

Recent developments in polymers derived from industrial lignin

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ABSTRACT: Lignin is an aromatic polymer that makes up 15–30% of the cell walls of terrestrial plants. While lignin's role in facilitating water transport through the vasculature, providing rigidity and acting as a defense against pests and pathogens is important for the plant's survival, industries that process plant biomass for the production of biofuels and bio-based chemicals have historically primarily been interested in the cell wall polysaccharides, especially cellulose. Consequently, lignin is generated in large quantities as a by-product that is often burned to generate heat and electricity, or that is used in low-value applications. It is becoming clear that, rather than treating it as waste, lignin is very suitable for the production of enhanced composites, carbon fibers, and nanomaterials, which offers both economic and environmental benefits. This review highlights recent uses of these polymers as adsorbents, flocculants, adhesives, anti-oxidants, energy storing films, and vehicles for drug delivery and gene therapy. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42069.

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INTRODUCTION

With the ability to access the large reserves of shale gas and oil in the United States, the importance of energy independence as the main motivation to pursue the use of plant biomass as a feedstock for the production of fuels and chemicals, as set forth in the Energy Independence and Security Act of 2007,¹ has declined. At the same time evidence in support of climate change as a result of the burning of fossil fuels is getting stronger, and cellulosic biofuels offer the potential to reduce transportation's contribution to greenhouse gas emissions.^{2,3} The use of plant biomass as a feedstock for fuels and chemicals has two additional benefits: its potential to boost local and regional economies through employment opportunities in biomass production and processing, and the potential to produce bio-based products with properties that are difficult to match with the use of petroleum-based chemicals or products that can be made at lower cost.^{4–7} Cellulose, and to a lesser extent, hemicellulosic polysaccharides, have been treated as the primary polymers of interest in biomass, while lignin, an aromatic polymer, has traditionally been viewed as a waste product that is best burned to generate heat or electricity.^{8,9} With biomass comprising of, depending on the source, 15–30% lignin, this practice renders a large source of bio-based chemicals underutilized. Furthermore, in light of the low price of natural gas, due largely to hydraulic fracturing (“fracking”), the economic benefit of burning lignin

has diminished.^{10–12} As a consequence, there is a renewed interest in the use of lignin for the production of bio-based chemicals and polymers with enhanced properties. This review summarizes the utilization of industrial lignin for the production of novel polymers, with an emphasis on developments since 2011.

LIGNIN BIOSYNTHESIS

Lignin is an aromatic polymer present in the cell walls of plants. It provides a hydrophobic surface to water-conducting cells in the plant's vasculature, provides structural support to fiber cells, and provides a physical barrier to invading pathogens and insect pests.^{13,14} Lignin is synthesized in the cell wall through oxidative coupling of monolignols, which are synthesized inside the cell and exported to the wall. Monolignols are synthesized from L-phenylalanine via a series of enzymatic reactions in which the amine moiety is removed, the aromatic ring is substituted with hydroxyl and methoxyl groups, and the carboxyl group on the propane side chain is reduced. The monolignol biosynthetic pathway was recently updated with the identification of the enzyme caffeoyl-shikimate esterase.¹⁵ The three most common monolignols are *p*-coumaryl alcohol (1), coniferyl alcohol (3), and sinapyl alcohol (6), which, once polymerized, result in *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl residues (S) (Figure 1). In mutants and transgenics in which the activity of

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specific monolignol biosynthetic enzymes has been altered, caffeyl alcohol (2), coniferaldehyde (4), 5-hydroxyconiferyl alcohol (5), and sinapaldehyde (7) can accumulate beyond background levels.^{16–19} The polymerization of monolignols via oxidative coupling is catalyzed by laccases and peroxidases, which generate monolignol radicals. As a result of delocalization of the radical electron, different chemical bonds, including ether and carbon–carbon bonds, can be formed between a monolignol and the growing lignin polymer (Figure 1).²⁰ Since chemistry,

rather than enzymes, controls the polymerization reactions, lignin has no regular structure, unlike the backbones of cellulose, starch and chitin.

LIGNIN AS A BY-PRODUCT OF BIOMASS PROCESSING

While the lack of a regular structure makes lignin an effective barrier against pests and pathogens, it also complicates the processing of biomass, necessitating high temperatures, pressures and

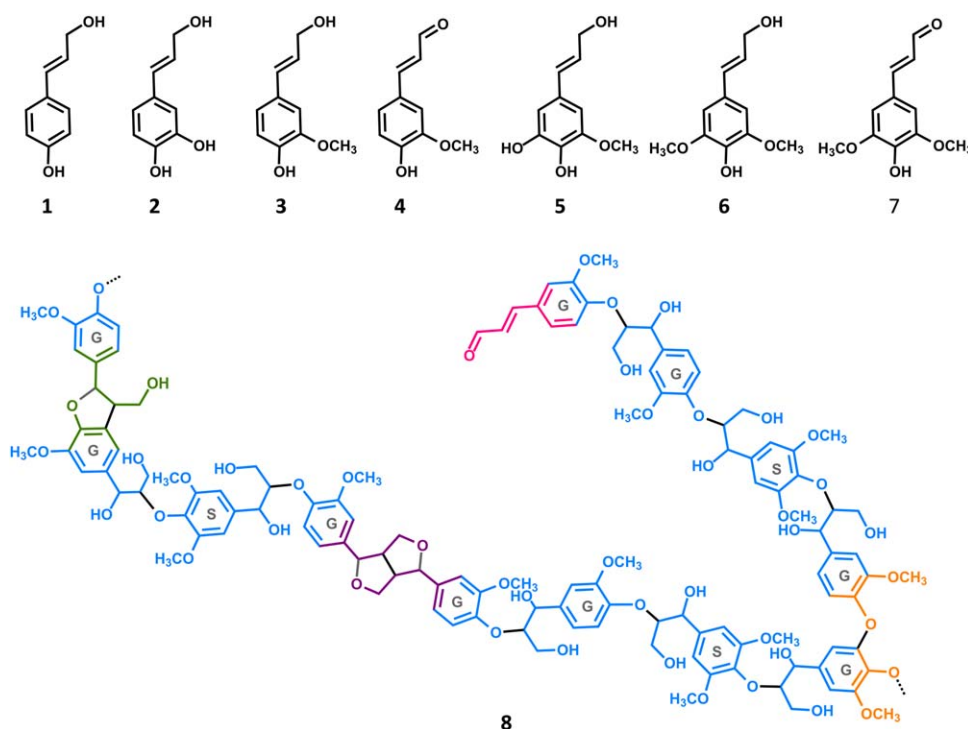


Figure 1. Lignin is formed from the oxidative polymerization of monolignols. The three most common monolignols are *p*-coumaryl alcohol (1), coniferyl alcohol (3) and sinapyl alcohol (6), but caffeyl alcohol (2), 5-hydroxyconiferyl alcohol (5), coniferaldehyde (4), and sinapaldehyde (7) can also serve as monomers for lignin. Structure 8 represents a fragment of lignin polymer from an angiosperm dicot, with guaiacyl (G) and syringyl (S) residues marked. The different interunit linkages are indicated in color: β -O-4 in blue, β - β' in purple, 4-O-5' in yellow, and β -5 in green. A coniferaldehyde end group is shown in magenta. The dotted lines indicate sites where additional monolignol radicals can be added to the polymer. Structure 8 is adapted from Ref. 30. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

various chemical catalysts. The oldest and most common biomass processing facilities are pulp and paper mills, which isolate cellulose from woody biomass, most commonly through the Kraft pulping process, which breaks down lignin by cooking wood chips in sodium hydroxide and sodium sulfide,²¹ the sulfite process, which generates lignosulfonate (LS), a water-soluble anionic polymer,²² or the organosolv process, which uses organic solvents to extract lignin fragments generated via acid-catalyzed degradation.^{23,24} The invention of the LignoBoost process²⁵ has enabled the large-scale purification of lignin from the so-called black liquor generated by the Kraft process, so that the lignin becomes available for down-stream applications. The LignoBoost process is based on lowering the pH of the black liquor to precipitate the lignin so that it can be separated from the inorganic contaminants present in the cooking liquor.

Lignin is also expected to be produced on a large scale as a byproduct of biorefineries that process plant biomass for the production of fuels and chemicals.²⁶ The most common biorefinery approach is to isolate the cellulose and hemicellulosic polysaccharides from the biomass, hydrolyze these polysaccharides to their monomers (saccharification), and then use microbial catalysts to convert the sugars to fuels (e.g., ethanol, butanol) or chemicals (e.g., L- or D-lactate, succinate). Commercial biorefineries use a thermo-chemical pretreatment in which the biomass is subjected to high temperature and high pressure, often in the presence of a catalyst.^{27,28} Acid-based thermochemical pretreatment hydrolyzes the hemicellulosic polysaccharides and redistributes the lignin, whereas alkaline pretreatment primarily dissolves the lignin. Both types of pretreatment make the cellulose more accessible to cellulolytic enzymes (cellulases) that can hydrolyze the cellulose to glucose. A difference between biorefineries and pulp and paper mills is that, depending on their location, the latter use predominantly softwood (pine, spruce) and hardwood (eucalyptus), whereas biorefineries process hardwood (poplar, willow), as well as various grasses (switchgrass, maize, sorghum, sugarcane, Miscanthus). The cell wall composition of grasses, including lignin composition, is distinct from those of woody species.^{22,29,30} The combined result of the variation in feedstock and processing method is that the resulting industrial lignin can vary substantially in molecular weight and chemical properties.^{31–35}

The thermal properties and behavior of Kraft and steam-explosion lignin, representing industrial lignins from the pulping industry and a biorefinery, respectively, have been compared to their chemically (purified) extracted counterparts, to assess their potential for the production of value-added products from these lignins.³⁶ The purified lignins were found to have similar thermal properties to one another. Meanwhile, their impurities significantly changed the thermal behavior of the lignins, and therefore their potential in value-added applications. The amount and nature of the impurities were governed by the extraction method and the source of the lignocellulosic material. The pulping extraction method generated more impurities compared to steam explosion. The ash content was affected the most, ranging from 0.45% for purified steam-explosion hardwood lignin to 36% for Kraft hardwood lignin. The amount of charred residue in purified lignins was much lower than that in lignins obtained directly

from the industrial residues. Based on the comparison of these two industrial lignins, steam-explosion lignin from biorefineries might have a higher potential for additional revenues, for example as a carbon fiber precursor, than Kraft lignin.³⁶

BIO-BASED POLYMERS FROM LIGNIN

Established applications of lignin include use as a cement additive to improve flow properties and enhance curing rates, use as adhesive, and use in drilling liquids for underwater oil wells.³⁷ Since the value of these products is relatively low, while large quantities of lignin are available, attempts are being made to develop additional uses of lignin that have the potential for higher revenues. Recent developments involving the use of lignin for the production of (co-)polymers with attractive features will be discussed below in more detail.

Lignin as a Copolymer in Biocomposites

The vast majority of commodity plastics like polyethylene (PE), polypropylene (PP), polymethylpentene (PMP) are polyolefins (produced from a simple olefin (alkene) with the general formula C_nH_{2n} as a monomer). While these polymers are light, their strength, stiffness and dimensional stability are limited, limiting their use in load-bearing structures.³⁸ Composites of olefins and other polymers that can compensate for the structural limitations of olefins are therefore of interest. Recently, various types of industrial lignins isolated from different plant species were evaluated for their suitability in composite production, and high-molecular-weight Kraft lignin was considered to be the most suitable for incorporation in polyolefins.³⁹ A higher molecular weight of the lignin improved lignin's affinity with the matrix. However, due to the presence of polar moieties and its complex structure, chemical modification of the lignin was recommended to improve the compatibility with polyolefins.³⁹

The large-scale use of bio-based polymers is of special interest due to the prospect of sustainability and bio-degradability. Polylactide (PLA) is a biodegradable polymer formed from the polymerization of microbially produced lactic acid, that suffers, however, from low impact strength, small elongation at break, suboptimal thermal properties, and poor UV light-barrier properties.⁴⁰ The development of lignin/PLA composites has been proposed as a way to enhance the thermal and mechanical properties of PLA.

Chung *et al.*⁴¹ improved miscibility between lignin and PLA by using a catalytic and solvent-free method to make a lignin/PLA copolymer. Lignin was activated by triazabicyclodecene (TBD) and lactide was graft-polymerized onto lignin resulting in a lignin-*g*-poly(lactic acid) copolymer. The authors were able to control the chain length of the PLA by changing the lignin/lactide ratio and pre-acetylation treatment. ¹H-NMR analysis revealed that the grafting capacity of lignin is very high and that grafting occurred preferentially on aliphatic rather than on phenolic hydroxyl groups. Spiridon *et al.*⁴² used compression molding of PLA pellets and industrial lignin—organosolv hardwood lignin or LignoBoost softwood lignin—to prepare lignin/PLA copolymers with a lignin content of approximately 7%. They showed that the addition of the lignin improved the thermal stability and mechanical properties of the polymer relative

to neat PLA. Simulated weathering analyses showed no negative impact of the lignin, although with time tensile and impact strength decreased. The effects of lignin on degradation of lignin/PLA composites submerged in an aqueous buffer solution was reported by Gordobil *et al.*,⁴³ who made copolymers via twin-screw extrusion using organosolv lignin (LO) extracted from almond shells and a commercially available alkaline lignin, both in native and acetylated form. The presence of lignin resulted in enhanced brittleness of the submerged samples, but also a reduced rate of degradation, with the acetylated lignin generally improving mechanical properties relative to the native lignin.

Lignin as Reinforcement for Polymers

Several polymer composite systems have been reported to use modified lignin particles as reinforcement for potential applications in the rubber industry. For example, Xiao *et al.*⁴⁴ prepared a lignin-layered double hydroxide (lignin-LDH) complex via an *in situ* preparation of LDH. They then used a melt compounding method to prepare styrene-butadiene rubber (SBR)/LDH composites. Mechanical analyses of the composites indicated that lignin-LDH/SBR outperformed LDH/SBR in terms of modulus, tensile strength, elongation at break and hardness. The elongation at break of the composites increased with the lignin concentration. They speculated that the moduli for these SBR composites improved due to the formation of shear zones that formed when the composites were placed under tension. The better stress transfer at the interface was enabled by the elastic deformation resulting from the high aspect ratio of lignin-LDH reinforcement. The enhancement was also ascribed to the improved dispersion of LDH particles in the rubber matrix in the presence of lignin, which was confirmed by TEM.

In a different study the mechanical properties of rubber reinforced with hexamethylenetetramine (HMT)-modified lignin were compared to those of a rubber reinforced with commonly used filler, carbon black (produced by the incomplete combustion of petrochemicals).⁴⁵ In this instance, lignin-reinforced composites did not achieve the performance of carbon black-filled rubber. The reason was ascribed to the differences in size of the particles: carbon black ranging from 10 to 500 nm, whereas lignin particle size was in the tenths-of-microns range. Moreover, poor interfacial adhesion among polar groups of lignin and the hydrophobic matrix could contribute to the reduced tensile strength.

Adhesives Derived from Lignin

As mentioned before, a traditional application of industrial lignin is its use as adhesive in wood panels. Due to the abundant presence of phenolic groups, lignin can potentially replace phenol in phenol-formaldehyde (PF) resins in wood composite adhesives.⁴⁶ Such adhesives can be used in the production of plywood, particleboard and other kinds of wood composites. PF is highly toxic chemical and an irritant of the eyes and respiratory tract. Moreover, PF resins can be very expensive, because of the fluctuating price of phenol. Therefore, replacing current synthetic PF resins based on petrochemicals offers great economic and health benefits. The chemical structure of industrial lignin does not, however, afford high reactivity and therefore

restricts the commercial applications of lignins as adhesives. Recently, Yuan *et al.*⁴⁷ investigated the use of modified ammonium lignosulfonate (MAL) and polyethylenimine (PEI) as a natural adhesive in manufacturing binderless fiberboard. The MAL/PEI composites had higher storage modulus and $\tan \delta$ than the unmodified ammonium lignosulfonate (UMAL)/PEI composites, and had better bonding strength characteristics.

The limited solubility of lignins in organic solvents is another factor restricting broad use of lignins as adhesives. The solubility of Kraft lignin in organic solvents was improved by partial depolymerization through base-catalyzed depolymerization in supercritical methanol.⁴⁸ The partially depolymerized lignin was then converted to lignin-based polycarboxylic acid (LPCA) in presence of succinic anhydride. LPCA has the potential to be used as a curing agent for a commercial epoxy in a temperature range similar to the commercial anhydride-based curing agents.

Lignin-Derived Adsorbents of Selected Heavy Metals and Toxic Organic Compounds

The variety of functional groups present in the structure of lignin allows the preparation of hybrid systems via combination with inorganic particles such as $MgO \cdot SiO_2$ ⁴⁹ or fumed silica.⁵⁰ Due to the resulting porous structures, the products can be used for the effective adsorption of harmful chemicals and heavy metals. An alternative to obtain porous structures is lignin-derived active carbon.⁵¹ Black liquor lignin from the pulp and paper industry was evaluated as a precursor for activated carbon. The lignin was carbonized in an oxygen-free atmosphere and the resulting carbon was then activated with steam. The pore structures of the lignin-based activated carbon were greatly affected by carbonization temperature, activation temperature and activation time. Methylene blue was used as a model compound to assess the potential of such activated carbon for dye wastewater treatment. The adsorption of a series of dye solutions at different concentrations in the presence of activated carbon was evaluated and used to determine that the optimal lignin-based activated carbon was obtained using a carbonization temperature of 450°C. The maximum adsorption capacity was such that lignin-based activated carbon is considered to have potential for use in dye wastewater treatment.

Lignin-Based Flocculants

Chemically modified lignin can be used as a flocculant. Flocculants, often positively charged molecules, are used to remove suspended solids from liquids by forming aggregates of colloids and other suspended particles that precipitate⁵² and play an important role in wastewater treatment and the removal of contaminants to prepare potable water.^{53,54} Environmentally friendly flocculants that are nontoxic and biodegradable are highly desirable. Rong *et al.*⁵⁵ investigated the flocculant properties of acrylamide grafted onto a lignin backbone. The resulting positively charged lignin-acrylamide (L-A) was evaluated for its ability to coagulate aluminum (Al). L-A markedly enhanced the removal efficiency of dissolved organic carbon, especially at low Al dosages, which reduced turbidity. The dissolved organic carbon removal efficiencies of aluminum sulfate and polyaluminum chloride at the Al dosage range selected in the study were improved more than 30% and 5% by L-A, respectively. L-A

drastically enlarged floc size, while floc strength and recoverability were also improved.⁵⁵

Lignin as an Antioxidant Additive for Food Packaging Material

Materials for food packaging must provide a barrier to minimize changes in composition prompted by environmental conditions, such as exposure to moisture, oxygen, or light. The selection of packaging materials should ideally balance food protection with other features, such as material and manufacturing costs, and the environmental impact of manufacturing and disposal. In this context, bio-based packaging has received considerable interest.^{56,57} Lignin has been of interest in food packaging applications because of its antioxidant activity, resulting from the presence of sterically hindered phenolic hydroxyl groups. Lignin has been added to PLA, as well as latex- and starch-based coatings, with the goal of improving the antioxidant activity of these polymers.

PLA-lignin films were prepared by twin-screw extrusion followed by thermo-compression using two different commercial sources of alkali lignins and different heat regimens.³⁴ Mechanical properties of the blends, however, were slightly diminished due to a counterbalancing effect between reinforcement by high-molecular-weight lignin and the plasticization by low-molecular-weight lignin. The antioxidant activity increased with increasing severity of the heat treatment due to the generation of free phenolic monomers during processing. The authors concluded that active packaging materials containing lignin as a natural antioxidant have equal mechanical and barrier performance as the original packaging material.³⁴

Fractionation of lignin with solvents exhibiting different polarity is a promising way to obtain homogeneous lignin products with significant antioxidant activity. The three soluble fractions extracted from commercial lignin by a sequential isolation with dichloromethane, methanol and a mixture of two solvents were compared to one another. The thermo-oxidative degradation of the model polyurethane (PU) elastomer samples was studied by thermogravimetric analysis (TGA) in the temperature range between 20 and 700°C. It was determined that, although all three fractions exhibited antioxidant properties, the most prominent activity was observed in the fraction extracted in dichloromethane/methanol.⁵⁸

Johansson *et al.*⁵⁹ included laccase from the white-rot fungus *Trametes versicolor* and LS in coating colors, and incorporated them in latex- or starch-based films and coatings on a foil or board. Oxygen levels were monitored in an airtight chamber at 100% relative humidity and shown to decline from 1% to 0.3% in the presence of laccase-containing coatings, while remaining unchanged in the no-laccase controls. Moreover, the water stability of latex-based coatings and starch-based films containing LS was enhanced after laccase-catalyzed oxidation of LS, due to the formation of polymerization products exhibiting lower water solubility. Furthermore, the storage modulus E' of starch-based films increased by 30%, which indicates that laccase-catalyzed polymerization of LS resulted in higher stiffness of the composite. Given that the beneficial impact of laccase on packaging properties requires a high-moisture environment, the

composite is recommended for active packaging of high-moisture foods like bread, fresh fish, and meat.⁵⁹

More recently, the same group investigated the oxygen-scavenging ability of laccase-containing coatings derived from alkali lignin (LA), hydrolytic lignin (LH), LO, and LS.⁶⁰ The oxygen-scavenging ability of coatings was evaluated in airtight, oxygen-containing containers with 92–100% relative humidity. Laccase-containing coatings derived from LS and LO displayed the highest oxygen-consumption rate, whereas coatings derived from LA and LH displayed minimal oxygen-scavenging capability. As a result of laccase activity, the molecular weight of the LO and LS dispersed in starch films increased, but much more so for LS than for LO. This could be due to the charged sulfonate groups enabling a better dispersion in the polar starch matrix, making more reactive groups accessible for polymerization.

LIGNIN AS A PRECURSOR FOR CARBON FIBERS

With increasing demands for the weight-to-performance ratio and the desire for low-cost materials, carbon fibers have attracted the attention of several major industries for years.⁶¹ The high cost of the carbon fiber precursors (such as polyacrylonitrile (PAN), pitch, rayon, phenolic resins) and their complex manufacturing processes, limit their large-scale applications.⁶² Moreover, the impact on the environment caused by toxic by-products such as hydrogen cyanide (during PAN processing) has raised serious concerns. Renewable, bio-based alternatives for carbon precursors are being developed, and the carbonized structure of lignin allows it to be used as renewable, low-cost graphitic carbon materials.⁶³ Lignin-based carbon materials such as fibers, mats, nanofibers, and mesoporous carbon have been successfully developed by a number of research groups, as discussed below. Depending upon processing methods, for example melt processing,^{64,65} dry-spinning,⁶⁶ or electrospinning,⁶⁷ it is possible to prepare lignin-based carbon fibers with a diameter ranging from several nanometers to sub-millimeter. The microstructure and properties of these carbon fibers can be easily tailored through the choice of chemical modification of lignin precursors and carbonization parameters.

LO was modified by incorporating different ester groups using dicarboxylic acid anhydrides.⁶⁴ The resulting carbon precursor was highly suitable to melt processing methods like fiber extrusion technique and conversion into microstructured carbons by oxidative stabilization and further carbonization. The results indicated a relationship between carbonization temperature and the structure of the carbons (graphitic vs. disordered structures). Chemical modification also played significant role in the microstructure formation. As such, carbon fibers made from phthalic anhydride-modified lignin were reported to have relatively high micro-scale porosity compared to carbon fibers made from unmodified lignin.

Nordström *et al.*⁶⁵ improved the spinability of softwood Kraft lignin by adding 10 wt % hardwood Kraft lignin permeate (HKLP) as a softening agent. To produce HKLP, black liquor was filtered through a ceramic membrane with a 15-kD molecular weight cut-off prior to isolation.⁶⁸ They further extruded fibers using 0.2 and 0.5 mm dies. Although the tensile strength

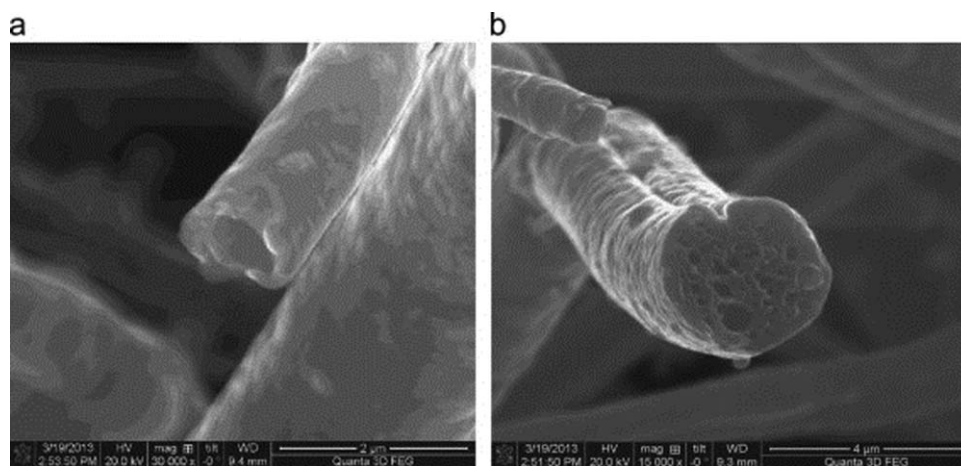


Figure 2. SEM images of carbonized lignin/PAN hollow fiber (a) and CNFs-lignin/PAN core-shell fiber (b). Reproduced from Ref. 67, with permission from [Elsevier].

(~ 300 MPa) of the produced lignin-based carbon fibers was still significantly lower than the values reported for commercially available isotropic carbon fibers (1720 MPa),⁶⁹ the stiffness (~ 30 GPa) was comparable.

Carbon fibers with smaller diameters can be prepared by the dry-spinning method. For example, Zhang and Ogale⁶⁶ successfully processed an acetylated softwood Kraft lignin into precursor fibers using the dry-spinning technique and then generated carbon fibers with a diameter of 7 μm . Limited acetylation of lignin hydroxyl groups enabled dry spinning of the precursor using acetone (solvent) followed by thermo-oxidative stabilization. The authors reported superior mechanical properties of lignin-based carbon fibers, with tensile modulus, strength, and strain-to-failure values of 52 ± 2 GPa, 1.04 ± 0.10 GPa, and $2.0 \pm 0.2\%$, respectively. These fibers could possess a high fiber-matrix interfacial bond strength when used in polymeric composites due to a highly reactive surface. Moreover, because of solvent diffusion during dry-spinning, fibers displayed a crenulated surface that can provide a larger specific interfacial area for enhanced fiber/matrix bonding in composite applications.⁶⁶

Lignin-based carbon nanofibers can also be produced via electrospinning. To synthesize alkali Kraft lignin/cellulose nanofibrils (CNFs), PAN was added as a co-spinning polymer to produce hollow fibers or fiber shells.⁶⁷ Lignin formed the shell of these electrospun fibers, while the CNFs formed the porous core. To improve dispersion of CNFs in non-polar solvents, the authors performed surface acetylation followed by the dispersion of CNFs in silicone oil. This suspension was stable and suitable for electrospinning to form the fiber core. The obtained hollow and core-shell fibers were subsequently carbonized without initiating obvious changes on the fiber microstructure. Both types of new fibers, particularly the porous core-shell, exhibited increased surface area and porosity compared to conventional solid fibers, while the fibers' structures were virtually maintained after the carbonization process, as evidenced in Figure 2, which shows the cross section of carbonized hollow and core-shell fibers.⁶⁷

Cellulose nanocrystals (CNCs; nanosized cellulose fibrils) were used to reinforce electrospun carbon fibers prepared from aque-

ous dispersions of softwood LA and poly(vinyl alcohol) (PVA) by Ago *et al.*⁷⁰ Dynamic mechanical analyses showed that the thermo-mechanical properties of lignin : PVA electrospun mats were enhanced after addition of lignin. This was attributed to the strong molecular interaction with PVA, and the addition of CNCs further improved these properties. The storage modulus E' in the glassy region below T_g mostly declined as the content of lignin increased. The molecular interactions between lignin and PVA restricted the segmental motion, and as lignin weight percentages increased from 0 to 50%, T_g shifted from 95 to 166°C.⁷⁰

LIGNIN FOR ENERGY STORAGE IN BATTERIES

A novel application for lignin-based carbon materials is their use as electrodes in lithium-ion batteries (LIBs). Carbon nanomaterials, such as graphene, carbon nanotubes, mesoporous carbons, and carbon nanofibers display excellent potential as electrode materials for applications in energy storage devices due to their high electrical conductivity and large and accessible specific surface area.⁷¹ A low-cost monolithic battery electrode was prepared from organosolv hardwood lignin by melt blowing 8–15 μm fibers onto a PE support that formed a lignin fiber mat with a thickness of 1.2 cm.⁷² This electrically interconnected three-dimensional architecture can function as current collector and lithium insertion material, permitting the reduction of costs and mass compared to the inactive materials used in conventional battery designs. The anode material exhibited adjustable electrochemical properties suitable for both high-power and high-energy applications. The resulting free-standing lignin-based electrodes displayed electrochemical properties comparable to the commercially available carbon-based anodes, but at substantially lower costs for materials and processing.⁷²

Another approach to using electrospun carbon mats for the anode in LIBs involved a blend of LO and polyethylene oxide (PEO).⁷³ Doping with nitrogen was shown to improve specific capacity as well as electrochemical conductivity of such mats. After thermal annealing in the presence of urea, the charge capacity was enhanced to as high as 576 mAh g^{-1} . For comparison, the theoretical value of the capacity of graphite is 372

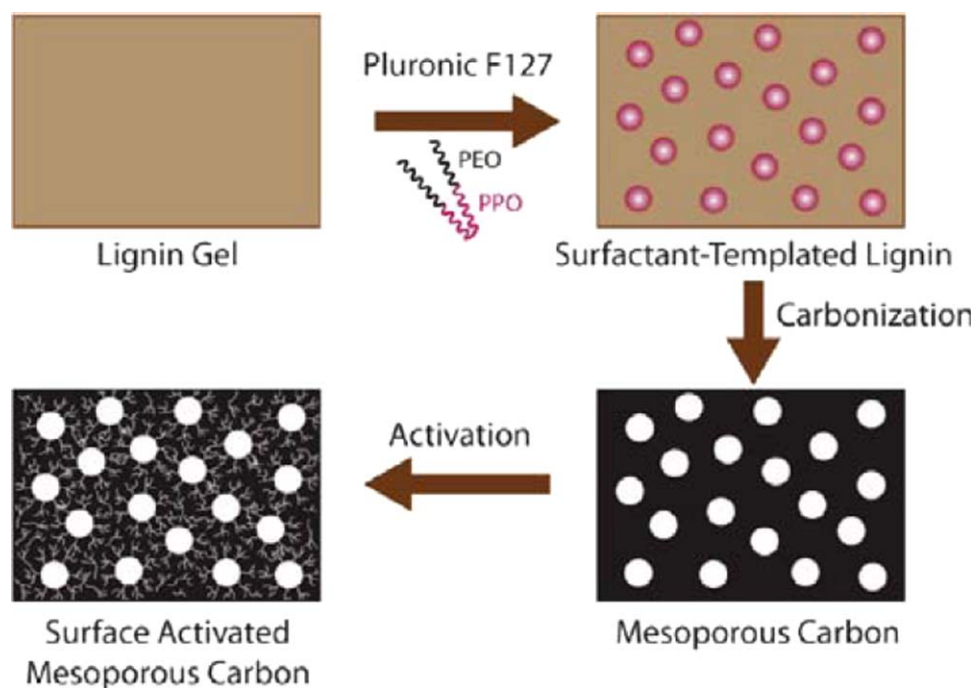


Figure 3. Schematic of surfactant-templated mesoporous and activated carbon synthesis from a lignin precursor. Reproduced from Ref. 74, with permission from [ACS Publications]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mAh g^{-1} . The carbon fibers without nitrogen doping demonstrated high specific capacity of 445 mAh g^{-1} at a current density of 30 mA g^{-1} (comparable to PAN-derived carbon nanofibers) and high cyclic stability at different current rates.

A recent report demonstrated the synthesis of mesoporous carbon from hardwood lignin.⁷⁴ Mesoporous carbons are carbon materials with 2–50 nm pores. Due to the availability of large volumes of mesopores and, therefore, large surface area, mesoporous carbons have a wide range of potential applications in membranes, fuel cells, supercapacitors, catalyst supports, chemical sensors, and sorbents. Phenolic resins are the main carbon precursor for mesoporous carbons, because the phenolic hydroxyl groups can form hydrogen bonds with the miscible segment of the block copolymer surfactants that further form micelles. The formed micelle domains generate the mesoporosity in the resultant carbon. Due to the abundance of hydroxyl groups, lignin is potentially a suitable precursor for mesoporous carbon. However, the branched and complex structure of lignin might make it challenging to control the porosity. The schematic of the synthesis of mesoporous carbon from lignin is shown in Figure 3. Mesoporous carbon was prepared from solvent-swollen gel of acid-treated, hardwood Kraft lignin in the presence of a templating agent (surfactant polyol Pluronic F127), which introduced micelles of surfactant in the lignin matrix. Mesoporosity was introduced by pyrolysis and carbonization during solvent removal and cross-linking of the matrix.⁷⁴ The gravimetric capacitance of the pure carbon was $77.1 \text{ Faraday g}^{-1}$, which was improved after activation to 102.3 and 91.7 F g^{-1} for CO_2 - and KOH -activated carbons, respectively.⁷⁴ While the gravimetric capacitance values are still lower than those of mesoporous carbons based on aque-

ous electrolyte ($100\text{--}200 \text{ F g}^{-1}$) without the presence of any pseudo-capacitance agents, they are on the same order of magnitude as single-walled or multiwalled carbon nanotubes ($50\text{--}100 \text{ F g}^{-1}$).⁷⁵

Besides use in LIBs, supercapacitors are used for electrochemical energy storage. Supercapacitors are more attractive energy storage devices than LIBs, due to their high power, long cycle life, fast charge/discharge rate, and safe operation. Two main types of supercapacitor exist: Pseudo-capacitors and electrochemical double-layer capacitors (EDLCs). A pseudo-capacitor is a type of supercapacitor that stores charge through a redox transfer at the electrode surface. Metal oxides (e.g., RuO_2 , MnO_2 , NiO , and CuO_2) and conducting polymers (e.g., polyaniline, polypyrrole, and polythiophene) have been investigated for use as pseudo-capacitive materials.⁷⁶ While pseudo-capacitors have increased energy density, power density and cycle life are limited compared to EDLCs.⁷⁷ The energy storage of EDLCs on the other hand, is limited by surface area and charge separation at the interface of electrode materials and electrolyte.⁷⁷ Hybrid supercapacitors that combine the advantages of both types have been developed by combining MnO_2 with carbon nanotubes.⁷⁷

This concept was taken further by the development of a renewable hybrid electrode consisting of lignin used as pseudo-capacitor and highly electron-conducting reduced graphene oxides (RGO) used as EDLCs.⁷⁸ RGO-lignin SCs were prepared by mixing of amphiphilic graphene oxide (GO) sheets and softwood sodium LS at different weight ratios. The two materials interacted through π - π stacking and hydrogen bonding. Reduction of the GOs with hydrazine resulted in electron-conducting lignin-RGO nanosheets, as represented in Figure 4. Interestingly, the reduction of GOs

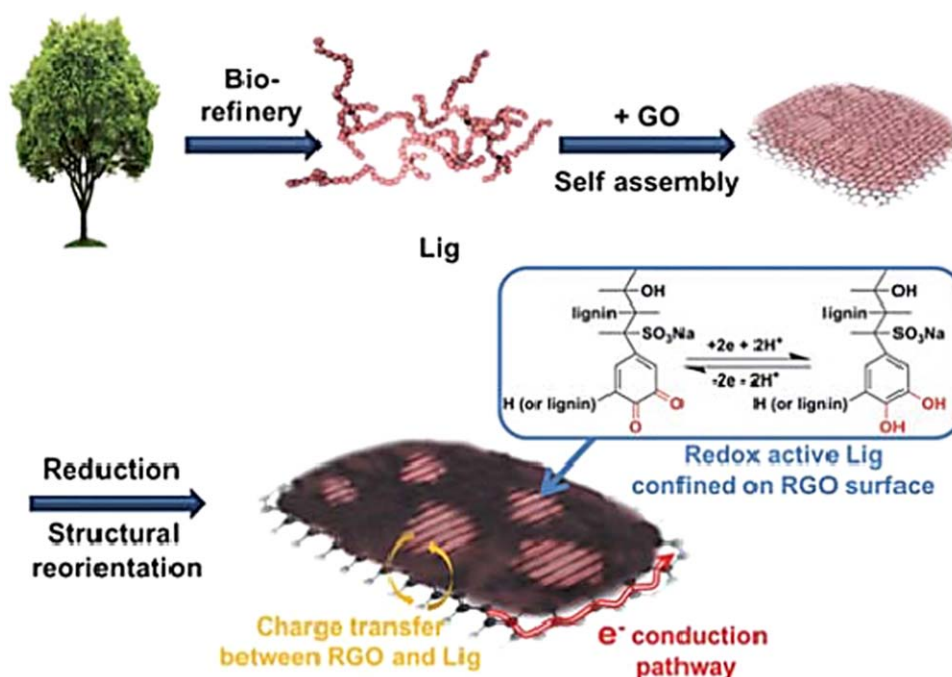


Figure 4. Energy-storage mechanism for lignin hybridized with RGO nanosheets. Reproduced from Ref. 78, with permission from [WILEY-VCH Verlag GmbH & Co]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

led to reorientation of the lignin and resulted in randomly distributed, discrete nanocrystals on the surface of the hybrid material, whereas RGOs not interacting with lignin were restacked into a few layers (Figure 5). The excellent capacitive

properties of the renewable hybrid electrodes were attained by generating the fast and reversible redox charge transfer of surface-confined quinone and the interplay with electron-conducting RGOs. Consequently, pseudo-capacitors with impressive rate and cyclic properties ($\sim 96\%$ retention after 3000 cycles) displayed a maximum capacitance of 432 F g^{-1} , which was close to the theoretical capacitance of 482 F g^{-1} , and six-fold higher than values obtained for RGO (93 F g^{-1}).⁷⁸

LIGNIN FOR BIOMEDICAL APPLICATIONS

Lignin for Controlled Drug Delivery

Hydrogels are attractive materials for tissue engineering due to their intrinsic structural and compositional resemblance to the extracellular matrix and, therefore, their high potential for cellular proliferation and survival. Hydrogels are three-dimensional (3D) networks of polymer chains formed when hydrophilic homopolymers, copolymers, or macromers crosslink to form insoluble polymer matrices. These structures can absorb liquid from one-fifth up to thousands of times their dry weight.⁷⁹ They are highly attractive for biomedical applications because they are generally biocompatible, while the aqueous medium in which they are embedded can protect cells, drugs, peptides and proteins from degradation. The aqueous environment can also promote transport of nutrients and metabolic products in and out of cells. Hydrogels can be injected *in vivo* as a liquid that further gels and crosslinks at body temperature and they can be easily modified with cell adhesion ligands for specific applications.^{80,81}

Xanthan gum is a polysaccharide that can be used for the production of biodegradable hydrogels, but it has limited reactivity and a narrow range in thermo-chemical properties. Copolymers between xanthan gum and lignin are expected to improve these

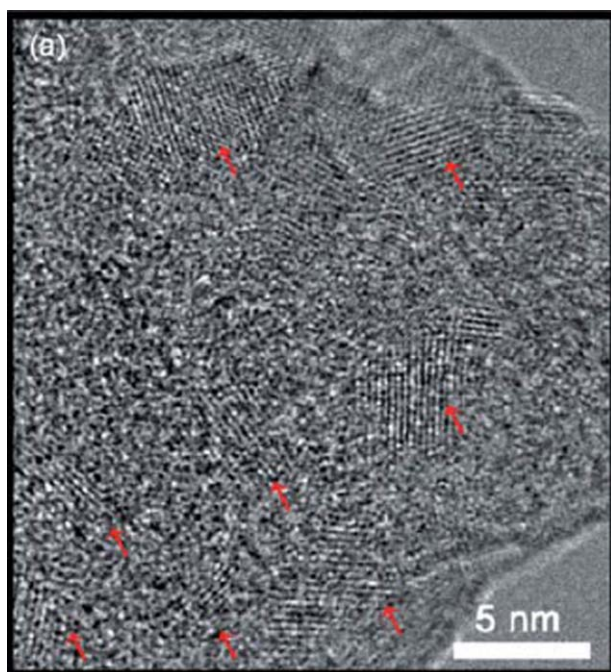


Figure 5. Field Emission Transmission Electron Microscopy image of RGOs/60 wt % lignin. Red arrows denote lignin nanocrystals confined on RGOs. Reproduced from Ref. 78, with permission from [WILEY-VCH Verlag GmbH & Co]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

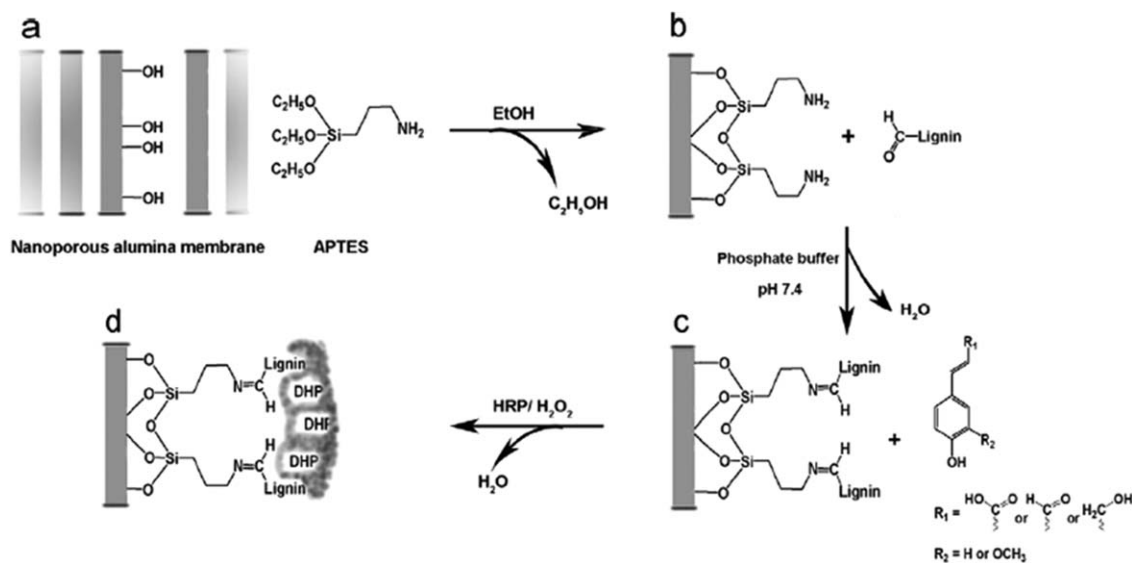


Figure 6. Schematic illustration of the synthesis of LNTs. (a) Activation of alumina membrane with APTES; the reactive sites are only shown on one of the pore walls. The inactivated (sputter-coated) upper and lower surfaces of the membrane are indicated by the dark-gray caps. (b) Schiff's base reaction between the amino groups on the APTES-activated membrane and aldehyde moieties in the thioglycolate lignin forms a base layer; only one pore wall is displayed. (c) Hydroxycinnamic acids, hydroxycinnamaldehydes or hydroxycinnamyl alcohols are added and (d) polymerize onto the lignin base layer through a reaction catalyzed by horseradish peroxidase (HRP)/H₂O₂ to form DHP. Reproduced from Ref. 87, with permission from IOP Publishing. All rights reserved.

features, while offering enhanced thermo-oxidative properties, and antimicrobial activity.⁸² Raschip *et al.*⁸³ reported on the development of superabsorbent xantham-gum-based hydrogels based on different types of lignin. These lignin-based semi-interpenetrating (semi-IPN) hydrogels were synthesized based on a crosslinking reaction with epichlorohydrin. The resulting hydrogels had a high swelling degree in an aqueous environment, with the source of the lignin influencing both the thermo-oxidative stability and swelling characteristics.

Lignin has also been used to prepare a thermo-responsive hydrogel that displays different gelling behavior at different temperatures.⁸⁴ This was achieved by reaction between acetic acid lignin with *N*-isopropylacrylamide (NIPAAm) in the presence of *N,N'*-methylenebisacrylamide (MBAAm) as the crosslinker and H₂O₂ as initiator. Differential scanning calorimetry (DSC) analysis demonstrated that the lower critical solution temperature of the hydrogels was approximately 31°C. The developed material contained pore sizes between 20 and 100 μm that were tunable by altering the lignin concentration.

The aforementioned mesoporous carbon lignin can potentially also be used as a controlled-release medium for functional molecules such as pharmaceuticals and therapeutic agents.⁸⁵ The experiments were conducted with captopril, a drug used for the treatment of hypertension and some types of congestive heart failure. The synthesized carbons possessed pore widths in a range of 2.5–12.0 nm. This modified carbon demonstrated adsorption and controlled release of captopril in simulated gastric fluid within 50 h as a result of the prevailing mesoporosity.⁸⁵ Due to the potential of large molecules to be adsorbed by mesopores, these carbons can be useful for such applications as dye adsorption, protein binding, pollution control, catalysis, molecular transport and other controlled-release applications.

Recently, Yiamsawas *et al.*⁸⁶ generated lignin–polyurea/polyurethane nanocontainers at the interface of stable water nanodroplets in an inverse mini-emulsion. These biodegradable nanocontainers with an aqueous core can potentially encapsulate hydrophilic substances such as bioactive drugs, or be used for advanced agricultural applications such as encapsulation of pesticides or fertilizers. Lignosulfonate sodium salt was dissolved together with sodium chloride to generate the dispersed phase, which was then combined with cyclohexane containing polyglycerol polyricinoleate (PGPR), the biocompatible surfactant. The poly-addition reaction at the interface of the mini-emulsion nanodroplets was initiated after a solution of toluene diisocyanate (TDI) in cyclohexane was added drop-wise to the previously prepared mini-emulsion.⁸⁶ The lignin nanocontainers displayed diameters in the range of 150–200 nm and were stable in organic or aqueous media over a long period of time (several weeks to months). Moreover, enzymatic degradation of lignin nanocontainers was evaluated by using laccase as a model enzyme, as well as a mixed enzyme cocktail extracted from fungi. In order to assess the biodegradability, the hydrophilic fluorescent dye sulforhodamine (SR101) was encapsulated in the lignin nanocontainers. Release of the dye following degradation of the capsule shell could be monitored based on fluorescence intensity. These biodegradable lignin nanocontainers are attractive for use in long-term drug release systems.⁸⁶

Lignin-Based Nanotubes for DNA Delivery

Our group has developed a protocol for the synthesis of lignin nanotubes (LNTs) and lignin nanowires (LNWs) with the potential to function as efficient, cost-effective, and biocompatible vehicles for the delivery of DNA and therapeutic agents.

The synthesis of LNTs and nanowires was based on crosslinking a lignin base layer to an alumina membrane, followed by

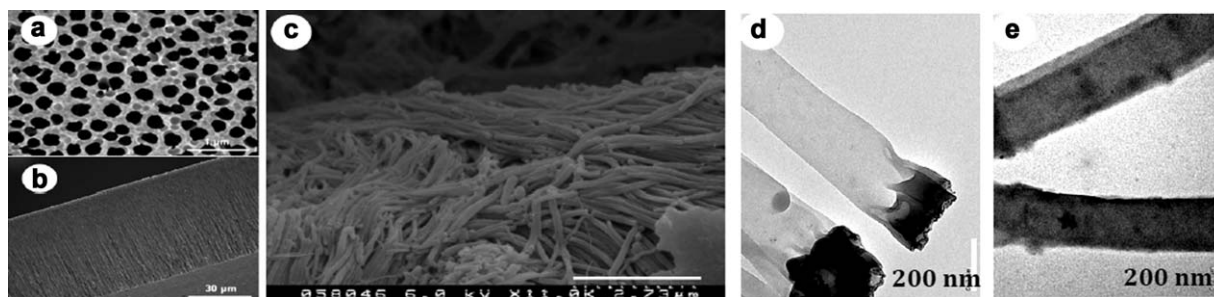


Figure 7. LNTs are synthesized in a sacrificial alumina template (a—top view; b—side view), which is dissolved in phosphoric acid to release them (c). Depending on the composition of the DHP liner, hollow tubes (d) or solid rods (e) can be manufactured. Reproduced from Ref. 87, with permission from IOP Publishing. All rights reserved.

peroxidase-catalyzed addition of dehydrogenation polymer (DHP; “synthetic lignin”) and dissolution of the membrane in dilute phosphoric acid.⁸⁷ A schematic illustration of the synthesis of LNTs is depicted in Figure 6. Depending upon type of the monomers used for the deposition of DHP, solid nanowires or hollow nanotubes can be synthesized (Figure 7) and easily functionalized with, for example, proteins, due to the abundance of reactive groups. As a result of their auto-fluorescence, LNTs allow label-free detection under UV radiation, while optical and physical properties of LNTs can be customized according to the monomers employed in the polymerization process.⁸⁷

It was recently demonstrated that LNTs can be used for the delivery of DNA into human HeLa cells in tissue culture without auxiliary agents.⁸⁸ These studies involved adding LNTs coated with cDNA encoding the green fluorescence protein (GFP) under control of the β -actin promoter to HeLa cells. After 48 h, fluorescent foci appeared that correlated with the increasing dose of DNA, indicating successful delivery and expression of the GFP cDNA (Figure 8). Compared to carbon nanotubes, the cytotoxicity of LNTs was substantially lower.

The efficacy of delivery was a function of the method with which the lignin had been isolated from the plant tissue. Confocal microscopy imaging revealed that the LNTs had penetrated the HeLa cells in all cases (Figure 8), but that the highest level

of expression was observed in those instances where the LNTs had penetrated the cell nuclei.

Once LNTs or LNW have been successfully tested in mice, functionalized LNTs able to target specific cells, tissues, or organs may serve as nanocarriers for DNA and therapeutic agents, which could include the use of LNTs for the tumor-specific delivery of anticancer drugs.

FUTURE PERSPECTIVES

While the applications discussed in the previous sections relied on the use of lignin as it was isolated during biomass processing, recent efforts have focused on degradation of lignin to low-molecular weight (C_6 - C_{12}) compounds that can be used as drop-in fuels, either pure or mixed with petroleum-based fuels. The major reasons for exploring lignin for this purpose are the higher energy content of lignin-derived fuels relative to ethanol, currently the most widely used biofuel, and the potential market size. Large-scale processing of lignocellulosic biomass will generate vast amounts of lignin, and even if the specialty applications discussed so far would be widely implemented, there will still be plenty of lignin left. With the current annual global consumption of petroleum amounting to 5.24×10^{12} L of which jet fuel represents approximately 3.03×10^{11} L (5.8%; 2010 data),⁸⁹ lignin as a source of liquid transportation fuels for

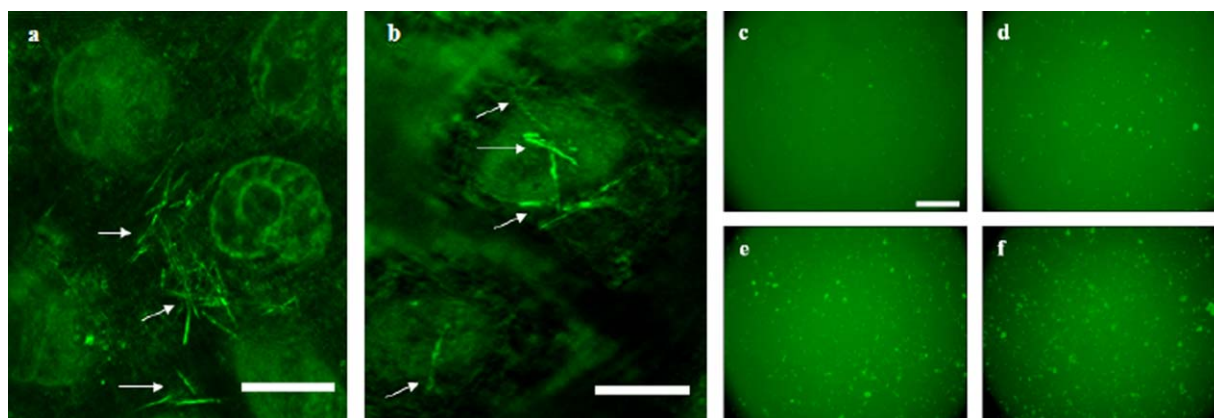


Figure 8. (a) Confocal microscopy image of DAPI-stained HeLa cells exposed to LNTs (marked by arrows) that were able to penetrate the cell, and (b) the nucleus. The efficiency of transfection of HeLa cells with a fixed concentration of 9.3 mg/mL LNTs is DNA-dosage dependent: (c) negative control; (d) 84 ng DNA (e) 294 ng DNA (f) 1.1 mg DNA. Scale bar $a = 15 \mu\text{m}$; scale bar $c = 200 \mu\text{m}$. Reproduced from Ref. 88, with permission from [ACS Publications]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

airplanes and other high-powered engines (ships, trucks) could address the desire to use more renewable resources for transportation, while at the same time offering biorefineries the opportunity to generate additional revenues from biomass processing.

Due to the many different types of chemical bonds in the lignin, and lack of a regular structure, relatively harsh conditions (temperature, catalyst) need to be applied to decompose the lignin, similar to the cracking of petroleum. A major challenge associated with the thermo-chemical decomposition of lignin is the formation of char, resulting from recondensation of lignin fragments. A number of excellent reviews have been published on this topic,^{90–93} and it remains an area of active research.

As the cultivation of dedicated energy crops expands in order to meet government mandates for renewable fuels, the available feedstock for the production of lignin-derived chemicals and polymers will increase as well. Lignin content and subunit composition have been shown to influence biomass recalcitrance,^{94–96} and there are many strategies to manipulate lignin biosynthesis *in planta*.^{15,97–99} Commercial production of these enhanced bioenergy crops, combined with different biomass processing schemes, will generate an array of lignin types that vary based on the relative proportions of lignin subunits, the distribution of interunit linkages, and the proportion of hydroxycinnamaldehyde end groups. This means that polymer-based applications of lignin will be able to utilize “designer lignin” with the optimal structure for that application. As the volume of bio-based polymers increases, a transition from market push to demand pull needs to occur.¹⁰⁰ Studies of consumer behavior towards ‘green’ products indicated that environmental sustainability is only one of several factors that are considered when selecting a product.^{101,102} This means that, along with educational efforts aimed at stimulating an awareness of the need for environmental sustainability, manufacturers need to develop bio-based products that also compete in terms of material properties and cost.

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