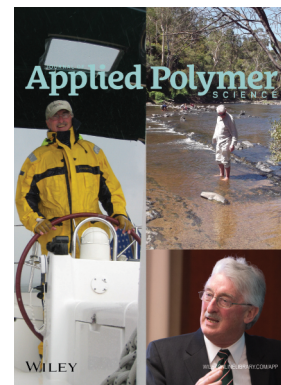


Special Issue: Sustainable Polymers and Polymer Science
Dedicated to the Life and Work of Richard P. Wool

Guest Editors: Dr Joseph F. Stanzione III (Rowan University, U.S.A.)
and Dr John J. La Scala (U.S. Army Research Laboratory, U.S.A.)



EDITORIAL

Sustainable Polymers and Polymer Science: Dedicated to the Life and Work of Richard P. Wool
Joseph F. Stanzione III and John J. La Scala, *J. Appl. Polym. Sci.* 2016, DOI: [10.1002/app.44212](https://doi.org/10.1002/app.44212)

REVIEWS

Richard P. Wool's contributions to sustainable polymers from 2000 to 2015
Alexander W. Bassett, John J. La Scala and Joseph F. Stanzione III, *J. Appl. Polym. Sci.* 2016,
DOI: [10.1002/app.43801](https://doi.org/10.1002/app.43801)

Recent advances in bio-based epoxy resins and bio-based epoxy curing agents
Elyse A. Baroncini, Santosh Kumar Yadav, Giuseppe R. Palmese and Joseph F. Stanzione III, *J. Appl. Polym. Sci.* 2016,
DOI: [10.1002/app.44103](https://doi.org/10.1002/app.44103)

Recent advances in carbon fibers derived from bio-based precursors
Amod A. Ogale, Meng Zhang and Jing Jin, *J. Appl. Polym. Sci.* 2016, DOI: [10.1002/app.43794](https://doi.org/10.1002/app.43794)

RESEARCH ARTICLES

Flexible polyurethane foams formulated with polyols derived from waste carbon dioxide
Mica DeBolt, Alper Kiziltas, Deborah Mielewski, Simon Waddington and Michael J. Nagridge, *J. Appl. Polym. Sci.* 2016,
DOI: [10.1002/app.44086](https://doi.org/10.1002/app.44086)

Sustainable polyacetals from erythritol and bioaromatics
Mayra Rostagno, Erik J. Price, Alexander G. Pemba, Ion Ghiriviga, Khalil A. Abboud and Stephen A. Miller, *J. Appl. Polym. Sci.*
2016, DOI: [10.1002/app.44089](https://doi.org/10.1002/app.44089)

Bio-based plasticizer and thermoset polyesters: A green polymer chemistry approach
Mathew D. Rowe, Ersan Eyiler and Keisha B. Walters, *J. Appl. Polym. Sci.* 2016, DOI: [10.1002/app.43917](https://doi.org/10.1002/app.43917)

The effect of impurities in reactive diluents prepared from lignin model compounds on the properties of vinyl ester resins
Alexander W. Bassett, Daniel P. Rogers, Joshua M. Sadler, John J. La Scala, Richard P. Wool and Joseph F. Stanzione III,
J. Appl. Polym. Sci. 2016, DOI: [10.1002/app.43817](https://doi.org/10.1002/app.43817)

Mechanical behaviour of palm oil-based composite foam and its sandwich structure with flax/epoxy composite
Siew Cheng Teo, Du Ngoc Uy Lan, Pei Leng Teh and Le Quan Ngoc Tran, *J. Appl. Polym. Sci.* 2016, DOI: [10.1002/app.43977](https://doi.org/10.1002/app.43977)

Mechanical properties of composites with chicken feather and glass fibers
Mingjiang Zhan and Richard P. Wool, *J. Appl. Polym. Sci.* 2016, DOI: [10.1002/app.44013](https://doi.org/10.1002/app.44013)

Structure–property relationships of a bio-based reactive diluent in a bio-based epoxy resin
Anthony Maiorana, Liang Yue, Ica Manas-Zloczower and Richard Gross, *J. Appl. Polym. Sci.* 2016, DOI: [10.1002/app.43635](https://doi.org/10.1002/app.43635)

Bio-based hydrophobic epoxy-amine networks derived from renewable terpenoids
Michael D. Garrison and Benjamin G. Harvey, *J. Appl. Polym. Sci.* 2016, DOI: [10.1002/app.43621](https://doi.org/10.1002/app.43621)

Dynamic heterogeneity in epoxy networks for protection applications
Kevin A. Masser, Daniel B. Knorr Jr., Jian H. Yu, Mark D. Hindenlang and Joseph L. Lenhart, *J. Appl. Polym. Sci.* 2016,
DOI: [10.1002/app.43566](https://doi.org/10.1002/app.43566)

Special Issue: Sustainable Polymers and Polymer Science
Dedicated to the Life and Work of Richard P. Wool

Guest Editors: Dr Joseph F. Stanzione III (Rowan University, U.S.A.)
and Dr John J. La Scala (U.S. Army Research Laboratory, U.S.A.)

Statistical analysis of the effects of carbonization parameters on the structure of carbonized electrospun organosolv lignin fibers

Vida Poursorkhabi, Amar K. Mohanty and Manjusri Misra, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.44005

Effect of temperature and concentration of acetylated-lignin solutions on dry-spinning of carbon fiber precursors

Meng Zhang and Amod A. Ogale, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.43663

Poly(lactic acid) bioconjugated with glutathione: Thermosensitive self-healed networks

Dalila Djidi, Nathalie Mignard and Mohamed Taha, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.43436

Sustainable biobased blends from the reactive extrusion of polylactide and acrylonitrile butadiene styrene

Ryan Vadori, Manjusri Misra and Amar K. Mohanty, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.43771

Physical aging and mechanical performance of poly(L-lactide)/ZnO nanocomposites

Erlantz Lizundia, Leyre Pérez-Álvarez, Míriam Sáenz-Pérez, David Patrocínio, José Luis Vilas and Luis Manuel León, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.43619

High surface area carbon black (BP-2000) as a reinforcing agent for poly[(-)-lactide]

Paula A. Delgado, Jacob P. Brutman, Kristina Masica, Joseph Molde, Brandon Wood and Marc A. Hillmyer, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.43926

Encapsulation of hydrophobic or hydrophilic iron oxide nanoparticles into poly-(lactic acid) micro/nanoparticles via adaptable emulsion setup

Anna Song, Shaowen Ji, Joung Sook Hong, Yi Ji, Ankush A. Gokhale and Ilsoon Lee, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.43749

Biorenewable blends of polyamide-4,10 and polyamide-6,10

Christopher S. Moran, Agathe Barthelon, Andrew Pearsall, Vikas Mittal and John R. Dorgan, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.43626

Improvement of the mechanical behavior of bioplastic poly(lactic acid)/polyamide blends by reactive compatibilization

JeongIn Gug and Margaret J. Sobkowicz, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.43350

Effect of ultrafine talc on crystallization and end-use properties of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)

Jens Vandewijngaarden, Marius Murariu, Philippe Dubois, Robert Carleer, Jan Yperman, Jan D'Haen, Roos Peeters and Mieke Buntinx, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.43808

Microfibrillated cellulose reinforced non-edible starch-based thermoset biocomposites

Namrata V. Patil and Anil N. Netravali, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.43803

Semi-IPN of biopolyurethane, benzyl starch, and cellulose nanofibers: Structure, thermal and mechanical properties

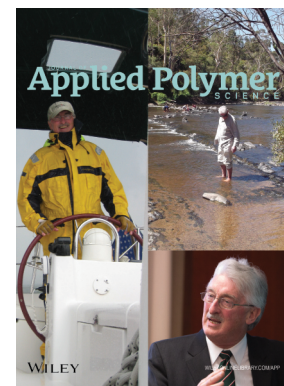
Md Minhaz-Ul Haque and Kristiina Oksman, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.43726

Lignin as a green primary antioxidant for polypropylene

Renan Gadioli, Walter Ruggeri Waldman and Marco Aurelio De Paoli, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.43558

Evaluation of the emulsion copolymerization of vinyl pivalate and methacrylated methyl oleate

Alan Thyago Jensen, Ana Carolina Couto de Oliveira, Sílvia Belém Gonçalves, Rossano Gambetta and Fabricio Machado, *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.44129



Recent advances in carbon fibers derived from biobased precursors

Amod A. Ogale, Meng Zhang, Jing Jin

Center for Advanced Engineering Fibers and Films, Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, South Carolina 29634

Correspondence to: A. A. Ogale (E-mail: ogale@clemson.edu)

ABSTRACT: High-performance carbon fibers (CFs) are currently produced primarily from polyacrylonitrile (PAN). However, the high cost of such CFs and the environmental concerns during its manufacturing (from PAN) are stimulating research on alternative bio-based precursors and environmentally friendly processing routes. This review summarizes the recent research studies on the pathways for converting cellulose and lignin (most abundant and renewable biomass) into suitable precursor fibers and CFs. The role of various bio-based precursors, fiber spinning routes, and process conditions on the final properties of CFs is discussed. Although bio-based CFs reported in the current research studies have limited strength and modulus to be considered for high-performance aerospace applications, further progress in precursor purification and optimized fiber processing may lead to their application in less demanding structural applications such as automotive and industrial. Even in their current state, a lack of graphitic crystallinity results in a lower conductivity for the resulting CFs and makes them suitable for ultrahigh temperature insulative applications. Furthermore, the noncrystalline form of carbon obtained from bio-based precursors clearly indicates a significant potential of carbon nanofibers, mats, and activated CFs in nonstructural applications that require a large specific surface area, such as electrochemical energy storage and purification. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43794.

KEYWORDS: biomaterials; cellulose and other wood products; fibers; structure-property relations

Received 13 February 2016; accepted 11 April 2016

DOI: 10.1002/app.43794

INTRODUCTION

Carbon fibers (CFs) possess outstanding specific strength and modulus, which is almost four times that of steel.^{1–3} The absolute tensile strength of CFs used in primary structural applications can approach 7 GPa, which is the highest value for any commercial reinforcing fibers. CFs possessing a high degree of graphitic content have a modulus as large as 830 GPa. Tensile strength and modulus of commercial CFs derived from polyacrylonitrile (PAN) and mesophase pitch are summarized in Table I (top two rows). In addition, when compared with metals like steel or titanium, CFs possess much lower specific gravity of only 1.8–2.2 and display much higher specific modulus and strength.¹ Even when compared with other strong polymer fibers (viz., Kevlar), CFs display much higher specific modulus and strength, which are retained at elevated temperatures. They are now being used commercially in structural, light-weight composites (e.g., fuselage and wings of Boeing 787 Dreamliner) for enhanced fuel efficiency and ergonomics. CFs are also being used in nonstructural applications because of their excellent

electrical and thermal conductivity. Furthermore, the heat treatment step can be altered to generate “activated” CFs with very large specific surface area, which have applications in gas separation, water purification, and electrical energy storage.

Unlike most polymers, carbon does not melt and cannot be directly extruded into a fiber form. Therefore, a single-step process for producing CFs does not exist. Rather, a suitable organic precursor material is first processed into “precursor fibers” that subsequently must be “stabilized.” The stabilization step is perhaps the most critical one because the precursor material must get thoroughly crosslinked into a thermoset without the individual filaments sticking to each other. Finally, the stabilized fibers are heat-treated in an inert environment at temperatures above 1000 °C to obtain CFs. The vast majority of high-performance commercial CFs are currently produced from the synthetic precursor PAN. The primary advantage of PAN is that it does not melt, and thus, its solution-spun fibers can be easily stabilized and subsequently carbonized at temperatures of 1200–1500 °C. The resulting CFs possess outstanding tensile strength

This article is dedicated in the fond memory of our colleague late Prof. Richard Wool with whom we had an opportunity to collaborate on a biomass-derived composites project, SERDP WP-1758.

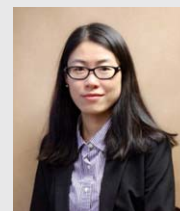
Amod A. Ogale and Meng Zhang contributed equally to this work as co-first authors.

© 2016 Wiley Periodicals, Inc.

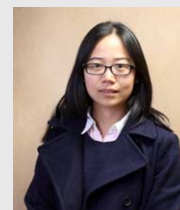
Amod A. Ogale is the Dow Chemical Professor and Director of the Center for Advanced Engineering Fibers and Films (CAEFF) at Clemson University. He is a Fellow of the Society of Plastics Engineers and received the 2013 Graffin Lecturer Award from the American Carbon Society. He has served as the principal investigator of more than 50 major federal and industry-sponsored projects. He has published more than 100 refereed papers and has graduated 40 PhD and MS students.



Meng Zhang received her B.S. and M.S. in Bioengineering and Biochemical Engineering from Tianjin University, China. She is currently a PhD student in Amod A. Ogale's group at Clemson University. Her research focuses on carbon fibers derived from lignin precursor. Her work covers polymer processing and rheology, polymer structure-property relationships, carbon fiber production, and composites.



Jing Jin received her B.S. in Chemical Engineering from East China University of Science and Technology in 2012. She is currently a PhD student in Amod A. Ogale's group at Clemson University. Her research focuses on the development of bio-based precursors, polymer synthesis and characterization, rheology analysis, fiber spinning, and microstructural analysis of carbon fibers.



of 3–7 GPa and a moderately high modulus of 200–300 GPa. However, the solution-based wet-spinning process itself involves the use of hazardous solvents, and the nitrile groups in PAN generate toxic byproducts (viz., hydrogen cyanide) during heat treatment.^{2,3} The environmental concerns and the related costs

associated with this process can be partially overcome by using bio-based precursors. Among naturally occurring biomass, lignin and cellulose are regarded as potential CF precursors because of their low cost and carbon-forming chemical structure. This article presents a review of the research strategies

Table I. Summary of the Tensile Properties of Carbon Fibers Obtained from Different Precursors

| Precursor type | Diameter (μm) | Modulus (GPa) | Tensile strength (MPa) | Reference |
|----------------------------------|----------------------------|-----------------|------------------------|-----------|
| PAN | 5-10 | 100-500 | 3000-7000 | 1-3 |
| Mesophase pitch | 5-15 | 200-800 | 1000-3000 | 1-3 |
| Various types of lignin | N/A | N/A | 150-800 | 4 |
| Steam-exploded hardwood lignin | 8 ± 3 | 40.7 ± 6.3 | 660 ± 230 | 5 |
| Organosolv hardwood lignin | 14 ± 1 | 39.1 ± 13.3 | 355 ± 53 | 6 |
| Hardwood kraft lignin/PEO | 33 ± 2 | 59 ± 8 | 458 ± 97 | 7 |
| Hardwood kraft lignin | 10 ± 1 | 28.6 ± 3.2 | 520 ± 182 | 8 |
| Hardwood kraft lignin | — | 82.7 | 1070 | 9 |
| Softwood/hardwood kraft lignin | 36-78 | 25-33 | 233-377 | 10 |
| Acetylated softwood kraft lignin | 6 ± 1 | 52 ± 2 | 1060 ± 70 | 11 |
| Lignin/PAN blend (25% lignin) | — | 217 | 2250 | 12 |
| Lignin/PAN blend (30% lignin) | 11 ± 1 | 230 ± 7 | 1720 ± 200 | 13 |
| Lignosulfonate-AN copolymer | 12-20 | — | 540 | 14 |
| Rayon | — | 720 | 1250 | 15,16 |
| Rayon | — | 70.7 ± 2.4 | 1500 ± 200 | 17 |
| Lyocell | — | 96.6 | 1070 | 18 |

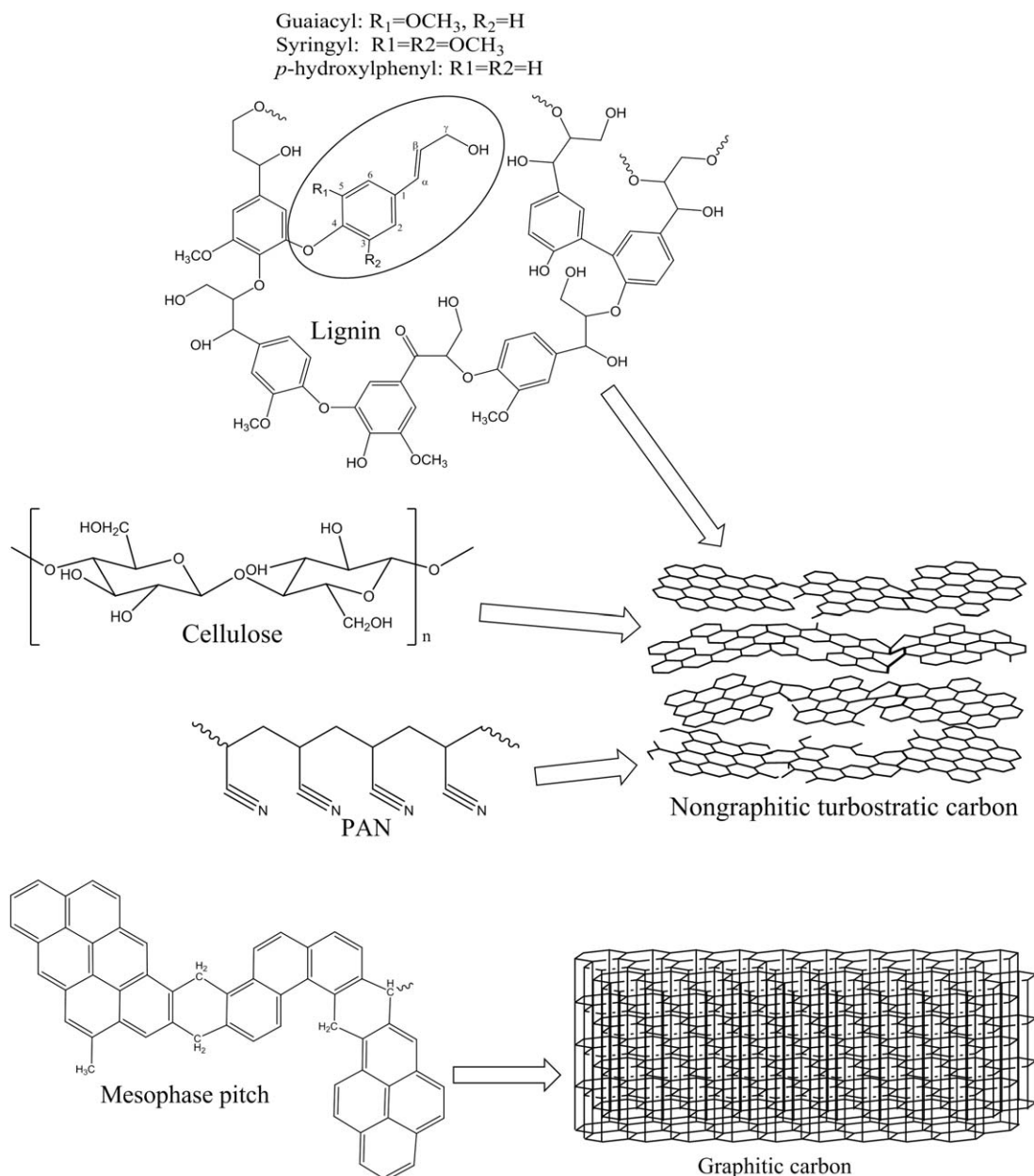


Figure 1. Schematic representation of chemical structure of lignin, cellulose, PAN, and mesophase pitch. A typical building unit of lignin is encircled. The first three precursors generate CFs with noncrystalline/turbostratic structure, whereas mesophase pitch generates graphitic/crystalline structure (adapted from Refs. 3 and 20).

proposed in the literature for converting such biomass into useful precursors and subsequent conversion into CFs.

Raw wood, an abundant source of biomass, nominally consists of 40–50% of cellulose, 23–32% of hemicellulose, and 15–30% lignin.¹⁹ A simplified schematic of lignin molecular structure is illustrated in Figure 1, with a typical building/repeat unit encircled.²⁰ Although its molecular structure can vary significantly, lignin is an amorphous and crosslinked polymer in its naturally occurring state. It is abundant in aromatic rings and consists of three primary precursor units: guaiacyl, syringyl, and *p*-hydroxyphenyl.²⁰ Guaiacyl is found predominately in softwood lignins, syringyl is found in hardwood lignins, and *p*-

hydroxyphenyl occurs mostly in annual crops.²⁰ The typical chemical structure of cellulose, also illustrated in Figure 1, is composed of β -D-glucopyranose units linked by 1–4 glycosidic bonds, with more than 10,000 glucopyranose units in wood cellulose and 15,000 in cotton cellulose.²¹ As further shown in Figure 1, lignin, cellulose, and PAN form a nongraphitic or turbostratic structure within the resulting CFs, whereas mesophase pitch forms a highly graphitic (crystalline) structure after heat treatment above 2400 °C.³

As noted above, high-strength CFs used in current structural composite applications are almost exclusively derived from PAN precursor fibers. The evolution of toxic byproducts

accompanied by the fact that a large amount of organic solvent is needed during the coagulation step, the production of PAN-based CF is not an environment-friendly procedure. Thus, the studies on CFs from a bio-based precursor have received increasing attention. However, unlike synthetically produced PAN, biomass typically contains a significant amount of ash/minerals. This is particularly deleterious for the tensile strength of the resulting CFs, because such minerals lead to defects within the fibers. Therefore, the separation of lignin and cellulose from biomass is important and is discussed next.

The crosslinked form of lignin within wood must be broken down to separate it from the cellulosic fibers. This requires drastic chemical breakdown of the chemical linkages and is accomplished by chemical pulping. The different pulping methods affect the processibility of various lignin precursors to CFs and the performance of the resulting CFs. In the soda pulping process, sodium hydroxide (NaOH, caustic soda) is used as the reactant for making cellulosic pulp and is mainly used for pulping of nonwood materials.²² Kraft pulping, based on soda pulping, has become the dominant commercial process²³ and uses NaOH and sodium sulfide (white liquor) to break down the lignin matrix. Cleavage occurs at the linkages that hold the phenylpropane units together, which leads to the generation of free phenolic hydroxyl groups in the resulting kraft lignin. After pulping, a waste liquor containing lignin is separated from cellulose. The cellulosic pulp is further treated by bleaching, washing, and drying and is used to produce paper. In another process, called sulfite process, a pulping liquor consisting of sulfur dioxide aqueous solution and suitable bases is prepared.²⁴ After washing, the resulting brown liquor is concentrated and typically burned to provide steam and to recover the inorganic chemicals.

Lignin can be precipitated by acidification of black liquor followed by a wash cycle.²² A series of studies have been reported based on a novel process of separating lignin from black liquors, called LignoBoost.²⁵ The LignoBoost process involves filtering the precipitated lignin and redispersing the filter cake by aqueous acid followed by filtration and washing. The ash content of kraft lignin from this process can be ~0.2 wt %.²⁶ Recently, Klett *et al.*²⁷ reported a process using hot aqueous acetic acid to purify and fractionate black liquor resulting in an “ultrapure” lignin with an ash content lower than 0.1 wt %, which can help to increase CF strength significantly in future studies.

Kraft and sulfite pulping are efficient processes, but suffer from several environmental issues such as emission of waste water and malodorous products (sulfur containing). In addition, sulfur is introduced into the resulting lignin, which can lead to defects in the resulting CFs. Organic solvent pulping is a good alternative to overcome such problems. Multiple studies have been conducted using various organic solvents such as methanol,²⁸ ethanol,²⁹ and acetic acid.³⁰ One of the well-developed processes is the Alcell process that uses 50% aqueous ethanol solutions. Lignin is recovered from the spent liquor by precipitation, and solvent is recovered later by evaporation and condensation.³¹ As there is no addition of inorganic moieties and sulfur during the process, Organosolv lignin has higher purity

when compared with kraft lignin and lignosulfonates. This is an important factor for the use of such biomass as CF precursor because metal impurities lead to defects during the carbonization step and reduces the strength of resulting CFs.

The vast majority of commercial CFs are produced in a continuous form for primary structural applications, that is, where the strength and modulus of these reinforcing fibers are critical. In contrast, carbon filaments in the form of nanofibers or mats consisting of discontinuous or randomly aligned filaments find use in nonstructural (or secondary structural) applications based on their extended surface area, outstanding chemical stability to harsh solvents, and thermal/electrical conductivity. Therefore, the remainder of the discussion in this article is focused on these two main classes of carbonaceous fibers: (i) continuous CFs and (ii) activated CFs (ACFs), nanofibers, and mats.

CONTINUOUS CARBON FIBERS: STRUCTURAL APPLICATIONS

CFs used in primary structural applications must be in their continuous form to provide the needed mechanical reinforcement. Thus, proper fiber spinning processes must be used to produce the precursor fibers in a continuous form and then suitably converted to continuous CFs. Fiber spinning processes that are in current commercial use can be classified into three main types: (i) melt-spinning, (ii) wet-spinning, and (iii) dry-spinning. Recent studies using such techniques for bio-based precursors and the resulting CF properties are discussed in this section. Because of the importance of minimizing the impact on environment, the development of green technologies for producing CFs from biomass is a topic of significant research and has resulted in several comprehensive review papers.^{9,32–34} Therefore, the following discussion will address more recent studies that have emerged within the past few years, while acknowledging pioneering developments of previous years. The focus here will be on the relationship between the fiber spinning methods used for biomass precursors and the resulting CF properties.

CARBON FIBERS DERIVED FROM MELT-SPINNING OF BIOMASS PRECURSORS

Melt-spinning of various types of lignins has received significant attention since 1990s. The primary advantage of melt-spinning is that it is a high-throughput process and can potentially lead to low-cost fibers because of its economy of scale. Melt-spinning is also an environmentally friendly process because it does not use solvents. A fusible precursor is extruded through a spinneret with small holes (100–500 μm) and drawn-down to fine fibers. The melt-spun precursor fibers, however, must possess some degree of reactivity such that the material within each filament can be adequately crosslinked during the “stabilization” step so that the fibers can survive the ultimate high-temperature carbonization step.

In one of the earliest studies, Sudo and Shimizu⁵ used methanol to extract lignin from a steam-exploded birch wood and modified it into a fusible material by hydrogenolysis. The lignin was

subsequently extracted with chloroform and carbon disulfide, and the insoluble fraction was capable of melt-spinning after a heat treatment. The resulting CFs from this process possessed a tensile strength of 660 MPa and a tensile modulus of 40.7 ± 6.3 GPa. Although precursor fibers were produced by melt-spinning, the process required significant chemical treatment as it was neither an economically nor an environmentally desired process.

Several studies have dealt with Organosolv lignin produced from acetic acid pulping. Tensile strength and modulus values of about 350 MPa and 39 GPa,⁶ respectively, were reported by Uraki *et al.*^{6,35,36} for CFs derived from hardwood-based lignin. Alcell lignin, derived from ethanol extraction, can be readily spun without any fractionation.⁷ Baker *et al.*³⁷ increased the T_g of Alcell lignin by heat treatment, which reduced the precursor fiber stabilization time from 14 h to 4 h and increased the strength of the resulting CFs from 338 to 710 MPa. Baker *et al.*³⁸ investigated another organic purified hardwood kraft lignin (HKL-OP), which was successfully spun using a pilot-scale unit; however, it suffered from fusing during carbonization. The CFs from HKL-OP displayed a tensile strength of 520 MPa. In another study by Baker *et al.*,⁹ an organic purified HKL was heat-treated to increase the T_g and to improve the flow properties. The resulting material had a narrower molecular weight distribution and could be fully stabilized. The resulting CFs had a tensile strength of 1.07 GPa, which is the highest strength obtained from melt-spun lignin precursors, as listed in Table I. As noted previously, Organosolv lignin has the advantage of high purity as no metal or sulfur content is added during separation, in contrast to kraft lignin and lignosulfonates. It is also readily melt-spinnable because of a relatively low T_g and stable melt viscosity. However, the low T_g and low reactivity are disadvantages during the stabilization step. Thus, the heat treatment strategy used by Baker *et al.*⁹ was an effective method to accelerate the thermo-oxidative stabilization step and to improve mechanical properties; however, this grade of lignin is not readily available commercially for process scale-up.

Melt-spinning of infusible lignins has also been investigated by the addition of synthetic thermoplastic polymers such as PEO, PET, PP, and PLA as the carrier polymers to facilitate flow.^{7,37,38} Hardwood lignin could be converted into CFs by this route; however, the fibers can display voids as a result of the carrier polymer leaving fibers as a fugitive component, and CFs had low strength and modulus of 703 MPa and 94 GPa, respectively.³⁹ Softwood kraft lignin (SKL) could not be converted into a fusible precursor even with the addition of PEO,⁷ likely due to the more crosslinked structure arising from the higher content guaiacyl groups that prevent it from adequately melting without any modification.

Nordström *et al.*⁴⁰ investigated selected grades of SKL and HKL separated by the LignoBoost process. Both lignins were successfully melt-spun into precursor fibers because of the removal of large molecular weight fractions by ultrafiltration. Using the fractionated SKL, the stabilization step could be completed within 45 min (heating rate of $15 \text{ }^\circ\text{C min}^{-1}$),⁴¹ which is among the fastest stabilization rates reported for lignin precursor fibers,

but resulted in a low strength of 377 MPa.¹⁰ The average fiber diameters were large (more than $30 \text{ }\mu\text{m}$), which likely resulted in the relatively low tensile properties. The inverse relationship of fiber strength and fiber diameter has been observed in prior studies on CFs because of their sensitivity to flow density.⁴² In another study using the LignoBoost approach,²⁵ SKL with a low ash content (0.02–0.04%) was converted to CFs with large diameter ($39 \pm 5 \text{ }\mu\text{m}$); however, the tensile strength was limited to about 500 MPa.⁴³ As noted previously, softwood lignin has more guaiacyl unit that crosslink more easily (when compared with the more linear hardwood lignin), and thus, it can be stabilized more rapidly. In addition, the LignoBoost process is a significant improvement with regard to reducing the ash content of kraft lignin. However, the large diameter and low tensile strength of CFs obtained from such SKL precursors indicate difficulties and the lack of process control during fiber spinning. CFs with small enough diameter ($<10 \text{ }\mu\text{m}$) are highly desired for enhanced mechanical properties.

Qin and Kadla⁴⁴ reported CFs obtained from melt-spinning of pyrolysis-derived lignin. Large voids displayed in the as-spun fibers and the resulting CFs had relatively low tensile strength of 370 MPa. Other solid components such as organoclay⁴⁵ and carbon nanotubes⁴⁶ have been added to lignin precursors; however, they have resulted in fiber strength below 500 MPa, which is quite low for primary structural applications.

Softwood lignin obtained by solvolysis of wood chips using polyethylene glycol and sulfuric acid had good flow properties for melt-spinning.⁴⁷ However, the precursor fibers were very difficult to stabilize, and the resulting CFs displayed a low tensile strength of only about 460 MPa, attributed to the porous and flabby structure within the fibers. After extensive chemical treatment, the strength could be increased to about 700 MPa. However, this is still fairly low on an absolute basis, and the harsh chemical treatment negates some of the environmental advantages of the use of biomass as a precursor.

As discussed above and also observed in other studies,⁹ the vast majority of CFs produced from melt-spun lignin and other biomass-derived precursors have displayed a low strength in the range of 0.3–0.8 GPa, significantly less than values such as 3 GPa displayed by T300 grade of CFs obtained from PAN precursors (*albeit* by wet-spinning). The melt-spun-derived CFs have suffered from the technical challenges of simultaneously satisfying two opposite characteristics: (i) the precursor must have a low enough T_g to be melt spun (a low-cost, high-volume route), but a high enough T_g to be stabilized rapidly (to retain low cost); and (ii) the precursor must have high enough chemical stability so that it can be melt-spun at elevated temperatures, but low enough chemical stability (i.e., adequate reactivity) to be crosslinked into a thoroughly stabilized state. As noted earlier, the stabilization step is often the most critical step in CF manufacturing, because the filaments must get internally crosslinked and yet should not stick to each during the crosslinking process. Otherwise, any minor surface fusion can lead to surface defects on CFs and reduce the strength drastically. A possible way around this conundrum is a precursor that can be dry-spun, a process where a low T_g is not required for the

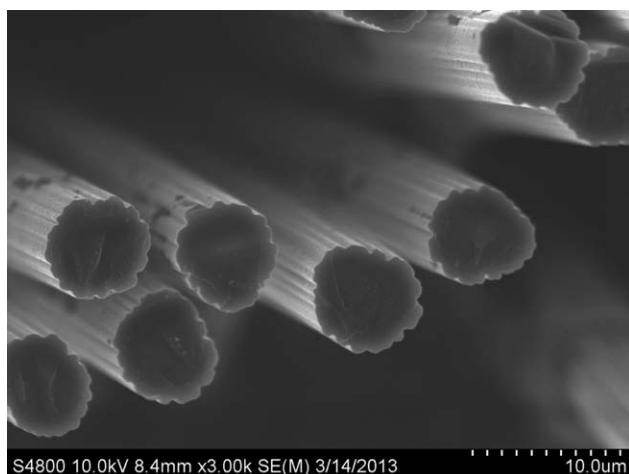


Figure 2. SEM micrograph illustrating the crenulated surface of CFs derived from acetylated softwood kraft lignin (Reprinted from Ref. 50, with permission from American Chemical Society).

precursor, but necessitates a solvent with high enough vapor pressure, a topic discussed in the next section.

CARBON FIBERS DERIVED FROM DRY-SPINNING OF BIOMASS PRECURSORS

In the dry-spinning process, a solid precursor/polymer is dissolved in a volatile solvent, and the heated solution is extruded out of a spinneret under pressure. Fibers are generated as the extrudate is drawn down and simultaneously solidified as the solvent evaporates. Otani *et al.*⁴⁸ used such a process to produce precursor fibers where water was used as a solvent with NaOH added to solubilize the lignin. CFs produced from this process had a tensile strength of 800 MPa. Defects were generated during the carbonization step because of the presence of residual NaOH.⁴

In the recent studies, we have produced CFs from dry-spinning of partially acetylated SKL.^{11,49,50} The partial acetylation allowed solubility of the lignin in acetone. The advantage of this process is that acetone was the only solvent, which is benign and can be recycled. The flow behavior of lignin/acetone solutions at various spinning temperatures and concentrations was investigated for potential scale-up of the process.¹¹ The as-spun fibers developed crenulated surface patterns because of the out-diffusion of acetone during solidification. For dilute lignin concentration below 2.00 g solid per milliliter of acetone, sharp crevices were generated that led to occlusions after carbonization, which reduced tensile strength of the resulting CFs. For lignin concentrations above 2.15 g solid per milliliter of acetone, precursor fibers developed relatively smooth crenulations without sharp crevices. The smooth crenulations on the resulting CFs provide up to 30% larger surface area for bonding with a matrix resin, for example, during composite production.¹¹

The dry-spun lignin fibers were stabilized and carbonized under tension,^{49,50} which provided enhanced carbon layer plane orientation within the resulting fibers. The resulting CFs retained the crenulated surface as displayed in Figure 2. The CFs derived from this process displayed a tensile modulus, strength, and

strain-to-failure values of 52 ± 2 GPa, 1.06 ± 0.07 GPa, and $2.0 \pm 0.2\%$, respectively. This strength value is among the highest reported in the literature for lignin-based CFs, as reported in Table I. In Figure 3, the wide-angle X-ray diffractogram from such lignin-based CFs is compared with those of PAN-based and mesophase pitch-based CFs. The 2-theta peak associated with carbon layer planes (0 0 2) for the dry-spun, lignin-based CFs is at $\sim 24^\circ$, indicating virtually no graphitic content (the peak appears at a 2-theta value less than that for PAN-based CFs). It should be noted that a higher graphitic crystallinity enhances lattice-dominated properties such as the modulus and thermal conductivity but adversely affects the tensile strength. The slow heating rate during thermal stabilization was accelerated by a UV/thermal dual stabilization approach.⁵¹ The precursor fibers were UV-irradiated for 15 min, which effectively shortened stabilization time from 40 down to 4 h. CFs derived from the fast stabilization process displayed a slight reduction in tensile strength; however, the absolute strength values were still fairly high (800 MPa) for lignin-derived precursors.

In addition to precursor modification, the above studies elucidate the importance of processing conditions during spinning and the following heat treatment, which has not been systematically studied in several previous studies on lignin-based CFs. Further ways to improve the tensile properties of such CFs obtained by dry-spinning of precursor fibers include the use of a lignin grade with high purity to reduce the defects, chemical modification of lignins to obtain a long-linear architecture of the precursor to facilitate molecular orientation during spinning, and applying tension during heat treatment in a continuous mode (rather than a batch mode used in research studies).

CARBON FIBERS DERIVED FROM WET-SPINNING OF BIOMASS PRECURSORS

The primary advantage of wet-spun precursor fibers, also obtained from solutions, is that the precursor does not have to possess thermal stability. The residual reactivity is effectively used for rapid crosslinking and thermo-oxidative stabilization of the precursor fibers to enable successful carbonization. Cellulose displays characteristics suitable for wet-spinning because

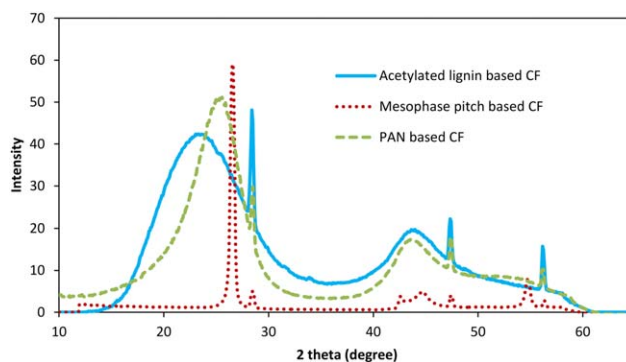


Figure 3. Wide-angle X-ray diffractograms comparing lignin, PAN, and pitch-based carbon fibers. Note: The very sharp peaks are for NIST-grade silica, which used a calibration standard for determining 2-theta peak positions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cellulose does not melt but can be dissolved in solvents to facilitate wet-spinning. It should be noted, however, that natural cellulose fibers, such as cotton or flax, in their native state are not good precursors for structural CFs because of their discontinuous form.⁵² Instead, regenerated cellulose fibers, such as rayon, have been used for conversion to CFs.^{15,16,53,54} Cellulose is mixed with a basic solution and treated with CS₂ to form cellulose xanthate that is dissolved in NaOH, and the solution is extruded through a spinneret followed by coagulation in a sulfuric acid solution.³ The as-spun rayon fibers have an irregular and porous cross section, which lead to low strength in the resulting CFs.⁵⁴ The rayon precursor fibers are stabilized in air at temperatures as high as 400 °C and carbonized under tension to generate molecular orientation. The resulting CFs can achieve a strength of 1.25 GPa and modulus of 720 GPa when graphitization was performed at 2800 °C; however, this stretching is a very expensive process.^{15,16}

Cellulose-based CFs have also been derived from Lyocell fibers that are obtained by a process that is environmentally more friendly than the xanthate process by using *N*-methylmorpholine *N*-oxide.^{18,55,56} In the dry-jet, wet-spinning process, the spinning solution is extruded into an air gap and drawn down (stretched) before entering the coagulation bath, which reduces voids and cracks in the resulting fibers by preventing a fast out-diffusion of solvent. The precursor fibers have a circular cross-sectional shape and less defects on surface when compared with rayon-based fibers. The resulting CFs displayed a strength and modulus as high as 1.07 GPa and 96.6 GPa, respectively.⁵⁶

Tencel™, a commercial lyocell fiber, has also been converted into CFs, but has led to a relatively low tensile strength of about 210 MPa,⁵⁷ which is not adequate for primary structural reinforcement purpose. Another commercial cellulose fiber, Bocell™, which is generated from wet-spinning of a liquid crystalline solution of cellulose in phosphoric acid, has been converted into CFs.⁵⁸ The Bocell™ fibers had well-developed molecular orientation and were heat-treated up to 2500 °C. Although no tensile properties were reported for CFs, the modulus of the skin was estimated at about 140 GPa and that of the core at 40 GPa using 2D Raman spectroscopy. Cordenka™, a commercial rayon fiber, has been graphitized at 2000 °C to obtain a strength of 1.5 GPa and modulus of 70.7 GPa.⁵⁹

Recent research studies have also investigated the use of ionic liquids (ILs) to produce cellulose-based precursor fibers.¹⁷ Imidazolium-based ILs with various cation and anion combinations were used as solvent for cellulose. The fibers were coagulated in a water-based bath. Sammons *et al.*⁶⁰ produced highly crystalline cellulose fibers from a 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) solution; however, no properties were reported for any resulting CFs. The combinations of cellulosic materials (cotton and viscose) with synthetic polymers (polyesters, polyamides, or PAN) have been investigated as a strategy to reduce synthetic content rather than eliminate them completely. Ingildeev *et al.*⁶¹ developed a method of using IL to produce cellulose/PAN fiber. The spinning dope was prepared by mixing both components in IL, and low-viscose blend solutions were wet-spun into precursor fibers. Not surprisingly, the overall car-

bon yield was better than that obtained from pure cellulose fibers. Although the very low vapor pressure of ILs make them attractive in some separation processes, the degradation products of ILs after prolonged use have not been investigated systematically and are a potential environmental hazard.

Unlike cellulose (a long-chain natural polymer), lignin recovered from the pulping process does not have a long and linear molecular architecture. Therefore, SKL does not have adequate extensional viscosity to be converted into fibers by wet-spinning. Thus, precursor fibers have been produced from a blend of lignin with synthetic polymers.^{62–65} Seydibeyoğlu used a PAN–lignin blend as a potential CF precursor to reduce the cost of precursor. Three different types of commercial Protobind lignins were dissolved in dimethyl acetamide together with homopolymers of PAN to form miscible blends that led to fibers with smooth surface⁶²; however, no CFs from this blend were reported. In another study, lignin sulfonate (LS)/PAN blend was wet-spun into fibers as a precursor candidate for low-cost CFs in which PAN serves as the framework and LS is used as an extender.⁶³ However, microporous structure was observed in precursor fibers, and the properties of CFs were reported. Liu *et al.*⁶⁴ used a gel-spinning technique for PAN/lignin and PAN/lignin/CNT precursor blends in a methanol coagulant bath at –50 °C with an air gap of 3 cm. The low coagulation temperature significantly reduced the counter-diffusion rate and lignin leaching. As displayed in Figure 4(a), fibers obtained from pure PAN displayed the typical kidney shape associated with out-diffusion of solvent. However, the lignin–PAN blend (30/70) led to a smoother/circular cross section and void-free cross section, as illustrated in Figure 4(b).⁶⁴ The presence of lignin led to lower cyclization activation energies (than those observed with pure PAN), which confirms that lignin can promote crosslinking during stabilization process.¹³ The large draw ratio (≈ 13) improved the degree of molecular orientation within the crystalline structure, and tensile strength and modulus of such gel-spun lignin/PAN-derived CFs were 1.72 ± 0.2 GPa and 230 ± 7 GPa, respectively, which represent attractive properties for CFs on an absolute basis. The advantage of gel-spinning technique is to minimize lignin diffusion for making void-free CFs from lignin/PAN blend. However, when compared with solution spinning, this process requires concentrated spinning dope and a low coagulation temperature, which affect spinnability. Recently, we have developed a method of controlling the coagulant composition to balance counter-diffusion rate of lignin during wet-spinning. As displayed in Figure 4(c,d), by the addition of about 2 wt % lignin in the coagulant, microvoids could be eliminated in fibers with lignin content as high as 50 wt %. This method may provide a simple and low-cost process to produce void-free, lignin/PAN-based CFs using the standard wet-spinning procedure. In addition, by using the blend approach and a standard wet-spinning process, Husman⁶⁵ investigated PAN polymers with higher molecular weight to minimize porosity. The average tensile strength was reported at 2.25 GPa and the tensile modulus at 217 GPa, which are among the highest values reported for CFs derived from lignin–PAN blends at 25 wt % lignin. It should be noted, however, that CFs produced from the lignin/PAN blend method possess

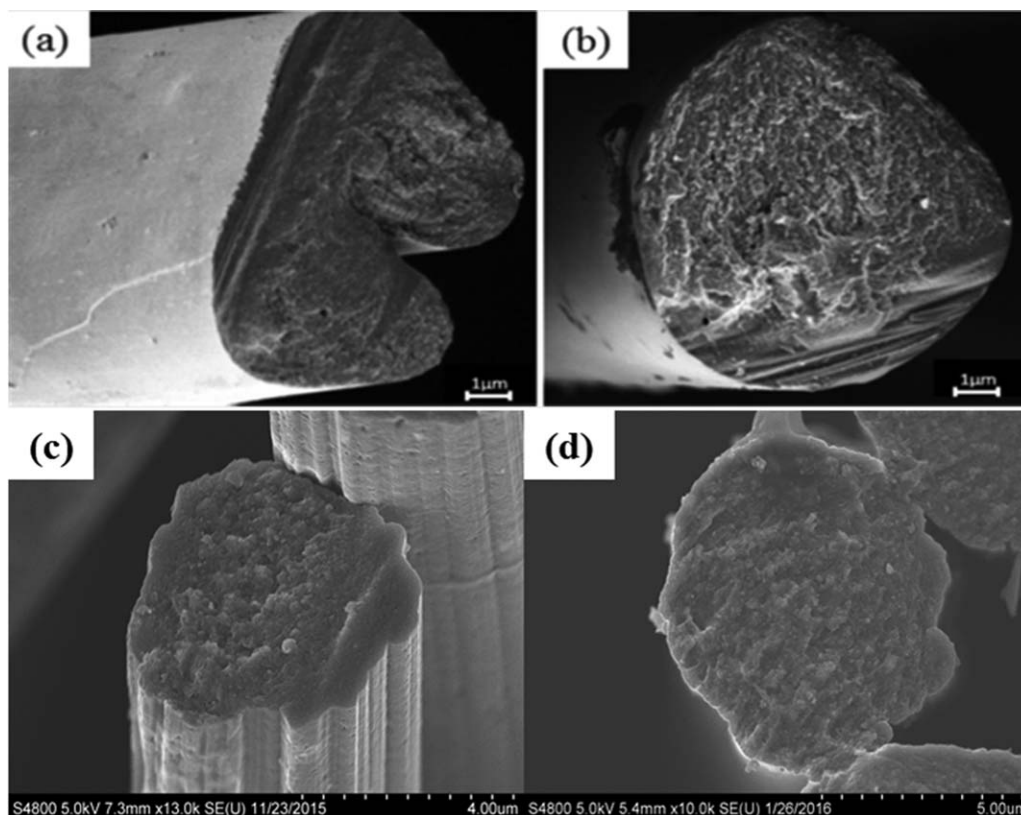


Figure 4. SEM micrographs of CF cross sections of (a) PAN, (b) lignin/PAN (30/70) carbonized at 1100 °C (Adapted from Ref. 64, with permission from the American Chemical Society), (c) lignin/PAN (35/65), and (d) lignin/PAN (50/50), carbonized at 1200 °C.

the strength associated primarily with the PAN-derived fraction, that is, the lignin component does not contribute significantly. Thus, no synergistic effects are found in the blends, with the CFs possessing tensile strength that is just a fraction based on the content of pure PAN (e.g., 75% of 3 GPa for pure PAN-based T300 = 2.25 GPa).

Although much work has been done to improve lignin-based CF properties by polymer blending, a few studies have made attempts to introduce acrylonitrile (AN) or PAN into lignin to develop CFs. Maradur *et al.*⁶⁶ prepared a copolymer using a hardwood lignin and AN in a two-step radical polymerization. The copolymer could be dissolved in DMSO, and the solution could be wet-spun. Thermal stabilization could be conducted at 280 °C; however, no tensile properties were reported for CFs. Similarly, Ramasubramanian¹² used butyrate SKL and Organosolv lignin to copolymerize with PAN and converted the copolymer into precursor fibers via wet spinning; however, no CF properties were reported. Recently, Xia *et al.*⁶⁷ prepared a ligno-sulfonate-AN copolymer as an alternative precursor. Wet-spun precursor fibers had a dense structure without any visible voids and defects; however, the resulting CFs possessed an average strength of only 540 MPa.

The incorporation of a synthetic monomer (AN) in a chain-like chemical structure of modified lignin appears to be a systematic approach of building a precursor “ground-up” and may ultimately lead to CFs with enhanced properties. However, the introduction of acrylonitrile or PAN (in blends) poses similar

environmental concerns as those posed by pure PAN-based CFs. Thus, future research studies need to develop environmentally friendly and cost-competitive precursors with very low ash content to reduce defects in the resulting CFs. Chemical modification of lignins need to be conducted to obtain a suitable molecular architecture to facilitate molecular orientation during spinning, stabilization, and carbonization steps. Such improvements should maximize applied tension and lead to CFs with strength and modulus approaching 3 and 200 GPa, respectively, if such bio-based CFs are to be used in primary structural composite applications.

ACTIVATED CARBON FIBERS, NANOFIBERS, AND MATS: NONSTRUCTURAL APPLICATIONS

In contrast to continuous CFs that are used for structural applications, discontinuous forms of carbon are ACFs, carbon nanofibers (CNFs), and CF mats. These forms have primary applications in nonstructural areas, such as energy storage devices and separation that use its high specific area. ACFs possess a large internal surface area because of their highly porous structure, which unfortunately leads to a drastic reduction in their strength. Nanofibers are prepared by electrospinning using electric force to draw fine fibers from polymer solution or melt. CF mats can also be produced by layer-by-layer electrospinning of precursors or melt-blown method. Currently, they are mostly produced from PAN precursors, and they pose the same environmental problems as PAN-based CFs. Therefore, there has

Table II. Surface Characteristics of Lignin and Cellulose-Based CF Mats/CNFs/ACFs

| | Specific area (m ² g ⁻¹) | Pore volume (cm ³ g ⁻¹) | Reference |
|--------------------|---|--|-----------|
| Lignin CF mat | ~8.2-37.4 | 0.0018-0.0151 | 68 |
| Lignin CNF | 524-1195 | 0.239-0.52 | 69 |
| Cellulose CNF | 289.9-511.5 | 0.073-0.1735 | 70 |
| Lignin ACF | >1400 | >0.91 | 71 |
| Cellulose ACNF | ~870-1120 | — | 72 |
| Viscose Rayon ACF | 681-1883 | 0.277-0.8 | 58 |
| Tencel ACF | 716-1557 | 0.297-0.627 | 58 |
| Liquified wood ACF | 2604.7 | 1.433 | 73 |

been a growing interest in developing ACFs and CNFs using biomass precursors (lignin and cellulose) because of their low cost and environmental friendly processing routes. As noted earlier for structural CFs, the development of ACFs and CNFs from biomass is an active research area and has been reviewed in several prior reviews.^{9,32,33} Thus, the discussion here will be limited to studies that have been reported recently.

Activated Carbon Fibers

ACFs are nominally 15 μm in diameter and have a large internal surface area (≈1,000 m² g⁻¹) because of internal pores, which also act as defects and result in mechanical weakening of fibers. Both chemical (KOH, NaOH, etc.) and physical (CO₂, steam, etc.) activation methods, as well as heat treatment conditions, have been investigated to optimize internal surface area and characteristics of ACFs, and a summary of these properties is presented in Table II. Shen *et al.*⁷⁴ developed a process of activating CFs using lignin-phenol-formaldehyde resin via melt spinning. Small molecules released during carbonization lead to the formation of macrovoids. It is interesting to note that although micro/macrovoids are highly undesirable for structural CFs, such “defects” are highly desirable for ACFs to achieve a large specific surface area. Hu *et al.*¹⁴ reported ACF mat material with maximum surface area of 1440 m² g⁻¹ via electrospinning of alkali lignin and alkali-metal hydroxide blended with PEO and activated by NaOH. A recent work by Hu *et al.*⁷⁵ also reported promising results on capacitance using lignin-based ACF supercapacitors.

Cellulose, the other abundant biomass, is also used to produce ACFs. Goldhalm⁵⁷ reported the properties (carbon yield, specific area, and total pore volume) of viscose rayon and Tencel™ ACF at different activation temperatures. Liquefied wood-based fibers, which are prepared from liquefied wood through melt-spinning and curing in acid solution, have been successfully used as precursors to make ACFs with high specific surface area.⁷¹ Ma *et al.*⁷⁶ reported ACFs melt-spun from liquefied wood followed by steam activation using wood charcoal as additive to achieve highly mesoporous structure. Wood charcoal is an amorphous carbon, which can be easily obtained from wood resource. With addition of wood charcoal, more unstable carbons were formed in the ACF matrix during steam activation, facilitating the formation of mesopores. With this method, 86.8% pore volume was from mesopores (2–4 nm), and a spe-

cific area exceeding 2600 m² g⁻¹ was achieved, which is the highest among cellulose-based ACFs as shown in Table II.

Huang *et al.*⁷⁷ developed a chemical/physical coupling two-step activation processing method using KOH activation, which provided more reaction points. This was followed by subsequent steam activation that developed microporosity and mesoporosity so that the resulting CF showed excellent adsorption characteristics. Porous CFs derived from wet spinning and carbonization process of cellulose obtained from rice straw and mulberry wood has been reported by Hwang *et al.*⁷³ Fibers were treated with KOH and stabilized in air at 300 °C before carbonization. This material exhibits high specific surface area of 2260 m² g⁻¹ and excellent hydrogen storage properties.

The use of ACFs in various applications, such as energy storage devices, has received significant attention. To date, ACFs based on PAN fabrics are produced in an energy-consuming and non-environmental friendly way. Moreover, the microporous structures of such ACFs are not targeted for storing aqueous electrolyte ions. Therefore, it is desirable to fabricate ACFs via simple and efficient processes from greener sources. In the future studies, ACFs produced from lignin must have well-controlled porosity and should have enhanced electrical conductivity to compete in their performance with commercial ACFs derived from synthetic precursors.

Carbon Nanofibers and Mats

CF mats have been prepared from hardwood and softwood lignin precursors via melt processing.⁷⁸ CFs within the nonwoven structure were about 40 μm in diameter with cylindrical hollow voids along with the fiber axis. Although the voids lead to a drastic deterioration of mechanical strength, the microscale voids increase the interfacial area when contacted with electrolytes for energy storage purpose.⁷⁹ Ruiz-Rosas *et al.*⁸⁰ prepared very fine lignin fibers (submicrometer) by electrospinning. The resulting CF mats had a surface area of 1195 m² g⁻¹, and micropore volumes of around 0.52 cm³ g⁻¹ were obtained. In another study, Tenhaeff *et al.*⁶⁸ reported that controlling the degree of fiber fusion is important because the fused CF mat structure has dual functions as active material and current collector in electrodes.

Dallmeyer *et al.*⁶⁹ reported kraft lignin-based CNFs by electrospinning with thermally induced interfiber bonding. Because the external surface area of a cylindrical fiber scales as the

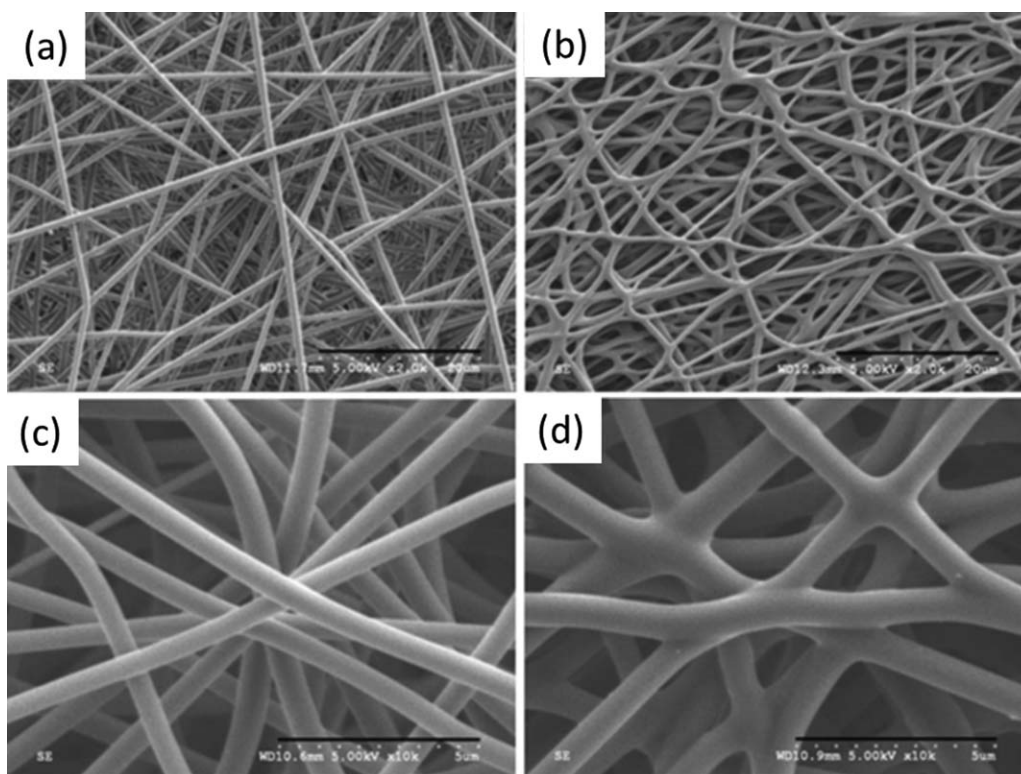


Figure 5. SEM micrographs of (a,b) nonbonded fibers and bonded fibers after stabilization and (c,d) nonbonded fibers and bonded mats after carbonization (Adapted from Ref. 69, with permission from Wiley).

reciprocal of the diameter ($4\pi DL/\pi D^2 L = 4/D$) and CNF diameters are almost two orders of magnitude smaller than that of ACFs, CNFs possess a large surface area even without any internal porosity. By controlling the heating conditions during stabilization, a variety of CNF morphologies have been obtained by using intrinsic differences in thermal softening behavior between different kraft lignin fractions, as illustrated in Figure 5. The interbonded CNFs show tensile strength of 74.1 ± 14.6 MPa and electrical conductivity of 19.6 ± 3.0 S cm^{-1} , which are higher than nonbonded ones (32.0 ± 9.0 MPa and 2.3 ± 0.4 S cm^{-1}), suggesting the potential of lignin-based CNFs as carbon electrodes.

CNFs prepared from lignin in combination with other polymers or particles exhibits some advantages over those obtained from pure lignin. Electrical conductivity of CNFs was reported to increase from 2.3 to 3.0 S cm^{-1} when 6 wt % multiwalled carbon nanotubes were incorporated into the electrospun SKL fibers.⁸¹ Ago *et al.*⁸² developed lignin-based fiber mats by electrospinning aqueous dispersions of lignin, PVA, and cellulose nanocrystals (CNCs). PVA held lignin and CNC together to avoid phase separation, and the addition of CNCs improved the thermal stability of composite electrospun fibers. Wang *et al.*⁸³ reported that fused CF mats obtained through the incorporation of certain proportions of low-melting-point polymer additive with organosolv lignin exhibit good electrochemical performance with specific capacity up to 445 mA h g^{-1} , which is comparable with that of PAN-derived CFs. Rios *et al.*⁸⁴ developed a method of preparing lignin-based CFs embedded with

core-shell silicon/SiO₂ via melt processing to make electrode for lithium ion batteries. The monolithic composite CFs exhibit capacities higher than 700 mA h g^{-1} because of their unique crystalline structure.

Another polymer of interest for blending with lignin is PAN. The electrospun PAN/lignin alkali nanofiber mats were prepared by electrospinning and cured by E-beam irradiation, followed by carbonization at 1000 °C.⁸⁰ Similarly, Ding *et al.*⁸⁵ reported process of low-cost electrospun CFs from organosolv and butyrate organosolv lignin/PAN blends. CF mats obtained from butyrate lignin/PAN (50–50) demonstrated the highest tensile strength and modulus of 83 ± 17 MPa and 6.1 ± 0.6 GPa when compared with those of pure PAN-based CF mats. Low-cost and bio-based carbon nanofibrous webs were fabricated from PAN/refined lignin (RL) that was extracted from hardwood lignosulfonate via electrospinning followed by stabilization and carbonization.⁸⁶ The CF mats display a reversible capacity of about 292.6 mA h g^{-1} with good charging rate capability (80 mA h g^{-1} at 1 A g^{-1}) and excellent cycling stability (247 mA h g^{-1} over 200 cycles at 0.1 A g^{-1}). Such CF mats show significant potential as electrode material for sodium ion batteries (SIBs) because of their enhanced performance.

Another interest in lignin/PAN polymer blend is CF with core-shell structure. Xu *et al.*⁸⁷ introduced a porous core-shell CF from lignin and cellulose nanofibrils prepared by electrospinning. Alkali kraft lignin/PAN blend was used as spinning material for shell of the fiber, whereas cellulose nanofibers were used

as core structure. The resulting CFs possessed solid shell and porous core structure with extended surface area.

Overall, lignin has a significant potential to produce CNFs and mats via melt process or electrospinning. The resulting CNFs and mats have relatively high specific surface areas and chemical functionality. In many cases, lignin-based CNFs and mats display improved spinning performance and electrical and thermal conductivities by blending with PEO, PAN, and CNCs.

Cellulose nanofibers have been produced by electrospinning of solution of cellulose⁸⁸ or its derivatives.⁸⁹ The drawback of the pure cellulose is that it has poor solubility in most common solvents because of its strong crystalline structure. In a study by Deng *et al.*,⁸⁹ cellulose nanofibers were prepared by electrospinning cellulose acetate, followed by deacetylation in a solution of NaOH in ethanol. Kuzmenko *et al.*⁹⁰ reported that incomplete regeneration of cellulose using a combination of NH₄OH and NH₄Cl increased carbon yield in the final CNFs by 20%. By using an IL as a cosolvent, Byrne *et al.*⁹¹ reported the preparation of PAN/cellulose acetate and PAN/raw cotton fibers by electrospinning. However, the long-term fate of ionic liquids and their environmental impact are somewhat unknown.

The effect of carbonization temperature (800–2200 °C) on graphitic microstructure of electrospun cellulose CNFs has been studied by Deng *et al.*⁸⁹ The development of graphitic crystallinity was observed for the CNFs starting at a relatively low temperature of 1500 °C, unlike that for CFs derived from micron-sized cellulose fibers. Such CNFs possessed a modulus of about 100 GPa that is suitable for semistructural applications. Liu *et al.*⁹² prepared primarily amorphous CNFs from electrospun cellulose nanofibers, followed by stabilization at 400 °C and carbonization at low temperatures of 800 and 1400 °C.

Electrospun cellulose-derived CNFs are promising materials in electrochemical and separation applications.^{72,93–95} One of the promising applications of cellulose-based CNFs is anode material for SIB. Luo *et al.*⁹⁶ reported promising electrochemical properties of cellulose-derived CNFs, including a high reversible capacity (255 mA h g⁻¹ at 40 mA g⁻¹), good rate capability (85 mA h g⁻¹ at 2000 mA g⁻¹), and excellent cycling stability (176 mA h g⁻¹ at 200 mA g⁻¹ over 600 cycles). Recently, core–sheath structured porous CNFs anode material for SIB was prepared by Zhang *et al.*⁷⁰ Because of the core–sheath structure and large interlayer spacing, these CNFs exhibit outstanding electrochemical performance, including a high reversible specific capacity (240 mA h g⁻¹ at 100 mA g⁻¹ over 100 cycles), excellent rate performance (146.5 mA h g⁻¹ at 1000 mA g⁻¹), and good cycling stability (148.8 mA h g⁻¹ at 500 mA g⁻¹ over 400 cycles).

It has been demonstrated that electrospun cellulose nanofibers are excellent precursors for CNFs. When compared with micron-sized cellulose-based CFs, graphitic structure formed at a lower temperature in these CNFs. Such unique structure enhances electrical conductivity of the cellulose-based CNFs. In summary, the combination of high electrical conductivity of resulting carbon, coupled with a large surface area offered by nanofibers, clearly shows the potential of CNFs/mats in future electrochemical applications.

CONCLUSIONS

The outstanding strength and modulus possessed by CFs derived from PAN (a synthetic, polymeric precursor) are their primary advantages; however, their high cost and environmental concerns during manufacturing serve as the primary stimuli for continued research on alternative precursors and processing routes. The natural abundance, renewability, and low environmental impact of lignin and cellulosic biomass are driving research toward their use as precursors for CFs. As discussed above, the properties of CFs are sensitive to the source of biomass that ultimately determines the precursor purity and routes available for fiber spinning (*viz.*, melt-spinning, dry-spinning, or wet-spinning). Current research studies on bio-based CFs report a maximum tensile strength and modulus of only about 1 and 50 GPa, respectively. These values are significantly lower than 3 and 200 GPa reported for typical PAN-derived CFs used in many commercial composite applications. Therefore, further improvements in precursor purification (ash content \ll 0.1 wt %), molecular structure control (elongated architecture), and continuous fiber processing (to minimize fiber abrasion/handling) need to be accomplished to enhance CF properties by about twofold to enable their commercial application in cost-sensitive structural composites including automotive and industrial.

The lack of graphitic crystallinity in CFs derived from bio-based precursors facilitates the generation of internal pores and large specific surface area when appropriate heat treatment conditions are used. It is evident from the literature studies that bio-based precursors can produce CNFs and ACFs with specific surface area exceeding 1000 m² g⁻¹. Thus, for nonstructural purposes, the combination of moderately high electrical conductivity and a large surface area offered by CNFs clearly shows the potential of CNFs/mats in future electrochemical applications. The ease and low cost of conversion of biomass into porous carbon show the potential of biomass in ACFs (*e.g.*, for gas and water purification) for applications of very significant and global societal importance.

REFERENCES

1. Bunsell, A. R.; Renard, J. In *Fundamentals of Fibre Reinforced Composite Materials*; Cantor, B.; Goringe, M. J.; Ma E. IOP Publishing: London, **2005**; pp 3–5.
2. Peebles, L. In *Carbon Fibers, Formation, Structure and Properties*; CRC Press: Boca Raton, **1995**; pp 7–24.
3. Edie, D. D.; Diefendorf, R. J. In *Carbon–Carbon Materials and Composites*; Buckley, J. D.; Edie, D. D., Eds.; Noyes Publications: Park Ridge, **1993**; pp 20–33.
4. Johnson, D.; Tomizuka, I.; Watanabe, O. *Carbon* **1975**, *13*, 321.
5. Sudo, K.; Shimizu, K. *J. Appl. Polym. Sci.* **1992**, *44*, 127.
6. Uraki, Y.; Kubo, S.; Nigo, N.; Sano, Y.; Sasaya, T. *Holzfor-schung* **1995**, *49*, 343.
7. Kadla, J.; Kubo, S.; Venditti, R.; Gilbert, R.; Compere, A.; Griffith, W. *Carbon* **2002**, *40*, 2913.

8. Thunga, M.; Chen, K.; Grewell, D.; Kessler, M. R. *Carbon* **2014**, *68*, 159.
9. Baker, D. A.; Rials, T. G. *J. Appl. Polym. Sci.* **2013**, *130*, 713.
10. Nordström, Y.; Joffe, R.; Sjöholm, E. *J. Appl. Polym. Sci.* **2013**, *130*, 3689.
11. Zhang, M.; Ogale, A. A. *J. Appl. Polym. Sci.* in press.
12. Ramasubramanian, G. Influence of Lignin Modification on PAN-Lignin Copolymers as Potential Carbon Fiber Precursors, M.Sc. Thesis, Graduate Thesis and Dissertations, Paper 13438, **2013**.
13. Liu, H. C.; Chien, A.; Newcomb, B. A.; Davijani, A. A. B.; Kumar, S. *Carbon* **2016**, *101*, 382.
14. Hu, S.; Hsieh, Y. *J. Mater. Chem.* **2013**, *1*, 11279.
15. Riggs, D. M.; Shuford, R. J.; Lewis, R. W. In Handbook of Composites; Lubin, G., Ed.; Springer: New York, **1982**; pp 196–271.
16. Bacon, R. *Chem. Phys. Carbon* **1973**, *9*, 1.
17. Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. *J. Am. Chem. Soc.* **2002**, *124*, 4974.
18. Wu, Q.; Pan, D. *Text. Res. J.* **2002**, *72*, 405.
19. Vakkilainen, E. In PaperMaking Science and Technology, Book 6B; Gullichsen, J.; Paulapuro, H., Eds.; Fapet Oy: Helsinki, **2000**; pp 6–34.
20. Sjostrom, E. Wood Chemistry: Fundamentals and Applications; Academic Press: New York, **1981**; pp 71–77.
21. Sjostrom, E. Wood Chemistry: Fundamentals and Applications; Academic Press: New York, **1981**; p 49.
22. Lai, Y. Z.; Sarkanen, K. V. In Lignins: Occurrence, Formation, Structure and Reactions; Sarkanen, K. V.; Ludwig, C. H., Eds.; Wiley: Toronto, **1971**; p 188.
23. Chakar, F. S.; Ragauskas, A. J. *Ind. Crops. Prod.* **2004**, *20*, 131.
24. Biermann, C. J. In Essentials of Pulping and Papermaking; Academic Press: San Diego, **1993**; p 93.
25. Tomani, P. *Cell. Chem. Technol* **2010**, *44*, 53.
26. Gellerstedt, G.; Sjöholm, E.; Brodin, I. *Open Agric. J.* **2010**, *4*, 119.
27. Klett, A.; Chappell, P.; Thies, M. C. *Chem. Commun.* **2015**, *51*, 12855.
28. Chang, P.; Paszner, L. U. S. Pat. 4,594,130 (**1986**).
29. Kleinert, T. N. *Tappi* **1974**, *57*, 99.
30. Nimz, H.; Casten, R. In Proceedings of the Third International Symposium on Wood and Pulping Chemistry, Vancouver, BC, Canada; **1985**; pp 265–266. by International Symposium on Wood and Pulping Chemistry, Vancouver, B.C.
31. Diebold, V. B.; Cowan, W. F.; Walsh, J. K. U.S. Patent 4,100,016 (**1978**).
32. Chatterjee, S.; Saito, T. *ChemSusChem* **2015**, *8*, 3941.
33. Frank, E.; Steudle, L. M.; Ingildeev, D.; Spörl, J. M.; Buchmeiser, M. R. *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 5262.
34. Dumanli, A. G.; Windle, A. H. *J. Mater. Sci.* **2012**, *47*, 4236.
35. Kubo, S.; Uraki, Y.; Sano, Y. *Holzforschung* **1996**, *50*, 144.
36. Kubo, S.; Uraki, Y.; Sano, Y. *Holzforschung* **1998**, *36*, 1119.
37. Baker, D. A.; Gallego, N. C.; Baker, F. S. Extended Abstract in the Book of Abstracts of the Fiber Society 2009 Fall Conference, University of Georgia, Athens, GA, USA, October 27–30, **2009**.
38. Baker, D. A.; Gallego, N. C.; Baker, F. S. *J. Appl. Polym. Sci.* **2012**, *124*, 227.
39. Kubo, S.; Kadla, J. *J. Polym. Environ.* **2005**, *13*, 97.
40. Nordström, Y.; Norberg, I.; Sjöholm, E.; Drougge, R. *J. Appl. Polym. Sci.* **2013**, *129*, 1274.
41. Norberg, I.; Nordström, Y.; Drougge, R.; Gellerstedt, G.; Sjöholm, E. *J. Appl. Polym. Sci.* **2012**, *128*, 3824.
42. Chae, H. G.; Choi, Y. H.; Minus, M. L.; Kumar, S. *Compos. Sci. Technol.* **2009**, *69*, 406.
43. Salmén, L.; Bergnor, E.; Olsson, A.; Åkerström, M.; Uhlin, A. *BioResources* **2015**, *10*, 7544.
44. Qin, W.; Kadla, J. *J. Appl. Polym. Sci.* **2012**, *126*, E204.
45. Qin, W.; Kadla, J. *Ind. Eng. Chem. Res.* **2011**, *50*, 12548.
46. Wang, S.; Zhou, Z.; Xiang, H.; Chen, W.; Yin, E.; Chang, T.; Zhu, M. *Compos. Sci. Technol.* **2016**, *128*, 116.
47. Lin, J.; Kubo, S.; Yamada, T.; Koda, K.; Uraki, Y. *BioResources* **2012**, *7*, 5634.
48. Otani, S.; Fukuoka, Y.; Igarashi, B.; Sasaki, K. U.S. Patent 3,461,082 (**1969**).
49. Zhang, M.; Ogale, A. A. *Carbon* **2013**, *69*, 626.
50. Zhang, M.; Ogale, A. A. In ACS Symposium Series: Polymer Precursor-Derived Carbon; Naskar, A. K.; Hoffman, W. P., Eds.; American Chemistry Society: Washington, DC, **2014**; Vol. 1173, pp 137–152.
51. Zhang, M.; Jin, J.; Ogale, A. A. *Fibers* **2015**, *3*, 184.
52. Bahl, O. P.; Shen, Z.; Lavin, J. G.; Ross, R. A.; In Carbon Fibers; Donnet, J. Bansal, R. C., Eds.; Marcel Dekker: New York, **1998**; p 31.
53. Bacon, R.; Cranch, G. E.; Moyer, R. O.; Watts, W. H. U.S. Patent 3,305,315 (**1967**).
54. Sisson, W. A. *Text. Res. J.* **1960**, *30*, 153.
55. Wu, Q.; Gu, S.; Gong, J.; Pan, D. *Synth. Met.* **2006**, *156*, 792.
56. Peng, S.; Shao, H.; Hu, X. *J. Appl. Polym. Sci.* **2003**, *90*, 1941.
57. Goldhalm, G. *Lenzinger Ber.* **2012**, *90*, 58.
58. Kong, K.; Deng, L.; Kinloch, I. A.; Young, R. J.; Eichhorn, S. *J. J. Mater. Sci.* **2012**, *47*, 5402.
59. Lewandowska, A. E.; Soutis, C.; Savage, L.; Eichhorn, S. *J. Compos. Sci. Technol.* **2015**, *116*, 50.
60. Sammons, R. J.; Collier, J. R.; Rials, T. G.; Spruiell, J. E.; Petrovan, S. *J. Appl. Polym. Sci.* **2013**, *128*, 951.
61. Ingildeev, D.; Hermanutz, F.; Bredereck, K.; Effenberger, F. *Macromol. Mater. Eng.* **2012**, *297*, 585.
62. Seydibeyoğlu, M. *J. Biomed. Biotechnol.* **2012**, *2012*, 1.
63. Dong, X.; Lu, C.; Zhou, P.; Zhang, S.; Wang, L.; Li, D. *RSC Adv.* **2015**, *5*, 42259.
64. Liu, H. C.; Chien, A.; Newcomb, B. A.; Liu, Y.; Kumar, S. *ACS Sustain. Chem. Eng.* **2015**, *3*, 1943.

65. Husman, G. Paper Presented at the 2014 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, June 17, 2014. Available from: http://energy.gov/sites/prod/files/2014/07/f17/lm048_husman_2014_o.pdf. Accessed on February 2, 2016.
66. Maradur, S. P.; Kim, C. H.; Kim, S. Y.; Kim, B.; Kim, W. C.; Yang, K. S. *Synth. Met.* **2012**, *162*, 453.
67. Xia, K.; Ouyang, Q.; Chen, Y.; Wang, X.; Qian, X.; Wang, L. *ACS Sustain. Chem. Eng.* **2016**, *4*, 159.
68. Tenhaeff, W. E.; Rios, O.; More, K.; McGuire, M. A. *Adv. Funct. Mater.* **2014**, *24*, 86.
69. Dallmeyer, I.; Lin, L. T.; Li, Y.; Ko, F.; Kadla, J. F. *Macromol. Mater. Eng.* **2014**, *299*, 540.
70. Zhang, Z.; Zhang, J.; Zhao, X.; Yang, F. *Carbon* **2015**, *95*, 552.
71. Liu, W.; Zhao, G. *BioResources* **2012**, *7*, 5552.
72. Naboka, O.; Rodriguez, K.; Toomadj, A. F.; Sanz-Velasco, A.; Toriz, G.; Lundgren, P.; Enoksson, P.; Gatenholm, P. *Mater. Sci. Forum* **2013**, *730*, 903.
73. Hwang, S.; Choi, W. M.; Lim, S. K. *Mater. Lett.* **2016**, *167*, 18.
74. Shen, Q.; Zhang, T.; Zhang, W.; Chen, S.; Mezgebe, M. *J. Appl. Polym. Sci.* **2011**, *121*, 989.
75. Hu, S.; Zhang, S.; Pan, N.; Hsieh, Y. *J. Power Sources* **2014**, *270*, 106.
76. Ma, X.; Zhang, F.; Zhu, J.; Yu, L.; Liu, X. *Bioresour. Technol.* **2014**, *164*, 1.
77. Huang, Y.; Ma, E.; Zhao, G. *RSC Adv.* **2015**, *5*, 70287.
78. Chatterjee, S.; Jones, E. B.; Clingenpeel, A. C.; McKenna, A. M.; Rios, O.; McNutt, N. W.; Keffer, D. J.; Johs, A. *ACS Sustain. Chem. Eng.* **2014**, *2*, 2002.
79. Chatterjee, S.; Clingenpeel, A.; McKenna, A.; Rios, O.; Johs, A. *RSC Adv.* **2014**, *4*, 4743.
80. Ruiz-Rosas, R.; Bedia, J.; Lallave, M.; Loscertales, I.; Barrero, A.; Rodríguez-Mirasol, J.; Cordero, T. *Carbon* **2010**, *48*, 696.
81. Teng, N.; Dallmeyer, I.; Kadla, J. F. *J. Wood Chem. Technol.* **2013**, *33*, 299.
82. Ago, M.; Okajima, K.; Jakes, J. E.; Park, S.; Rojas, O. J. *Bio-macromolecules* **2012**, *13*, 918.
83. Wang, S.; Yang, L.; Stubbs, L. P.; Li, X.; He, C. *ACS Appl. Mater. Interfaces* **2013**, *5*, 12275.
84. Rios, O.; Martha, S. K.; McGuire, M. A.; Tenhaeff, W.; More, K.; Daniel, C.; Nanda, J. *Energy Technol.* **2014**, *2*, 773.
85. Ding, R.; Wu, H.; Thunga, M.; Bowler, N.; Kessler, M. R. *Carbon* **2016**, *100*, 126.
86. Jin, J.; Yu, B.; Shi, Z.; Wang, C.; Chong, C. *J. Power Sources* **2014**, *272*, 800.
87. Xu, X.; Zhou, J.; Jiang, L.; Lubineau, G.; Chen, Y.; Wu, X.; Piere, R. *Mater. Lett.* **2013**, *109*, 175.
88. Lu, P.; Hsieh, Y. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2413.
89. Deng, L.; Young, R. J.; Kinloch, I. A.; Zhu, Y.; Eichhorn, S. J. *Carbon* **2013**, *58*, 66.
90. Kuzmenko, V.; Naboka, O.; Gatenholm, P.; Enoksson, P. *Carbon* **2014**, *67*, 694.
91. Byrne, N.; Leblais, A.; Fox, B. *J. Mater. Chem.* **2014**, *2*, 3424.
92. Liu, Y.; Qin, W.; Wang, Q.; Liu, R.; Liu, H. *J. Mater. Sci.* **2015**, *50*, 563.
93. Deng, L.; Young, R. J.; Kinloch, I. A.; Abdelkader, A. M.; Holmes, S. M.; Haro-Del Rio, D.; David, A.; Eichhorn, S. J. *ACS Appl. Mater. Interfaces* **2013**, *5*, 9983.
94. Pugazhenthiran, N.; Sen Gupta, S.; Prabhath, A.; Manikandan, M.; Swathy, J. R.; Raman, V. K.; Pradeep, T. *ACS Appl. Mater. Interfaces* **2015**, *7*, 20156.
95. Chen, L.; Huang, Z.; Liang, H.; Gao, H.; Yu, S. *Adv. Funct. Mater.* **2014**, *24*, 5104.
96. Luo, W.; Schardt, J.; Bommier, C.; Wang, B.; Razink, J.; Simonsen, J.; Ji, X. *J. Mater. Chem.* **2013**, *1*, 10662.