P NMR using preparation and analysis methods previously reported. (24, 25) NMR Spectra were recorded on a Bruker AVANCE 500 MHz spectrometer at 25 °C. Lignin molecular weights were determined in DMF with size exclusion chromatography (SEC) on a Waters GPC II Liquid Chromatograph equipped with a Model 590 Pump and R401 Differential Refractometer. Polystyrene standards were used with Waters Styragel® 4E and 5E mixed bed columns.

Reactive Mixing and Torque-Rheological Characterization of Lignin-Rubber Composites. Melt-mixing of NBR composite blends was conducted at 140 °C and 50 rpm using a Brabender Plasti-Corder® torque rheometer fitted with a half-size (30 cc) mixing bowl and high-shear, twin roller blade attachment. A general procedure for the preparation of a composite is as follows. NBR was masticated for 2 min in the preheated mixer to bring to working temperature, followed by the addition of CB for 6 min. At 8 min, lignin and PEO powders were gently mixed in a plastic weigh boat and added to the mixer. At 20 min, BA was added to the mixer, followed by the addition of DCP at 24 min. Mixing was stopped at 36 min, followed by removal of the composite with brass tools and air cooling of the mixed mass. The amount of PEO, BA, and DCP varied across each sample. All composite blends had a mass between 25 and 26 g. Time-resolved temperature and torque data were collected for each run.

Compression Molding and Specimen Preparation. The bulk masses of mixed composite materials were placed in a 80 mm \times 80 mm \times 1.5 mm aluminum frame, covered with a Teflon-coated glass fiber mat as a release surface, and pressed between flat hot platens at 190 °C and 30,000 psi in a laboratory heat press for 30 min. Following water cooling under pressure to room temperature over 15 min, the molded coupons were removed from the press and the aluminum frame. Ten dumbbell-shaped tensile testing specimens were cut from the resulting coupon using an ASTM D638-V die.

Tensile Testing. Specimens were tested on an MTS Alliance RT/5 twin screw tensile tester equipped with a 2000 kN load cell, precision extensometer, pneumatic grips, and a crosshead speed of 500 mm/min (per ASTM standard D412). Tensile modulus, yield stress and yield elongation (if any), failure stress, and elongation at break were recorded. Results reported are the average of at least five test specimens. Samples that failed outside of the gauge area were not included in analyses.

Sample Swelling, Gel Content, and Gel Composition Analysis. Disc-shaped specimens were cut from each 1.5 mm compression molded sheet with a 9/16" round leather punch, each having a mass of ~300 mg. Discs were immersed in 50 mL of THF for 24 hours, with masses recorded at intervals up to 240 minutes (4 hours) at which point swelling had equilibrated. After swelling, samples were dried at 80 °C for 24 hours and final masses recorded to determine gel content of each sample. Total gel content for each sample is reported as the average of three measurements.

Thermal Analysis. Calorimetric analysis of composite blends was completed using a TA Instruments Q2000 differential scanning calorimeter (DSC) under nitrogen flow of 50 mL/min.

Samples of ~8 mg were heated to 190 °C and held for 10 min to erase thermal history, cooled to -75 °C, then heated to 250 °C. All heating and cooling rates were 10 °C/min. PEO crystallinity and T_g's were determined with TA Universal Analysis software. Thermogravimetric analysis (TGA) of each blend was completed using a TA Instruments Q500 thermogravimetric analyzer under nitrogen and air. Samples of about 5 mg were heated to 105 °C and held for 10 min, cooled to 25 °C, and heated to 800 °C at a rate of 10 °C/min. Dynamic mechanical analysis (DMA) was performed using a TA Instruments Q800 fitted with a dual cantilever clamp. Samples were hot pressed at 190 °C to films about 0.4 mm thick and cut into 5 mm × 30 mm strips. Testing was performed at a frequency of 1 Hz, an oscillating amplitude of 0.1 % strain, and a heating ramp from -75 to 250 °C at a rate of 3 °C/min.

Electron Microscopy. Thin sections of samples were obtained at -70° C using a Leica ultramicrotome equipped with a cryochamber and a diamond knife. Sections were picked up on lacey carbon copper grids obtained from Electron Microscopy Science and analyzed using a Zeiss Libra 120 transmission electron microscope at an operating voltage of 120 kV.

3. Results and Discussion

3.1. Lignin Characterization

Lignin molecular weights were determined by SEC. SKL was found to have $M_n = 5,587$; $M_w = 195,956$; and a PDI of 35.1. HSL was found to have $M_n = 2,987$; $M_w = 160,784$; and a PDI of 53.8. Lignins were characterized by ¹³C and ³¹P NMR using the most current methods for sample preparation and data acquisition (24, 25) and the results are summarized in Tables 1-2.

Lignin Functional Groups per 100 Ar													
ID	CO NC*	CO Conj	CO Total	COOR NC*	COOR Conj	COOR Total	OMe	ArH	DC, %†	S/G	Oxygen. Aliph.	Satur. Aliph.	Sugars
SKL	6	5	11	13	1	14	87	218	82	N/A	72	106	1.5
HSL	6	9	15	18	2	20	136	196	46	1.38	73	110	5
ID	OH Pr	OH Sec	OH Aliph Total	PhOH 5-Free	PhOH 5-Subst	PhOH Total	Total OH	H Units	β-Ο-4	β-5	β-β	Side Chain Length	M _{Ar} g/mol
SKL	37	22	59	40	38	78	137	3	6	2	2	203	169
HSL	25	19	44	19	65	84	128	3	6	1	2	218	208

Table 1. ¹³C NMR functional group analysis of lignins

Lignin Functional Groups in mmol/g											
ID	CO NC*	CO conj	CO total	COOR nc*	COOR conj	COOR tot	OMe	ArH	Oxygen. Aliph.	Satur. Aliph.	Sugars
SKL	0.40	0.28	0.68	0.74	0.06	0.79	5.14	12.9	4.25	6.26	0.09
HSL	0.34	0.39	0.73	0.87	0.10	0.97	6.54	9.40	3.49	5.29	0.24
ID	OH Pr	OH Sec	OH Aliph Total	PhOH 5-free	PhOH 5-subst	PhOH total	Total OH	H units	β-Ο-4	β-5	β-β
SKL	2.18	1.30	3.48	2.36	2.24	4.61	8.09	0.18	0.35	0.12	0.12
HSL	1.20	0.91	2.12	0.91	3.13	4.04	6.16	0.14	0.29	0.05	0.10

Lignin Functional Groups in mmol/g									
			PhOH						
ID	Aliphatic OH	5	G non	п	PhOH	Total OH	СООН		
		substituted	condensed	11	total				
SKL	2.17	1.83	2.16	0.16	4.16	6.33	0.57		
HSL	1.76	3.07	0.95	0.07	4.10	5.86	0.71		

Table 2. ³¹P NMR functional group analysis of lignins

*non-conjugated; †degree of condensation(25)

The results (Table 1-2) correlate with expected functional group quantities based on the general subunit prevalence as explained earlier, showing a higher concentration of methoxy groups, 5-substituted phenolic structures, and general oxygen-containing moieties in the HSL sample. As expected from the lignin biological origin, HSL contains significant amount of S-units that naturally results in a higher amount of OMe-groups and protonated aromatic carbons (Ar-H). Also expectable (but not always), the degree of condensation (DC) of SKL is significantly higher than that of HSL. In addition, HSL has relatively high amount (for pulping lignins) of carbohydrates.

The most substantial difference between SKL and HSL is significantly higher amounts of aliphatic OH groups in the SKL, especially by the 13C NMR data; this difference will be even higher if one subtracts the contribution of carbohydrates OH (carbohydrates contribute with approximately 10 aliphatic OH per 100 Ar meaning that true lignin aliphatic OH in HSL will be 44-10=34/100 Ar). Considering that HW native lignins have higher amounts of aliphatic OH than native SW lignins(25), this indicates that the hardwood lignin underwent more severe transformations during pulping than the softwood one. This is also supported by the amount of β -O-4 units; although the value are the same in HSL and SKL, the amounts of β -O-4 units in native HW lignins are significantly higher than that in SW native lignins and, therefore, more β -O-4 moieties were cleaved during the pulping of the hardwood feedstock.

Although the amount of total phenolic OH (PhOH) is similar in both lignins, the amounts (and ratio) of 5-substituted PhOH (S-units and 5-condensed G-units) and 5-free PhOH (G-noncondensed) are significantly different; SKL has significantly higher amount of non-condensed Gunits (more than twofold) where 5-position is available for various chemical reactions. Overall, the lower DC in the HSL samples, rendering those chains less crosslinked and more flexible, and higher concentration of 5-substituted phenols in HSL samples supports our findings that HSL composites have lower tensile strength but better ductility due to a reduction in reactivity with NBR and a generally more flexible chain. These findings are discussed in detail in the following sections.

3.2. Mechanical Properties of Multicomponent Lignin Elastomers

Lignin–NBR melt-processable rubber before and after partial cross-linking of rubber.

Tensile testing of the lignin–polymer composites containing 40–55 % lignin by mass showed a wide range of properties depending on the additives chosen and the type of lignin used. The compositions studied are shown in Table 3. The base rubber is NBR containing 33 mol % acrylonitrile (NBR-33); without any additives or thermal and shear history, this material exhibits

less than 1 MPa tensile strength.

Our prior study (16) with blends of NBR-33 and lignin suggests that use of lignin increases the modulus of the binary blends; however, at significantly high lignin loading the ductility of the composition deteriorates. Binary lignin/NBR blends of 40/60 to 60/40 wt. % ratios offered good mechanical properties. In this study we describe the effect of lignin in NBR-33 blends, cured and uncured, and with and without additives. The compositions shown in Table 3 use units of additive loadings in parts per hundred rubber (pphr).

Tensile testing of molded specimens shows that for a binary blend of NBR and SKL (blend SKL1, 120 pphr lignin), there is a unique interaction resulting in peak tensile strength of 3.7 MPa and 525 % elongation at break, indicative of cross-linked structure formation with some degree of reinforcement. This behavior is different from that of neat NBR or its analogous binary blend with HSL (1.3 MPa, >2500 % elongation) (composition HSL1). Apparently SKL offers better interaction with the NBR matrix.

DCP is a well-known rubber cross-linking peroxide (13, 18). The low amount of 2.5 pphr was intentionally selected so the final materials could be processed over multiple thermal cycles, indicative of thermoplasticity, and not become thermosets, as rubber-based compounds traditionally are prepared. The addition of DCP resulted in improved tensile failure strength of 8.8 MPa and 125 % elongation at break for the softwood lignin blend (SKL 2). DCP cross-linking also improved the tensile strength of the corresponding blend with HSL (4.6 MPa and 230 % elongation at break). It may be noted here that the hardwood lignin, being an inherently melt-processable low-viscosity material, produces a relatively softer, lower strength but more extensible blend with NBR-33.

Lignin–NBR melt-processable rubber with optional CB reinforcement and enhanced dispersion of lignin phase by PEO.

The introduction of 40 pphr CB loading in blends along with DCP increased tensile strength significantly for both types of lignin. For example, blends SKL 3 and HSL 3 had tensile strengths of 13.7 MPa and 7.9 MPa at 50 % and 95 % ultimate elongations, respectively. This represents a 55 % and 70 % strength enhancement in peroxide cross-linked binary compositions of NBR-33/SKL and NBR-33/HSL, respectively. As expected, particulate reinforcement in the network-structured matrix obtained by peroxide cross-linking further reduced the compounded resin's extensibility. This behavior is in agreement with the existing state-of-the-art for particulate-reinforced rubber systems (20).

	Ingr	edients (p	arts p	er 100 p	arts N	NBR)	Tensile properties			
ID	NBR	Lignin	СВ	PEO	BA	DCP	Stress, MPa (Std. Dev.)	Break Strain, % (Std. Dev.)	Modulus, MPa (Std. Dev.)	
Hardwood Soda Lignin Compositions										
HSL 1	100	120					1.28 (0.12)	>2500	8.2 (1.6)	
HSL 2	100	120				2.5	4.63 (0.80)	227 (80)	16.5 (2.9)	
HSL 3	100	120	40			2.5	7.86 (0.9)	96 (52)	110.5 (23.6)	
HSL 4	100	120	40	20		2.5	13.26 (1.18)	69 (21)	273.0 (29.7)	
HSL 5	100	120	40	20	7	2.5	7.27 (0.5)	109 (25)	250.7 (33.6)	
HSL 6	100	120	40	12	7	2.5	7.66 (0.43)	135 (16)	157.5 (35.0)	
HSL 7	100	120	40		7	2.5	16.69 (2.85)	84 (21)	89.1 (17.3)	
HSL 8	100	120	40	20	7		5.55 (0.33)	147 (57)	157.1 (15.8)	
HSL 9	100	120		20	7	2.5	3.49 (0.50)	183 (56)	75.6 (20.6)	
Softwood Kraft Lignin Compositions										
SKL 1	100	120					3.76 (0.37)	526 (96)	10.4 (0.8)	
SKL 2	100	120				2.5	8.82 (1.63)	126 (35)	29.9 (8.9)	
SKL 3	100	120	40			2.5	13.68 (1.48)	54 (18)	141.0 (25.7)	
SKL 4	100	120	40	20		2.5	12.61 (0.93)	16 (17)	448.6 (92.0)	
SKL 5	100	120	40	20	7	2.5	25.15 (1.26)	9 (5)	1001.3 (311.9)	
SKL 6	100	120	40	12	7	2.5	20.69 (2.99)	11 (2)	593.9 (138.0)	
SKL 7	100	120	40		7	2.5	13.01 (2.60)	33 (6)	51.14 (9.27)	
SKL 8	100	120	40	20	7		18.52 (4.06)	21 (17)	690.9 (167.6)	
SKL 9	100	120		20	7	2.5	6.32 (0.22)	151 (11)	48.4 (3.7)	
				Contr	ol Cor	npositio	n – No Lignin			
Control	100		40	20	7	2.5	4.80 (0.43)	81 (12)	13.4 (1.1)	

Table 3. Formulations and tensile properties of NBR-33-based HSL and SKL lignin resins

With the tensile properties of these partially cross-linked and reinforced systems characterized, we sought to increase adhesion and compatibility in the blends and to enhance the degree of lignin dispersion in the NBR matrix. PEO has been shown to be highly compatible with lignin (21, 22). Our prior study showed that NBR-33 forms immiscible blends with lignin (16). Since the solubility parameters of NBR-33 (19.2–20.3 MPa^{0.5}) and PEO (17.6–20.2 MPa^{0.5}) are similar, PEO is expected to plasticize NBR-33 effectively (26). Also, our previous study has shown that PEO compatibilizes thermoplastic blends of lignin and acrylonitrile-butadiene-styrene resin.(27) Therefore, we hypothesized that the presence of PEO in the blends would enhance lignin dispersion and would increase performance of CB-reinforced partially cross-linked lignin/NBR-33 blends. Accordingly, SKL 3 and HSL 3 blends were further modified with 20 pphr loading of PEO to obtain compounds SKL 4 and HSL 4, respectively.

Tensile stress–strain profiles of the HSL and SKL compositions discussed above are displayed in Fig. 4*A-B*. It is clear that inclusion of 20 pphr PEO in the NBR/lignin/DCP/CB compositions for both HSL and SKL enhanced the modulus of both samples, with a further gain in strength observed in hardwood sample HSL 4 (13.3 MPa strength and 70 % elongation). The softwood sample, however, exhibited reduced strength and elongation (12.6 MPa, ~20 % elongation) but also exhibited yielding behavior, necking, and low extensibility, an unexpected result and uncharacteristic mechanical behavior of rubber-based materials. It is apparent that the softwood lignin/NBR blend in the presence of PEO becomes less compatible. Even though PEO loading is very low (20 pphr based on rubber content and 7 wt. %), it very likely forms an excluded phase morphology that exhibits characteristic yield stress. A detailed discussion on such contrasting behavior is presented in a later section and supported by morphological data.



Fig. 4. Tensile stress–strain plots of NBR-33 rubber blends containing (*A*) hardwood (HSL) and (*B*) softwood (SKL) lignin. The composition HSL 1 elongates more than 2500 %; here, x-axis in (*A*) is shown truncated.

Lignin–NBR multiphase thermoplastic composition further modified with BA for secondary network formation.

BA is known to form gels with polyols through hydrogen bonding and esterification reactions (19). Lignin hydroxyl groups should also be able to form a hydrogen bonded network in the presence of BA, as BA has been shown to react readily with phenolic groups on lignin derivatives through the formation of borate esters (28). BA can also react with hydroxyl end groups of PEO for ester formation; however, in this case high molecular weight PEO makes such probability very low. Hydrogen bonding between hydroxyl groups of boric acid and ether linkages in PEO is a more probable bonding scheme. Traditional studies of rubber-based vulcanizates have theoretical limits of strength, modulus, and elongation that can be achieved with cross-linking and rigid reinforcement. (29, 30) A way of overcoming these limitations that has seen growing interest in recent years is to introduce a secondary, interpenetrating network within the rubber matrix. By adding BA, we sought to create such a network composed primarily

of thermally labile hydrogen bonds between the OH groups of Lewis-acid BA, and the oxygen atoms in both PEO and lignin. This behavior is similar to that of classic polyvinylacetate (PVAc) and polyvinylalcohol (PVOH) gels cross-linked with BA—the same reactions taking place in the well-known "slime" or "flubber" demonstrations common in the chemistry classroom.

BA is also known to form hydrogen bonds with nitrile groups and to exhibit Lewis acid-base interactions with the nitrile segments in NBR (31). In the hardwood lignin/NBR matrix, BA addition to the PEO-modified blend (HSL 5) resulted in lower tensile strength and elongation (7.27 MPa, 109 % elongation) than that observed in the sample with only PEO (HSL 4). Although the strength was reduced, HSL 5 showed unexpected necking behavior, similar to SKL 4, this time with greater extensibility. In the softwood lignin/NBR matrix, BA addition to the PEO blend (SKL 5) exhibited the same necking behavior as SKL 4, but with twice the tensile strength (25.2 MPa) and about half the elongation (9 %). This dramatically enhanced strength and the accompanying modulus (1 GPa) make the material behave like glassy polymers such as ABS. This surprising result, to the best of our knowledge, is the first report of rendering an inherently elastomeric composition to glassy plastic by the addition of a Lewis acid. Also, this is the first report to obtain a multiphase thermoplastic material with >40 % unmodified or asreceived lignin and to achieve a strength and modulus of this magnitude.

To further understand the interaction of lignin, PEO, and BA in these blends, we prepared samples with each lignin containing half the amount of PEO and no PEO. In the hardwood blends HSL 5, HSL 6, and HSL 7, decreasing PEO content resulted in an increase in tensile strength with a reduction in modulus. With no PEO, the hardwood sample containing BA (HSL 7) showed increased tensile strength and elongation in comparison with HSL 4 containing neither additive. In contrast, softwood blends SKL 5, SKL 6, and SKL 7 with decreasing PEO content resulted in the opposite behavior, reducing tensile strength. Also opposing the results observed in the hardwood sample, the softwood blend containing only BA as an additive (SKL 7) resulted in a decrease in strength and elongation compared to the blend without (SKL 4). The tensile stress–strain profiles of these compositions of hardwood and softwood lignin–rubber blends containing BA and varying PEO content are shown in Fig. 5*A-B*.



Fig. 5. Tensile stress-strain plots of (A) hardwood and (B) softwood lignin-rubber blends containing boric acid and

varying polyethylene oxide content.

To examine the role of peroxide cross-linking and CB reinforcement in the NBR matrices, the best performing SKL composition (SKL 5) and its HSL analogue (HSL 5) were prepared without peroxide (SKL 8 and HSL 8) and without CB (SKL 9 and HSL 9). Omitting peroxide reduced the strength in both compositions proportionally, by about 25 %, while the removal of CB caused a more dramatic reduction of >50 % in strength for both lignin types. Further, to understand the effect of lignin itself as the hard rigid segment in the composition, we prepared the same composition without lignin. The composition showed poor strength (4.8 MPa) and low ductility (<100 % elongation). This is interesting as in the case of hardwood samples, the presence of lignin increased both strength and elongation over the no-lignin sample.

3.3. Torque Rheology During Melt-Mixing of Components

Figure 6A and Fig. 6B show the time-resolved torque measurements of select hardwood lignin and softwood lignin blends, detailing the base matrix resin consisting of NBR, CB, lignin, and DCP as well as the addition of BA, PEO, and the combination of the two. The graphs show the time period after the addition of NBR, CB, lignin, and PEO and the attainment of a homogenous state with stable torque, followed by the addition of BA, then DCP. The torque rheology data corresponds to the reactions or interactions that occur during mixing cycles.

In hardwood lignin blends, DCP addition in the presence of PEO showed a minor increase in torque over the remaining mixing time (HSL 4). Addition of BA in the presence of PEO (HSL 5) showed a steady increase in torque over the remaining mixing time, but any change upon the addition of DCP was indiscernible. HSL 7 showed no change in torque upon addition of BA and a minor increase in torque that quickly plateaued upon the loading of DCP.

In the softwood lignin blends, additions of BA and DCP produced significantly different results. While the addition of DCP to the most basic matrix (SKL 3) showed an expected increase in torque due to cross-linking of the rubber, the amount of change was considerably greater than that of the hardwood lignin sample (HSL3), suggesting improved interaction between the rubber matrix and SKL. It should also be noted that hardwood lignin melts well but softwood lignin does not; therefore, a softwood-lignin-filled NBR matrix behaves like a particulate-filled matrix that is expected to have higher viscosity and hence torque. In the presence of PEO (SKL 4), the rate of torque rise slowed, likely due to the plasticization of the matrix by PEO. PEO addition may cause disruption of the rubber network and some occlusion of possible reaction sites on the lignin molecules by the hydrogen bonding activity of PEO. BA addition without PEO present (SKL 7) showed no effect on torque; however, the vulcanization behavior of DCP seemed to accelerate, with torque cresting and falling to a plateau. BA addition in the presence of PEO (SKL 5) resulted in a sharp rise in torque, followed by an even sharper effect as observed upon the addition of DCP. This dramatic increase in torque suggests that a large amount of network formation occurred, likely through vulcanization of rubber with itself and the lignin, and through the creation of a secondary network of hydrogen bonding with BA, PEO, and lignin.



Fig. 6. Time-resolved rheological data during sample blending of (A) hardwood lignin samples and (B) softwood lignin samples. Samples containing softwood lignin show a much greater response to all additives than do those samples containing hardwood lignin.

To test the hypothesis that network formation could be effected through introduction of BA alone, additional blends were made using each lignin and all components except DCP (HSL 8, SKL 8). Addition of BA at 16 min to the softwood sample (SKL 8) showed a continuing increase in torque over the next 20 min until mixing ended. This increase is similar to other well-known rubber cross-linking behaviors, but in our attempt here, this was made possible without the use of a free radical initiator. We believe that this network is composed mostly of hydrogen bonding interactions, and perhaps a small amount of borate ester condensation with unhindered hydroxyl groups present on the softwood lignin molecules. In the hardwood sample (HSL 8), the torque mixing profile remained relatively unchanged in the absence of DCP, most likely due to the higher degree of hindered phenols present in hardwood lignin species.

The average tensile strength of the SKL 8 specimens was 18.52 MPa, quite a bit lower than the best performing SKL 5. The tensile strength deviation of 4.06 in SKL 8 suggests that these samples were more heterogeneous than SKL 5, as the sufficient cross-linking of the rubber and lignin phases achieved with DCP was absent. The average tensile strength of the HSL 8 specimens was 5.55 MPa, with a deviation of 0.33 MPa. This further suggests that upon the addition of DCP, less cross-linking interaction was achieved between hardwood lignin and the NBR phase than between softwood lignin and NBR.

3.4. Thermal Analysis of the Compositions

First heating DSC scans of both HSL and SKL blends containing PEO showed a small melting endotherm at 60–70 °C due to melting of PEO crystalline phase. These endotherms disappeared, however, in blends containing both PEO and BA. We suggest that BA interrupts the crystallization of PEO through the formation of a hydrogen bonded network.

These samples were analyzed by DMA to understand their phase morphology. Figure 7*A-B* present the loss tangent spectra for the selected HSL and SKL samples, respectively. For each lignin type, all cross-linked, CB-reinforced lignin/NBR binary blends showed a tan δ peak near -15 °C, representative of the T_g of NBR, and a depression of 2–4 °C in T_g for samples containing PEO. It is evident that loading of PEO plasticizes NBR phase, as we suggested earlier. All of these results are consistent with our observations of torque rheology during the mixing of each sample. Base matrix samples HSL 3 and SKL 3 showed a second Tg associated with relaxation of the lignin phase (T_{g2}) at 200 °C and 215 °C, respectively.

Addition of PEO to the HSL matrix (HSL 4) resulted in a large plasticization effect (in lignin phase), reducing T_{g2} to 110 °C (a drop of 90 °C), followed by rubbery flow of the sample at 125 °C, beyond which DMA data collection could not be completed due to sample rupture. It is possible that the lignin–PEO interaction created a phase that melted near that temperature, as PEO melts at 65 °C and HSL begins to demonstrate viscous flow at 140 °C. PEO addition to SKL 4 resulted in a T_{g2} of 138 °C (a drop of 77 °C), similar to the HSL sample but without the loss of strength due to flow of the lignin–PEO phase. This again supports the high viscosity and torque rise observed during mixing of SKL samples compared to the HSL series.

BA addition without PEO in HSL 7 and SKL 7 erased any trace of T_{g2} in both samples, suggesting that hydrogen bonding and/or borate ester formation between BA and lignin are able to create physical or chemical cross-links sufficient to reduce or eliminate significant softening of the lignin phase. This change in second phase T_g is consistent with our prior report on gradual increase in T_g of lignin with increase in its cross-link density, achieved by cross-linking with formaldehyde (5). Addition of PEO and BA together to these materials (HSL 5 and SKL 5) maintained a secondary networked structure that includes lignin, as evidenced again by the lack of sharp T_{g2} .



Fig. 7. DMA loss tangent spectra of (A) hardwood lignin and (B) softwood lignin blends.

Figures 8*A*-*B* show the storage moduli spectra of HSL and SKL compositions, respectively. It is clear that PEO addition had opposite effects; PEO plasticized NBR-33/HSL matrix but surprisingly reinforced NBR-33/SKL matrix. With increasing temperature, the storage modulus in HSL 4 remained similar to that of the base resin HSL3; however, beyond the melting temperature of PEO, the modulus decreased steadily with increase in temperature. In contrast, PEO addition to SKL 3 increased storage modulus (of SKL 4 formulation) beyond the T_g of NBR, although a precipitous drop was observed starting at about 90 °C.

In samples doped with BA (HSL 7, SKL 7), storage modulus was maintained over a larger temperature range compared to the base matrix as a result of physical/chemical cross-linking via hydrogen bonds/borate ester formation between BA and lignin. The combination of BA and PEO in materials (HSL 5, SKL 5) showed no notable change in storage modulus in the hardwood sample (HSL 5) compared to that with only BA (HSL 7). The softwood sample (SKL 5) maintained a higher storage modulus than any other sample over the entire temperature range, with a large increase observed at the high temperature region (>90 °C) compared to the blend containing only BA (SKL 7). This elevated storage modulus supports our hypothesis of secondary networked structure formation that causes extended dispersion of relatively rigid lignin in SKL 5 and is consistent with materials exhibiting interpenetrating network morphology (32).



Fig. 8. Dynamic mechanical storage moduli plot of representative (*A*) hardwood lignin and (*B*) softwood lignin blends.

3.5. Electron Microscopy

Transmission electron microscopy of a 50/50 blend of NBR and softwood lignin shows noninterconnected lignin aggregates between 0.2 and 2 μ m having an elliptical spheroid shape (Fig. 9). This "islands in the sea" morphology has been described in other lignin polymer blends (16, 27).



Fig. 9. Transmission electron micrograph of NBR-33/SKL 50/50 blend.

Figures 10*A-F* show the phase morphology of additional selected specimens using transmission electron microscopy. Compositions of hardwood and softwood blends show CB as collections of small black particles in the 50–100 nm size range. The aggregates of these particles are dispersed in the NBR phase, providing an easy distinction between the lignin and NBR phases. In hardwood blend HSL 7, the addition of BA caused the lignin particles to reduce, become more uniform in size (500–1000 nm), and maintain a more spherical shape (Fig. 10*A*). After PEO addition to this composition (HSL 4), the lignin domains became elongated and tended to form an interconnected structure, demonstrating the beginning of a continuous two-phase material rather than highly dispersed islands. This observation confirms that PEO addition enhances deformability of the lignin phase in an NBR matrix (Fig. 10*B*). In the presence of PEO and BA together in sample HSL 5, lignin aggregates became very large and elongated, with some small amount of interconnectivity (Fig. 10*C*).

In softwood blend SKL 7, the addition of BA showed some interconnecting spheroidal lignin domains between 200 and 1000 nm in size, exhibiting the same behavior as HSL 7 but also suggesting the formation of a two-phase nearly co-continuous morphology (Fig. 10*D*). PEO addition (SKL 4) brought lignin to nearly a continuous phase, with no real discernable beginning or end to any individual aggregates of the CB-loaded rubbery phase (Fig. 10*E*). The addition of PEO and BA together in SKL 5 showed CB even more well-dispersed, demonstrating that the lignin and NBR phases had become a fully co-continuous, interpenetrating network (Fig. 10*F*). This fully interpenetrating network is supported by the exceptional mechanical properties demonstrated by this sample and our earlier DMA results.



Fig. 10. TEM images. (*A*) HSL 7, the hardwood lignin matrix with BA, showing spherical lignin domains; (*B*) HSL 4, the hardwood lignin matrix with PEO, showing elongation and interconnection of lignin domains; (*C*) HSL 5, the hardwood lignin matrix with BA and PEO, showing great elongation and interconnected lignin domains; (*D*) SKL 7, the softwood lignin matrix with BA, showing interconnected spheroidal domains; (*E*) SKL 4, the softwood lignin matrix with BA and PEO, showing elongated, interconnected domains; (*F*) SKL 5, the softwood lignin matrix with BA and PEO, showing elongated, interconnected domains; (*F*) SKL 5, the softwood lignin matrix with BA and PEO, showing an interpenetrating network of lignin and rubber.

3.6. Sample Swelling, Gel Content, and Gel Composition Analysis.

All samples excluding HSL & SKL 6 (reduced PEO loading) and HSL & SKL 9 (removal of carbon black) were subjected to a swelling study to determine gel content. THF was chosen as a solvent as it readily dissolves all polymeric ingredients: lignin, NBR, and PEO. The HSL composites took up solvent at a faster rate (Fig. 11) than the SKL composites, with exception of samples not containing DCP (HSL 1,8 & SKL 1,8). The HSL samples that contained no DCP (HSL 1 & HSL 8) disintegrated after 24 hours. Any remaining gel had the consistency of slime and pieces smaller than 1mm in size.

The most intriguing information obtained from this experiment is the comparison in swelling rate, swelling ratio, and final gel content of the simple binary blends of lignin and NBR, and those binary blends with DCP added. HSL 1 and SKL 1 took up solvent the fastest, with HSL 1 disintegrating after 2 hours. SKL 1 had the largest swell ratio and samples remained a nearly perfect disc shape, indicating the largest molecular weight between crosslinks but enough crosslink density to maintain dimensional stability. SKL 2 on the other hand, swelled to a lesser degree, had an oblong egg shape, and generally high gel content indicative of a higher degree of crosslinking.



Fig. 11. Swelling of lignin-NBR composites over time, with final gel content. (A) HSL composites, (B) SKL composites.

ID	Composition	Gel	Std. Dev.							
	Hardwood Cal Analys	Content								
	Haruwoou Ger Allarys	515								
HSL 1	HSL/NBR	N/A	N/A							
HSL 2	HSL/NBR/DCP	39 %	1 %							
HSL 3	HSL/NBR/CB/DCP	49 %	1 %							
HSL 4	HSL/NBR/CB/PEO/DCP	56 %	1 %							
HSL 5	HSL/NBR/CB/PEO/BA/DCP	55 %	4 %							
HSL 7	HSL/NBR/CB/BA/DCP	57 %	4 %							
HSL 8	HSL/NBR/CB/PEO/BA	42 %	5 %							
Softwood Gel Analysis										
SKL 1	SKL/NBR	64 %	1 %							
SKL 2	SKL/NBR/DCP	77 %	4 %							
SKL 3	SKL/NBR/CB/DCP	79 %	1 %							
SKL 4	SKL/NBR/CB/PEO/DCP	77 %	1 %							
SKL 5	SKL/NBR/CB/PEO/BA/DCP	78 %	1 %							
SKL 7	SKL/NBR/CB/BA/DCP	75 %	< 1%							
SKL 8	SKL/NBR/CB/PEO/BA	72 %	2							

Table 5. Gel Content of NBR-33-based HSL and SKL lignin resins

The gel content (Table 5) of all HSL samples was between 0 and 57%, with the non-DCP multi-component composition losing more than 50 % of its mass, and the HSL 1 binary sample completely disintegrating. In representative SKL compositions, composite gel content was between 64 and 79 %. Again, the non-DCP composition lost the most mass, however SKL 1 showed higher gel content than any other sample with HSL. These gel content values correlate

with our earlier assumptions that the SKL lignin reacts stronger with the NBR matrix, especially in the presence of DCP, due to the presence of more non-condensed G-subunits. A chemical explanation of this reactivity is presented in section 3.7.

3.7. Networked Structure Formation and Lignin-NBR Grafting.

Based on the results discussed earlier, we find that softwood lignin exhibits more torque during mixing in an NBR matrix, particularly in the presence of DCP, a free radical generator. Softwood lignin, being predominantly made of coniferyl-alcohol based phenylpropanoid units (G-type lignin structures), has fewer methoxy groups and is likely more reactive than the more substituted and hindered hardwood lignin, where syringyl-alcohol units (S-type lignin structures) dominate. Also, it appears that in the presence of PEO, softwood lignin/NBR-33 blends form a more co-continuous phase morphology, in contrast with hardwood lignin/NBR-33 blends, which remain phase separated. This fundamental difference and subsequent reactivity with BA and further reinforcement of the NBR phase by CB helps to produce multiphase high performance material from as-received lignin and commodity nitrile rubber. A recent study showed that inclusion of PEO in hardwood lignin results in formation of significantly longer lignin cylindrical structural units by formation of hydrogen-bonded networks of anisotropic segments of hardwood lignin molecules. This, however, does not affect the radius of gyration of the lignin dispersed units in a solvent. A similar case with softwood lignin results in cylindrical structural units of larger diameter and slightly longer length; however, that significantly reduces the radius of gyration of lignin dispersions (34). This study suggests that hardwood lignin forms an extended, flexible chain conformation in the presence of PEO, and that softwood lignin shrinks in size, likely due to less compatibility with PEO, and forms chain-folded morphology. Thus, the presence of PEO allows lignin to form rigid aggregates that interact favorably with NBR in the presence of free-radical-generating species. BA further enhances compatibility among all components through formation of the secondary network structure discussed earlier.

Our hypothesis is that lignin is being grafted to NBR during the reactive blending process. There is precedent for this type of reactivity, as recently demonstrated in a reactively blended alloy of lignin and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) that used DCP as a radical-generator.(33) It is also well-known that lignin, with many hindered phenolic structures, functions well and a such has been well studied as an antioxidant with uses in polymeric systems.(34) In our system, we propose that DCP accelerates the reactivity between NBR and lignin through the mechanism outlined in Scheme 1 – forming the primary network of this polymer system. Based on earlier swelling data and mechanical properties of SKL 2, it is plausible and very likely that this mechanism can be initiated simply from spontaneous radical formation along the NBR chain that occurs under high-temperature, high-shear processing as a result of either chain scission or attack by molecular oxygen.(35)



Scheme 1. Plausible reaction between lignin and nitrile rubber in presence of free-radicals generated from an initiator or thermal shearing of unsaturated rubber.

After radical generation and/or proton abstraction occurs on both the lignin and rubber molecules (Scheme 1, steps 2 & 3), those radicals can then terminate (Scheme 1, step 4), grafting lignin to the polymer chain. Based on our observations of the increased reactivity in softwood lignin, and the higher concentration of non-condensed G subunits and unoccupied 5 positions on the softwood lignin molecules, we suggest that this is the most likely point of attachment. While the radical species on lignin can be stabilized at the 1, 3, or 5 positions through resonance, the sterically hindered nature of 1 and 3 reduce the likelihood of attachment here. Furthermore, radical species at those positions are tertiary in nature and as such, more stable and less prone to reactivity – a concept readily exploited in hindered phenolic antioxidants like butylated hydroxytoluene (BHT).(36) Predominant S subunits in HSL reduce extent of such reaction between HSL lignin and NBR; thus, those compositions have significantly lower gel content.

4. Conclusions

Reactive mixing has been demonstrated to be an effective method for increasing the compatibility of lignin and nitrile-containing butadiene rubber. The introduction of carbon black as a traditional rubber reinforcement, along with polyethylene oxide as an adhesion promoter and hydrogen-bond acceptor, and boric acid and dicumyl peroxide as cross-linkers, produces a range of materials with high elongation when used with hardwood lignin, and high tensile strength near that of ABS when used with softwood lignin. All materials can be compression molded and recycled, owing to the number of thermal processing cycles during mixing and compression. Unique to this work is the finding that the combination of all components in a commodity-grade 33 % acrylonitrile-containing butadiene matrix, using softwood lignin, produces a thermoplastic material with a two-phase interpenetrating network of exceptional strength and modulus. To date, we have found no reports of lignin thermoplastics of this quality that have been produced with greater than 30 % lignin without the use of solvent-based chemical modification. This research opens new opportunities for using lignin not simply as a filler, as in previous research, but as an independent polymeric phase in polymer blends, and expands upon the opportunities available for the future commercial valorization of lignin into greener durable products.

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