Rigid Oligomer from Lignin in Designing of Tough, Self-healing Elastomers

Mengmeng Cui*,†, Ngoc A. Nguyen†, Peter V. Bonnesen‡, David Uhrig‡, Jong K. Keum§, and Amit K. Naskar*,†

†Carbon and Composite Group, Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

‡Center for Nanophase Materials Science, Oak Ridge National laboratory, Oak Ridge, TN 37831, USA

§Neutron Science Directorate, Oak Ridge National Laboratory, Oak Ridge National Laboratory, Oak ridge, TN 37831, USA

ABSTRACT: Converting lignin into well-defined compounds is often challenged by structural complexation and inorganic contamination induced by the pulping process. In this report, instead of breaking down lignin into small molecules, we extracted a uniform and rigid oligomer from lignin waste stream. The multifunctional polyphenol oligomer containing carboxylic acid, alcohol and phenol groups, is highly reactive and brings stiffness into material matrix. Tough and self-healing elastomers are economically prepared from this oligomer by a reaction with epoxy-terminated polyethylene glycol, without needing any solvent. Specifically, the polyaromatic backbone's rigidity enhances the elastomer's toughness, and the multiple polar substituents form a network of hydrogen bonding that heals the elastomer. Many other applications, including adhesives, hydrogels, coating, and metal-scavengers, are envisioned based on this oligomer's unique properties.

Being the second-most-abundant terrestrial polymer that makes 25-35% of woody biomass, lignin is usually underutilized as a byproduct in the biomass processing industries, such as paper manufacturing and biorefining.[1,2] Only less than 2% of the 50 million tons of lignin produced annually by the pulping industry was converted into useful chemicals.[3] Due to lignin's abundance, sustainability, and low cost, there is increasing interest in converting lignin into value-added chemicals. Recently, progress was achieved in catalytic conversion of mildly-modified lignin into defined aromatic compounds.[4,5] However, the catalytic processes are less effective towards lignin from pulping industries because: 1) hash conditions of pulping methods significantly modify the structure of lignin, leading to complex mixtures after catalytic conversion;[6] 2) lignin from pulping industries is often contaminated with sulfur that poisons the metal catalyst. Therefore, new methods are needed to better accommodate current pulping processes. Here, we report a uniform lignin oligomer that is simply extracted out of lignin from different wood sources and pulping processes. The extraction method largely maintained the polyaromatic backbone of lignin, yet the functionality can be unambiguously determined, so the oligomer exhibits high thermal and mechanical performances, making it a unique building block for polymer materials.

The oligomer was obtained by directly extracting lignin from pulp manufacturers with acetonitrile. To fully understand the effect of extraction, we developed a new method to characterize lignin compositions by combining several nuclear magnetic resonance (NMR) techniques (Figure 1, Figure S1 and S2). Both original and extracted lignin have an almost identical degree of substitution (DS) for alcohol and phenol (around 1.20 per aromatic ring) and a similar DS for aldehyde (~0.40). The major difference comes from carboxylic acid and methoxy groups. The extraction enriches the DS for carboxylic acid by five times (0.80 vs. 0.17) and decreases the DS for methoxy by half (0.75 vs. 1.40), suggesting a slightly higher reactivity after extraction. Very similar compositions were obtained when we change the lignin source from hard wood to soft wood or change the pulping process (Figure S3). From a chemistry perspective, lignin's substituted polyaromatic nature and plentiful functional groups[7-9] resemble 3,4-dihydroxyphenylacetic acid (DOPAc), a derivate of 3,4-dihydroxyphenylalanine (DOPA) that is responsible for the strong adhesion of mussel[10] and frequently used for coating,[11] adhesives,[12] tough materials,[13] particles,[14] metal scavenging,[15] and self-healing.[16]

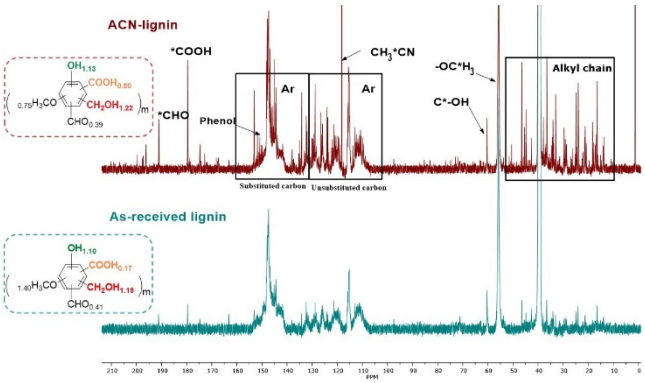

Figure 1. Average degree of substitution (DS) for each functional group of as-received lignin and ACN-lignin as characterized by ^{13}C-NMR in d^6-DMSO.

The distinct feature of extracted lignin (ACN-lignin) lies in its uniformity and high glass transition temperature (T_g). The weight average molecular weight of ACN-lignin is narrowly distributed around 2200 g/mol, but its T_g is as high as 96.6°C. The as-received lignin has a much broader polydispersity (1.83 vs. 1.16) and does not exhibit detectable glass transition (Figure S4). Therefore, the ACN-lignin is a rigid and uniform oligomer consisting of ~10 aromatic repeating units substituted by carboxylic acid, alcohol, phenol, and some methoxy and aldehyde. Compared with the as-received lignin, ACN-lignin is highly polar with significantly increased carboxylic acid and reduced methoxy, which makes the ACN-lignin more reactive for preparation of functional materials.

From a materials perspective, lignin has a high theoretical Young's modulus of 2.31~4.65 GPa.[17] The ACN-lignin's high mechanical strength, combined with its chemical versatility, offers us a unique opportunity to address a standing challenge in self-healing materials. Many self-healing materials[18] rely on judiciously designed supramolecular interactions, such as hydrogen-bonding,[19,20] π-π stacking,[21] metal-ligand interactions,[22,23] ionic interactions,[24,25] and host-guest interactions.[26] These weak interactions afford quick and spontaneous self-healing but also lead to unsatisfactory mechanical properties. One solution is to introduce dual phases into the material, a hard phase bringing in stiffness and a soft phase for self-healing.[27-29] The ACN-lignin is a naturally occurring rigid building block surrounded by functional groups that are able to form hydrogen bonding. Thus, it holds potential to mitigate the trade-off between mechanical properties and self-healing dynamics.

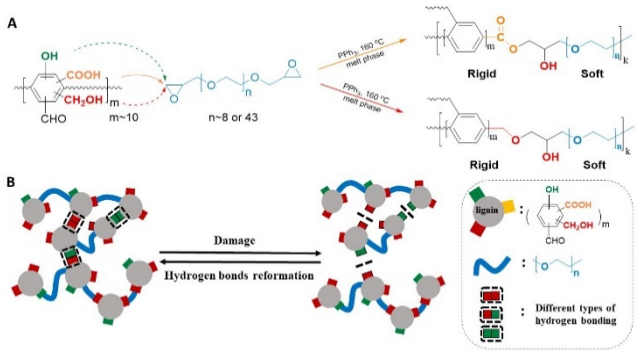

Figure 2. Preparation and schematic illustration of the self-healing elastomer from ACN-lignin. (**A**) Two dominant reactions between ACN-lignin and diglycidyl ether polyethylene glycol (PEG) at melt-phase. (**B**) Schematic illustration of a network formed by coexisting covalent bonds and non-covalent bonds.

Self-healing elastomers are prepared by reacting diglycidyl ether terminated polyethylene glycol (PEG) with the ACN-lignin at melt phase (Figure 2A).[30] Without generating by-product, the reaction leads to a network consisting of both covalent and hydrogen bonds (Figure 2B). The covalent bonds are formed by reactions of the epoxy in PEG with the carboxylic acid, alcohol, and phenol in lignin. At the same time, the product of these reactions (esters, ethers, and secondary alcohols) further mingle with the starting materials and form abundant hydrogen bonds. The functional groups reacted with glycidyl ether in an order from carboxylic acid to alcohol to phenol, and generated secondary alcohols. Therefore, the total amount of hydrogen bonding donor and acceptors remained unchanged during the reaction (Figure S5).

The produced network contains both hard phases of lignin and soft phases of PEG. While the hard phase provides the material with stiffness, the soft phase allows chain movement and material ductility. The coupling of soft PEG with the ACN-lignin lowers the T_g, and the resulting material is expected to exhibit high toughness. The presence of hydrogen bonding further contributes to the toughness and dissipates the energy by rupturing and sacrificing themselves during force loading, which has been demonstrated in hydrogel and elastomer systems.[31-35] The dynamic nature of hydrogen bonds allows them to reform after the force loading and to self-heal the materials. Therefore, the material is both tough and self-healing due to: (1) the coexistence of hard phase and soft phase in the material and (2) the coexistence of covalent bonds and hydrogen bonds in the network.

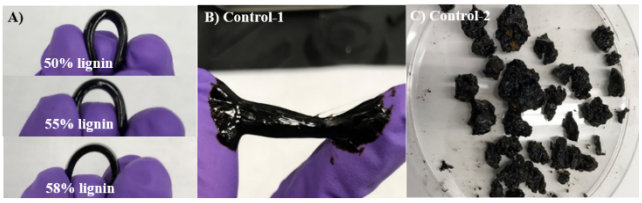

Figure 3. Physical appearance of products from reactions

between diglycidyl ether PEG and: A) ACN-lignin, B) DOPAc, and C) as-received lignin.

Three samples with different lignin-to-PEG ratios are prepared, and all of them behave like elastomers (Figure 3A). While the control sample 1 prepared with 55% DOPAC is very sticky and shows adhesive properties (Figure 3B), the control sample 2 prepared with as-received lignin appears as chunks that lacks elasticity (Figure 3C).

Unlike materials formed by supramolecular interactions, the synthesized elastomer exhibited both stiffness and toughness. ACN-lignin is the key to this remarkable mechanical property, as seen from the fact that both the elastic modulus and the tensile stress increased significantly when lignin content increased (Figure 4A, B). For the 58% lignin sample, the elastic modulus was as high as 86 MPa while the tensile stress was around 12 MPa (Table 1). The material was also highly stretchable with stiffness. For example, the elastomer with an elastic modulus around 19 MPa can be stretched by 2200% before break. The high stretchability comes from the unfolding and sliding of polymer chains that are enabled by the break and rejuvenation of hydrogen bonds during stretching[23].

The contribution of ACN-lignin is further exemplified by its absence from the system. The Control-1 sample showed very low strength and stiffness (Figure 4A inset) because the low molecular weight of DOPAc does not provide as much mechanical strength, and the less reactive phenol groups did not build up molecular weight in the product either. The Control-2 sample was prepared from as-received lignin whose molecular weight is higher than the ACN-lignin. The product contained large lignin domains and showed brittleness and very limited self-healing characteristics.

A uniform phase structure is also critical here for the toughness, as phase-separated lignin domains will produce a brittle material, especially for the sample with a high lignin composition. Small angle X-ray scattering (SAXS) (Figure 4C) did not reveal any peak from 1 nm to 100 nm, indicating formation of a uniform and homogeneous material.

Another requisite for high mechanical performance is a sufficient polymer chain length to achieve chain entanglement. The material exhibited both stiffness and toughness after a two-hour reaction, but if the reaction time was reduced to 20 min (Figure S6a), it only showed poor toughness due to incomplete reaction (Figure S6b). The lack of physical entanglement leads to serious strain softening and lack of strain hardening, which reduces the material's toughness

Table 1. Three self-healing elastomers and the control sample.

Entry	Lignin (or DOPAc) (wt%)	T_g (°C)	Tensile Stress (MPa)	Elastic Modulus (MPa)	Elongation at Break (%)
Elastomer 1	50%	-5.4	0.96±0.11	4.26±0.22	1345±2
Elastomer 2	55%	6.9	4.48±0.33	18.70±1.55	2231±433
Elastomer 3	58%	16.8	12.20±0.75	86.13±13.21	354±52
Control-1	55% DOPAc	-5.0	~0.011	~0.43	~230

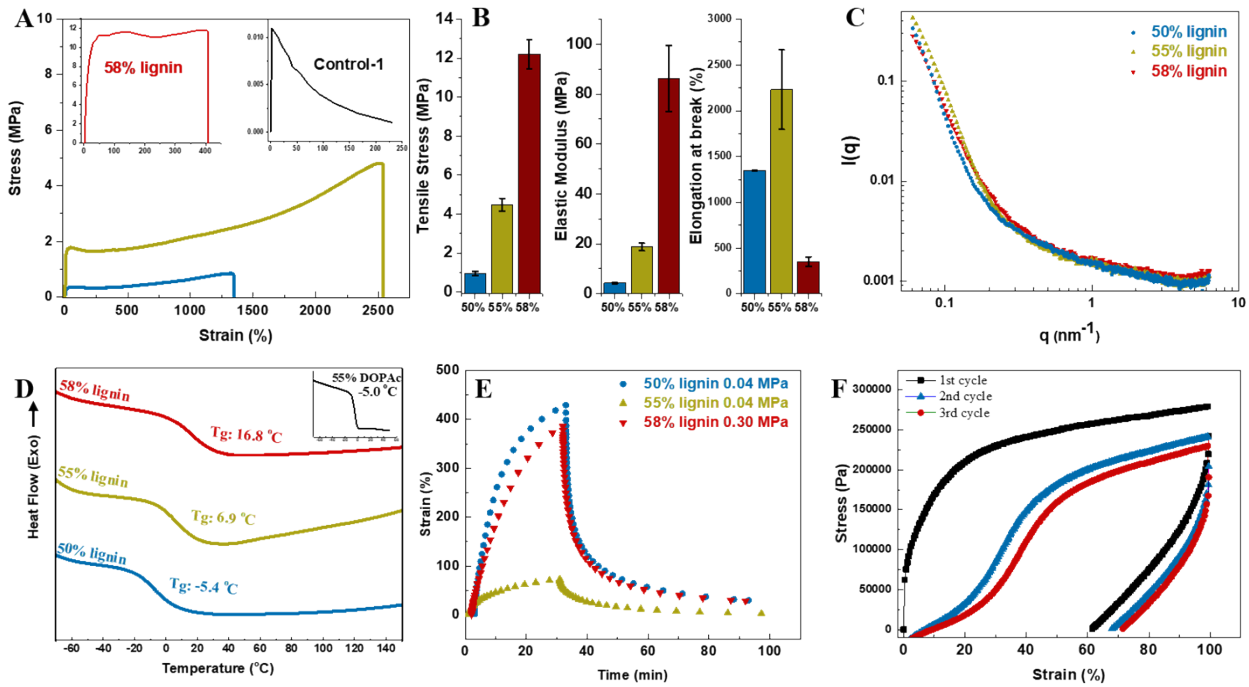

Figure 4. Mechanical properties and glass transitions of three self-healing elastomers in different compositions (50% lignin: blue; 55% lignin: yellow; 58% lignin: red). (**A**) Stress-strain curves of three elastomers and Control-1 with DOPAc. (**B**) The change of tensile stress, elastic modulus, and elongation at break of elastomers as the lignin composition increases. (**C**) X-ray scattering of three elastomers, all showing uniform structures. (**D**) DSC thermograms of three elastomers. The inset is the Control-1 with 55% DOPAc. (**E**) Creep recovery of three elastomers at different conditions: the 50% lignin sample and 55% lignin sample at 0.04 MPa at 20°C, and the 58% lignin sample at 0.30 MPa at 35°C. (**F**) Cyclic stress-strain test of the 55% lignin sample.

Naturally, a higher lignin loading enhances the T_g of the material (from −5.4°C to 16.8°C) (Figure 4D), and further increasing lignin content beyond 58% leads to glassy materials. This is ascribed to both the rigidity and network forming ability of lignin. All three elastomers are amorphous, perhaps because the branched and irregular structure of lignin suppress the potential crystallization of PEG segments (Figure S7). Accordingly, the material's optimal working temperature depends on its composition and the desired mechanical property.

For example, all three samples displayed good shape recovery after they were stretched by a fixed stress for 30 min. (Figure 4E). Both the 50% lignin and 55% lignin elastomers can recover ~90% in one hour at ambient temperature. Even when the sample was stretched to a high strain of ~1000%, an 88% recovery was observed for the 55% lignin sample (Figure S8b). Under similar conditions, however, only 50% recovery was observed for the 58% lignin sample (Figure S8c), because its T_g is close to the room temperature. Raising the temperature to 35°C relaxes this elastomer faster and approximately 90% recovery was observed.

The energy dissipation capability of this material is shown by pronounced hysteresis. The area between the loading and unloading curves corresponds to the energy dissipated per unit volume of material during deformation (Figure 4F). The high tan δ (1.75) also indicates an effective energy absorption property (damping characteristics) of the elastomers (Figure S9).

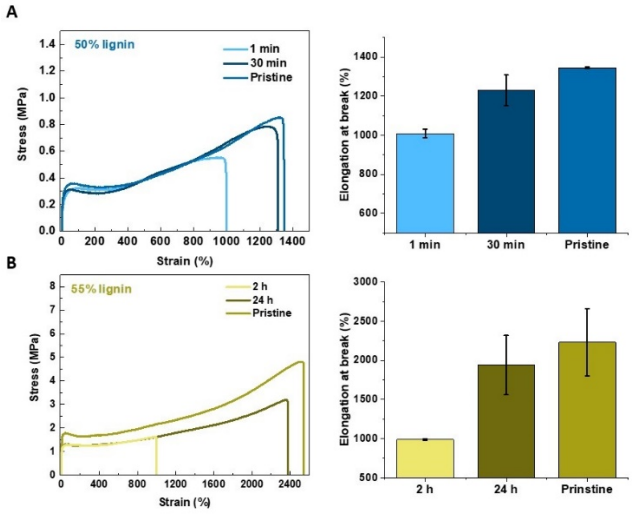

Figure 5. Recovery of mechanical properties of self-healed elastomers. Stress-strain curve and recovery performance of (**A**) the elastomer with 50% ACN-lignin in 1 min and 30 min at room temperature, and (**B**) the elastomer with 55% ACN-lignin in 2 h and 24 h at 37°C.

The self-healing ability of this elastomer series is tunable by composition, ranging from instant self-healing at room

temperature to slow self -healing at body temperature. The 50% lignin material exhibited instant self-healing at room temperature (21.5°C). The cut elastomer self-healed immediately after the cut surfaces contacted each other (Movie S1), while the elastomer was not obviously sticky to other materials. In 1 min., over 50% recovery was observed for the elongation at break (Figure 5A). And the material was almost fully recovered in 30 min. The rapid self-healing benefits from plentiful hydrogen bonds as well as the low T_g of PEG. In comparison with previously reported materials, the 50% lignin material exhibited instant self-healing and maintained equally good or better stiffness and toughness; this indicates that our design rationale by using ACN-lignin successfully averted the aforementioned trade-off. As the lignin content increased, the self-healing became slower due to an increased T_g. The 55% lignin sample required 24 h to self-heal at body temperature (37°C) to get ~90% recovery (Figure 5B, Movie S2). Even higher temperature is required for the 58% lignin material exhibit obvious self-healing.

In summary, we obtained a valuable oligomer from the lignin waste stream by solvent extraction. The lignin oligomer has a uniform composition, rigid structure and diverse functional groups, showing potential to serve as a renewable building block offering both mechanical property and self-healing ability. Its advantages are exemplified by a series of elastomers derived from the lignin oligomer and PEG, with tunable properties ranging from instant self-healing at room temperature to a tough elastomer with slower self-healing. Particularly, the two design parameters in the material, i.e., the coexistence of covalent and hydrogen bond and the coexistence of copolymerized hard and soft phases, not only endow the material with self-healing ability but also make the material tough and strong. The elastomers also feature >50% of lignin composition and an efficient melt-phase preparation that excludes solvent usage or waste generation. Rigid, reactive, sustainable and affordable, this tailored lignin is expected to be useful in self-healing, adhesives, hydrogels, elastomers, and many other applications in both frontier research and industrial development.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge via the Internet at http://pubs.acs.org."

Additional characterization data (PDF)
Movie of instant self-healing (mp4)
Movie of tensile test of tough elastomer (mp4)

AUTHOR INFORMATION

Corresponding Author

*E-mail: cuim@ornl.gov (M. Cui), naskarak@ornl.gov (A. K. Naskar)

Author Contributions

M.C. and A.K.N. conceived the idea and designed the project; M.C., N.A.N., P.V.B., D.U. and J.K.K conducted the experiments; M.C., N.A.N., P.V.B., and A.K.N analyzed the data; M.C. and A.K.N. drafted the manuscript.

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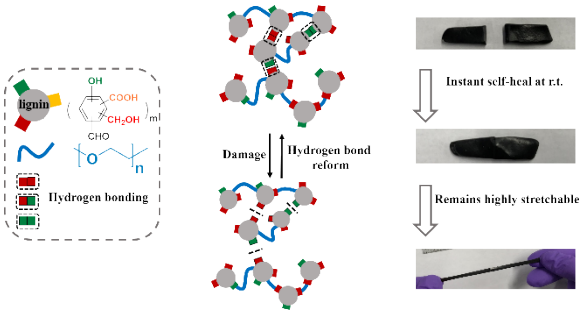
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