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REVIEW

Recent Advances in Low-Cost Carbon Fiber Manufacture from Lignin

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ABSTRACT: The confluence of two US energy policy mandates, the 2012 Corporate Average Fuel Economy Standards and Renewable Fuels Standard #2, provide the opportunity to examine the possibility of high-value materials from lignin with increased depth. In this case, the desire to provide lighter, low-cost materials for automobiles to reduce fuel consumption, and to improve the economics of biorefineries for fuel production, have led to an increased interest in low-cost carbon fiber manufacture from lignin. For this review the authors provide the context of subject matter importance, a cost comparison of potential low-cost carbon fibers, a brief review of historical work, a review of more recent work, and a limited technical discussion followed by recommendations for future directions. As the available material for review is limited, the author includes many references to publicly available government documents and reviewed proceedings that are generally difficult to locate. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 713–728, 2013

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INTRODUCTION

Carbon fibers are currently manufactured from polyacrylonitrile (PAN) precursors while small amounts are derived from pitches, notably mesophase (MPP). However, due to the high cost of these petroleum-based precursors and their associated processing costs, carbon fiber remains a specialty product and as such has been limited for use in aerospace, sporting goods, high-end automotive, and specialist industrial applications.[1,2] Investigations towards the manufacture of low-cost carbon fiber have been limited to a small number of organizations owing to the magnitude of the effort required, a limited availability of expertise, equipment provision and cost. Such efforts have typically involved the reduction of cost by using lower cost materials, by reducing the cost of processing, or by using a combination of the two.

In 2012, the U.S. government legislated through updated Corporate Average Fuel Economy (CAFE)[3] standards that the average fuel economy of cars and light trucks sold in the U.S. for model year 2017 will be 35.5 mpg and will increase to 54.5 mpg for model year 2025. The most effective way to increase fuel economy is to decrease vehicle weight through the use of smaller engines, smaller bodies, and by lowering the level of luxury. However, EPA[4] data suggests that consumer demands have historically dictated automobile manufacture, so that while great progress has been made in automotive technologies which could have substantially increased fuel economy, the demand for faster, safer, quieter vehicles with more capacity and features has substantially increased weight and therefore only resulted in modest increases in fuel economy. U.S. Department of Energy (DOE) studies have identified several materials that could be used for the light-weighting of vehicles, one of the most promising, PAN-based carbon fiber reinforced composites, could offer as much as 60% part weight reduction, but at up to ten times the cost.[5] The manufacturing cost of a suitable grade of carbon fiber is highly dependent on oil price, with around 51% being precursor cost, 18% utilities, 12% depreciation, 10% labor and 9% represented by other fixed costs (Figure 1); in 2010 the cost was over US\$30/kg.[6] The automotive industry requires suitable carbon fiber be less than \$11–\$15.40/kg, have a tensile strength of 1.72 GPa (250 ksi; 176 kg-f/mm^2), and a modulus of 172 GPa (25 Msi; 17.6×10^3 kg-f/mm^2) for it to be attractive for wider utilization. Consequently, the DOE has invested well over US\$100M over the last 10 years to examine possible routes towards the provision of suitable low-cost carbon fiber, representing possibly the largest single investment towards that goal.

To reduce carbon fiber manufacturing costs DOE emphasis has been towards lowering processing costs through advanced oxidation techniques,[7–10] the potential use of textile grade PAN precursors,[7–10] and the synthesis of new melt-spinnable PAN precursors;[11,12] the progress to date in each case providing carbon fiber with strengths of 2.52 GPa (365 ksi; 257 kg-f/mm^2) and 1.03 GPa (150 ksi; 105 kg-f/mm^2), respectively. Researchers have also developed a process by which polyolefins can be converted to carbon fiber[13] with reported strengths of 0.758 GPa (110 ksi; 77.3 kg-f/mm^2)[12,14] and up to 1.39 GPa (201 ksi; 141

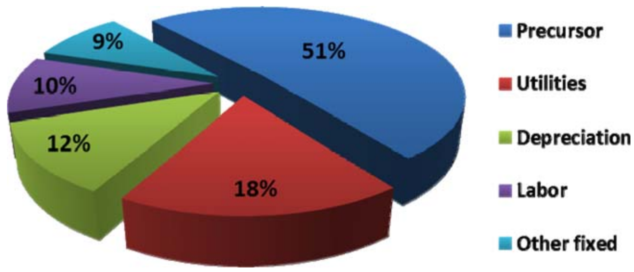

Figure 1. Separation of cost elements in the manufacture of carbon fiber from PAN.[5] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

kg-f/mm^2) with a modulus of 149 GPa (21.6 Msi; 15.2×10^3 kg-f/mm^2).[15] Another DOE program,[16,17] involves the manufacture of carbon fiber from lignin and is directed towards cost reduction through the very low cost of the renewable precursor. The best lignin-based carbon fiber samples produced to date had an average strength of 1.07 GPa (155 ksi; 109 kg-f/mm^2), moduli of 82.7 GPa (12 Msi; 8.44×10^3 kg-f/mm^2), and extensibilities of 2.03%;[15] and were manufactured using a modified technical lignin. These lignin carbon fibers were projected to cost much less than any other known method of carbon fiber production.[18–20] Efforts to further increase strength have been restricted by the unavailability of suitable lignins (i.e., lignins that meet stringent melt spinning requirements) to allow for multifilament melt spinning and conversion trials. There is now, however, a possibility this could change.

Towards Lignin Utilization

As a part of overall U.S. energy policy, the Renewable Fuels Standard (#2) mandates the production of 36 billion gallons of renewable transportation fuels by 2022, with almost 50% produced in the Southeast U.S.[21] Conversion of cellulosic feedstocks into ethanol and advanced fuels (e.g., butanol) has therefore been recognized as a necessary component of the overall biofuel strategy, so that 16 billion gallons is required from lignocellulosic biomass. Switchgrass and hybrid poplar are both attractive dedicated energy crops because of their high biomass yields and their ability to grow on significant U.S. acreage; including land that is considered marginal for production of corn and other major crops. One of the main barriers to the development of the biomass-to-liquid fuels industry is price competitiveness with oil refining to gasoline. In mature fuel and bulk chemical industries, the feedstock often represents 50% or more of the total cost; this is true for gasoline and ethanol derived from corn, and it will be true for cellulosic-derived biofuels.[22] There is therefore significant opportunity to reduce costs associated with biofuel production by the development of co-products that have higher values than the target fuel itself.

Numerous pretreatment methods[23,24] have been proposed to reduce lignocellulosic biomass recalcitrance and make the cellulosic component more accessible for hydrolysis. These approaches have been developed and optimized with a single goal—the production of a sugar stream that can be converted into fuel. In this context, a typical model biorefinery produces two product streams; a saccharide stream for fuel production and a waste lignin stream that is used for low-value thermal energy. In most cases the lignin stream passes through the whole process and therefore has a high level of impurities and ill-defined properties for use as a product. For a lignocellulosic feedstock biorefinery to be economically viable and sustainable, it must be able to use a variety of resources and utilize all major lignocellulosic components to generate valuable products.[25] Therefore biomass fractionation is now proposed, and this could be achieved through the use of organosolv techniques,[26–29] ionic liquid technologies,[30,31] green liquor processes,[32,33] or through the repurposing of defunct kraft mills as biorefineries.[34,35] In consideration of the potential for clean lignin streams to become available, there is a growing effort to now find uses[36,37] for lignins that will enable a biofuel economy to be competitive with oil refining. Several products have been identified and include: direct replacements for petroleum derived chemicals,[38] phenol derivatives,[39] polymer blends,[40,41] adhesives,[42] polyurethanes,[43] epoxy resins,[44] conducting polymers,[45] and antioxidants.[46] Of particular interest is the possibility of manufacturing carbon fiber from lignin, and this is illustrated by plotting the frequency of lignin-based carbon fiber articles and patents by year (Figure 2).

A Cost Perspective

According to DOE figures, the estimated cost of a suitable lignin precursor for carbon fiber manufacture, accounting for simple purification and high-speed melt-spinning, is conservatively ∼$0.85/kg[17,47,48] ($1.52/kg, adjusting for a carbon fiber yield of ∼55%, based on precursor fiber).[18] This is substantially lower than the proposed cost of other potential precursors such as textile grade PAN at $2.2–$6.6/kg[14] (depending on the grade used; $4.4-$13.2/kg adjusting for yield ∼50%); melt-spun PAN at $3.15/kg[12] ($6.3/kg, yield of ∼50%); and polyethylene at $1.1–$1.65/kg[14] ($1.57–$2.36/kg, yield ∼70%); however, the latter process requires additional precursors and costly environmental remediation during conversion.[49] The differences in cost between lignin and the other potential precursors would increase further if an increased oil price were to be accounted for; lignin has no such limitation. According to additional figures,[12,14] the production cost of conventional PAN carbon fibers are estimated to be $25.15/kg, while those from textile grade PAN are, depending on the grade, $12.25 to $25.43/kg; from melt-spun PAN are $17.40/kg, and with advanced conversion processes, $13.44/kg. No estimate has been provided for polyethylene-based low-cost carbon fiber. Carbon fiber manufactured at lower scales from any of these precursors would almost

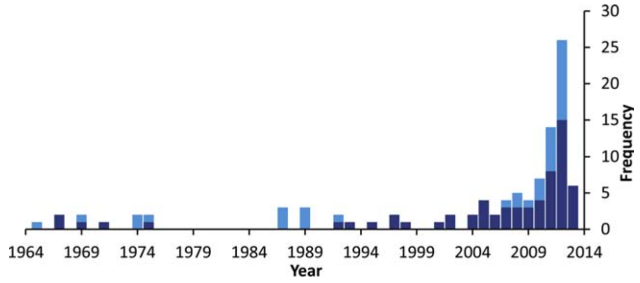

Figure 2. Frequency of journal articles (dark) and patents (light) by year; to 01/31/2013. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

certainly be close to the automotive target costs of \$11–\$15.40/kg, but still less than half the cost of equivalent commercial polyacrylonitrile based carbon fibers.

The DOE estimate provided for the manufacturing cost of lignin-based carbon fiber is \$6.27/kg and accounts for some reduced costs in processing but only a 35% carbon fiber yield. If an increase in carbon yield to 55%[20] is accounted for, the potential cost is reduced to around \$4/kg. Furthermore, since lignin is already substantially oxidized, oxidative thermostabilization of thermoplastic lignin fiber to thermoset lignin fiber could proceed more quickly (minutes)[16] than for PAN (hours),[50] which would further reduce energy consumption and cost.

LIGNIN CARBON FIBER MANUFACTURE

The currently preferred method for the manufacture of carbon fiber from lignin[2] (Figure 3) involves the preparation of a suitable lignin that is melt-spun into fiber under an inert atmosphere. The lignin fiber is then oxidatively thermostabilized and carbonized. The integrity of the lignin fiber during oxidative thermostabilization depends on its ability to crosslink, so that the glass transition (T_g) of the material is maintained above the process temperature, ultimately rendering it infusible. The process is complex and careful control of the lignin, spinning conditions, treatment temperatures, and ramping profiles are required to obtain carbon fiber of superior strength. Lignin, which is naturally partially oxidized, demands critical control of the melt-spinning step. The lignin has to be prepared in such a way to have a low enough melt flow temperature (T_s, the softening temperature at which liquid flow is observed under low shear) for it to be melt spun without polymerizing during extrusion, but a high enough T_g for fiber stabilization to proceed at an acceptable rate. Thus a narrow thermal window of opportunity exists for manufacturing carbon fiber from lignin by way of melt extrusion. However, lignin does have advantages over other precursors (MPP and PAN): it is very inexpensive, a renewable product, and is already substantially oxidized so that it can be oxidatively thermostabilized at potentially much higher rates than either MPP or PAN.

Historical Lignin Carbon Fibers

Otani et al.[51] in 1965 described several methods of forming fiber from lignin (hardwood kraft, softwood kraft, and alkali softwood lignins) by both melt-spinning and dry spinning, and their conversion to carbon fiber, graphite fiber, and activated carbon fiber. Using a one pot melt-spinning method (i.e., short residence time), they were able to obtain hardwood kraft lignin fiber of 20–30 μm diameter at rates of 15 m/min and with a reported strength of up to 8000 kg-f/cm^2 (0.785 GPa, 114 ksi, 80 kg-f/mm^2; patent example). Similarly, they could produce a carbon fiber from a 1 : 1 mixture of alkali-pulped softwood lignin and alkali-pulped hardwood lignin with strengths of up to 7000 kg/cm^2 (0.686 GPa, 99 ksi, 70 kg-f/mm^2; patent example). They also described several other methods using additives and/or post-treatments to facilitate activation. Consequently, lignin carbon fiber enjoyed a brief period of small-scale commercialization extending into the early 1970s under the name of Kayacarbon by Nippon Kayaku.[52] The precursor fiber was manufactured by the dry spinning of an alkali lignin solution which passed through a heated chamber prior to spooling; poly(vinyl alcohol) was added to improve fiber integrity. Tomizuka et al.[53] reported on the morphology and voids in graphitized Kayacarbon fibers by small angle X-ray and density studies. Similarly, Johnson et al.[54] examined them by high-angle X-ray diffraction and electron microscopy concluding that they had a heterogeneous fine structure, with both continuous and discontinuous inclusions of graphitic structure, which was more pronounced than carbon fibers from other precursors of the time.[55]

Presumably, Kayacarbon left the market since other precursor materials developed more rapidly, at lower cost and with higher strengths, making it less competitive. It is notable that the lower-cost melt spinning route was not taken, but this may have been due to problems in transitioning from small scale single fiber extrusion equipment to larger multifilament facilities

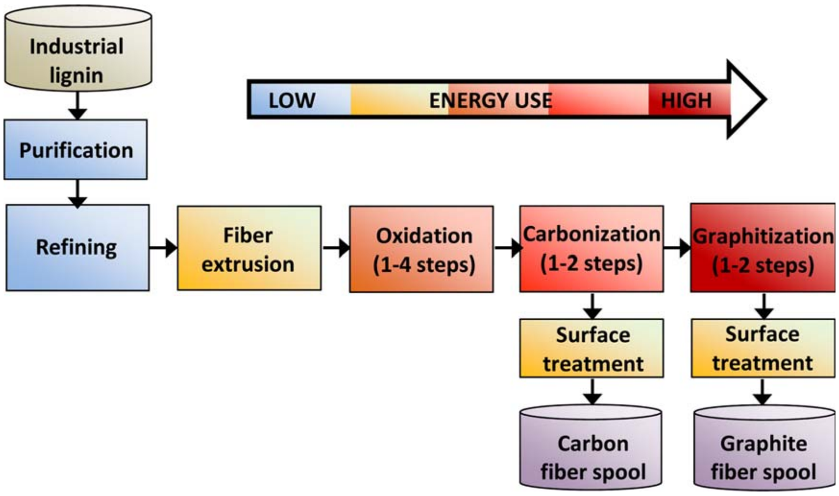

Figure 3. Schematic of carbon fiber production from an industrial (technical) lignin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with significantly longer residence times, which could potentially cause the lignin to polymerize during extrusion. Otani[56] also authored an article describing methods of carbon fiber production from various precursors, including lignin, and also the physical properties required for various industrial applications.

Several patents were awarded over the two following decades. Gould[57] described methods by which an improved carbon fiber could be made by extracting pulp waste lignin with an alcohol, followed by demethoylation, and then polymerization by irradiation or thermal treatment prior to conversion. The same year, Mansmann[58] described several methods for the co-spinning of lignin sulfonates with PEO (predominantly by dry spinning, as Otani had) with rapid subsequent conversion to carbon fiber, providing fibers with strengths of up to 0.834 GPa (121 ksi; 85.1 kg-f/mm^2); some examples were given in which salts were added to improve conversion kinetics.

Ten years later, Sudo[59,60] described the preparation of lignins by the high pressure steam treatment of wood with subsequent organic solvent or alkali extraction. The resulting lignins were first hydrocracked to reduce molecular weight and complexity, and then treated to increase molecular weight to provide a precursor for melt-spinning. Conversion of the lignin fibers resulted in carbon fibers with strengths in the range of 30–80 kg/mm^2 (0.29-0.78 GPa; 42.7–114 ksi) and of 10–40 μm diameter. Sudo[61] also suggested an alternative preparation of lignin whereby treatment with phenol in the presence of p-toluenesulphonic acid yielded a melt spinnable product. Conversion of the melt spun fiber gave carbon fibers with strengths in the region of 52.8 kg-f/mm^2 (0.518 GPa; 75.1 ksi). Sudo then described additional carbon fiber processes that used steam-exploded lignins that were treated by hydrogenolysis[62] (0.660 GPa; 65.3 ksi; 45.9 kg-f/mm^2) or a more simple phenolysis (0.450 GPa; 65.3 ksi; 45.9 kg-f/mm^2),[63] in what are possibly the first publications on manufacturing carbon fiber from lignin in the accessible literature.

Ito[64] suggested an alternative method for the preparation of lignins suitable for carbon fiber manufacture using the high temperature extraction of wood chips with a mixture of water and cresols. The solvents were recovered by evaporation and the lignins melt-spun to give thermoplastic fiber that could be rendered infusible at 3°C/min to 200°C. Ichikawa[65] described another lignin preparation in which lignins were phenylated but were then coextruded with various amounts of pitch (isotropic) to improve carbon fiber properties.

Uraki,[66–68] in the late 1990s, applied an aqueous acetic acid pulping method to birch which gave lignins that were more directly suitable for melt-spinning due to a limited acetylation. These were subsequently either heat treated or fractionated by pH inversion using acetic acid to give derivative lignins with further improved melt-spinning efficacy and increased molecular weights. Conversion of the melt spun fibers to carbon fibers with strengths of up to 0.355 GPa (51.5 ksi; kg-f/mm^2) and moduli of 39.1 GPa (5.67 Msi; 3.99×10^3 kg-f/mm^2) were reported. The conversion of these carbon fibers to activated carbon fiber was later evaluated.[69]

Advances in the New Millennium

Much of the preceding work was elaborate and therefore would most likely have been too expensive for commercial manufacture. Several groups have more recently investigated the production of carbon fibers from lignin directed towards improving the melt-spinning of lignin fiber and their conversion to carbon fiber with lower cost. The literature can be separated into three main areas: (1) carbon fiber from lignins without any additives or chemical modifications applied prior to extrusion; (2) carbon fiber from lignins that were either coextruded, or chemically modified prior to extrusion; and (3) efforts directed towards the manufacture of submicron carbon fibers from lignin.

Carbon Fiber from Lignin

Uraki,[70] in continuing earlier work,[62,63,66–69] described the preparation of carbon fiber from a lignin recovered by the acetic acid catalyzed fractionation of Todo Fir. The lignin was extracted with solvent and melt-spun on single filament apparatus.[63] Single fibers could be oxidatively stabilized at rates of up to 3.0°C/min to 250°C, and carbonized at 180°C/min to 1000°C to give carbon fibers with strengths of 0.15 GPa (21.8 ksi; 15.3 kg-f/mm^2); direct carbonization was also reported. The purpose of this work, however, was to examine lignin-based carbon fiber activation, and they reported increased efficacy compared with conventional carbon fibers.

Kadla[71] later reported carbon fiber preparation from three lignins, an organosolv hardwood lignin (Alcell^{TM}; Lignol Innovations), a softwood kraft lignin (Indulin AT^{TM}; MeadWestvaco) and a hardwood kraft lignin (experimental; MeadWestvaco). The lignins were desalted prior to any measurements and/or extrusion and the hardwood-based samples were treated at 145°C for 1 hour to remove potential volatiles. It was reported that while the hardwood lignins were readily melt spun into fiber, the softwood lignin had low thermal stability and therefore crosslinked during extrusion, and this was in agreement with the findings of Kubo.[67] Alcell lignin with a $T_{g(\mathrm{onset})}$ of 68.2°C could be single-filament spun at between 138–165°C to give lignin fibers that were oxidatively thermostabilized at a rate of 0.2°C/min to 250°C. Subsequent carbonization at a rate of 3°C/min to 1000°C, gave fibers with 0.388 GPa strength (56.3 ksi; 39.6 kg-f/mm^2), 40 GPa modulus (5.80 Msi; 4.08×10^3 kg-f/mm^2), and 1.00% extensibility, and in 41.8% yield based on the starting Alcell fibers (as per convention, this author will adjust and provide yields compared to precursor fiber material). Similarly, the hardwood kraft lignin with a $T_{g(\mathrm{onset})}$ of 83.3°C was spun at 195–228°C, providing fibers that were oxidatively thermostabilized at a rate of 2.0°C/min under similar conditions. Carbonization of the thermoset fibers gave carbon fibers with 0.422 GPa strength (61.2 ksi; 43.0 kg-f/mm^2), 40 GPa modulus (5.80 Msi; 4.08x10^3 kg-f/mm^2), and 1.12% extensibility, and in 48.1% yield.

Braun[72] later noted that little information was available concerning the effect of oxidative thermostabilization on lignin T_g and therefore presented data concerning the chemical and polymeric changes that occur during thermal conversion. Homogenized hardwood kraft lignin strands were extruded,[71] ground and directly heat-treated at various rates and to differing

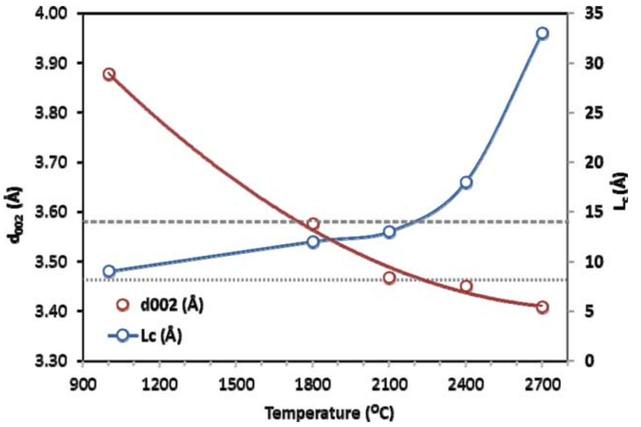

Figure 4. Graphitic structure evolution in Alcell-based carbon fiber as a function of heat treatment temperature.[19] PAN-based T300 is provided for comparison, where ······· is d_{002} spacing and ------- is stacking height, L_c. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperatures, while changes in elemental composition, functional groups, molecular weights, and thermal properties were examined and compared. They found that the oxidative thermostabilization process was consistent with autocatalysis and that increased oxygen contents occurred at treatment temperatures of up to 250°C, followed by decreasing contents with incrementally increased temperatures. Continuous heating transformation diagrams, based on kinetic and T_g data, showed that to avoid softening during heat treatments, the oxidative thermostabilization of that particular lignin would have to take place using rates of less than 0.06°C/min. This was a far lower rate than had been used previously (2°C/min) for the same lignin when spun and thermally treated as a single filament,[71] but was consistent with later findings[2] using a very similar lignin when multifilament extrusion was used to prepare the fibers; (an explanation for this is offered later).

Baker[73,74] later described the properties of two lignins, an experimental hardwood kraft lignin and an organic purified derivative of the same ($T_g \sim 86°C$; OP86). While the kraft lignin was not readily melt-spinable, the organic purified lignin was, and continuous lignin tows could be spun to diameters as low as 10 μm and with high speed. However, conversion of the lignin fiber tow proceeded slowly with rates of oxidative thermostabilization as low as 0.01°C/min being required before carbonization was possible. The resulting carbon fibers were of low yield (32%), had a low strength of 0.517 GPa (75 ksi; 52.7 kg-f/mm^2), and were therefore similar in strength to those previously reported. Owing to a limited availability of OP86, attention turned towards an organosolv lignin, Alcell^{TM}. The use of a thermal pretreatment to increase Alcell T_g and T_s was employed to examine resulting changes in the kinetics of conversion of the lignin fiber into carbon fiber. Ultimately, the tensile properties and yield of the carbon fibers were improved by these treatments, giving 0.710 GPa (103 ksi; 72.4 kg-f/mm^2) and 41%, respectively, in comparison to the original Alcell based carbon fibers, which had a strength of 0.338 GPa (49 ksi; 34.5 kg-f/mm^2) and a yield of 31%. The multifilament tow processing time was, however, reduced significantly from 14 days to 14 h, thereby establishing a firm link between lignin fiber T_g and permissible oxidative thermostabilization rates.[74] Furthermore, the lignin based carbon fibers formed highly graphitic structures[16,17] upon treatment to temperatures greater than 2100°C (Figure 4), though it was unknown if they had developed the highly oriented graphitic structures that MPP or PAN based carbon fibers develop since there were no improvements in strength observed. This suggested that there was a lack of orientation and continuity in the structure which could only be improved with the use of a more suitable lignin precursor.

In continuing work,[18,75] Baker determined that the use of a thermal pretreatment to adjust the T_g and melt flow properties of a lignin starting material would be more effectively employed using a lignin with a more narrow molecular weight distribution. Therefore, attention returned to OP86, which owing to the method of manufacture was determined to have more favorable molecular weight properties than Alcell. The thermal pretreatment of OP86 gave a selection of lignins with varying T_g and T_s properties, which were evaluated for their multifilament melt-spinning properties. The resulting lignin fiber tows were studied for their oxidative thermostabilization and carbonization properties (Figure 5). Ultimately, the best carbon fibers produced had average tensile strengths of 1.07 GPa (155 ksi; 109 kg-f/mm^2) compared with the original lignin-derived carbon fibers with a strength of 0.517 GPa; and with carbon yields as high as 55% compared with the original lignin with 33% yield[76]. However, the oxidative thermostabilization times for these particular fiber tows was long at around 6–12 h, although some higher T_g fiber samples could be treated in as little as 13 min, with oxidative thermostabilization from 25°C to 250°C at 20°C/min. Unfortunately, these latter fibers had much reduced tensile properties and this was due to their relatively poor melt-spinning performance.

The same researchers[77] also evaluated high T_g softwood lignins plasticized with low T_g hardwood lignins and found that optimum levels of addition could give continuously spun multifilaments with accelerated conversion times. Other evaluations using both the single filament and multi-filament spinning of lignin mixtures such as PET, PE, PAN, MPP, and various other plasticizers were also done; however, no improvement was to be found in the mechanical properties of the resulting carbon fibers.

Researchers at Innventia AB have more recently explored the manufacture of carbon fiber from lignins obtained from their Lignoboost process.[78,79] The process is designed to work alongside traditional kraft pulping processes to recover high purity lignins from a portion of the lignin-rich stream that would normally be incinerated in a recovery boiler to recover pulp mill chemicals and provide energy. The process involves the treatment of industrial black liquor with carbon dioxide which causes precipitation of lignin, which is slurried, washed with dilute acid and recovered. Therefore the resulting lignin is relatively free of carbohydrates and salts compared to traditional kraft lignins. Nordstrom[80] described the properties, single-filament melt spinning, and processing of four lignins prepared from both softwood (SK) and hardwood kraft (HK) liquors

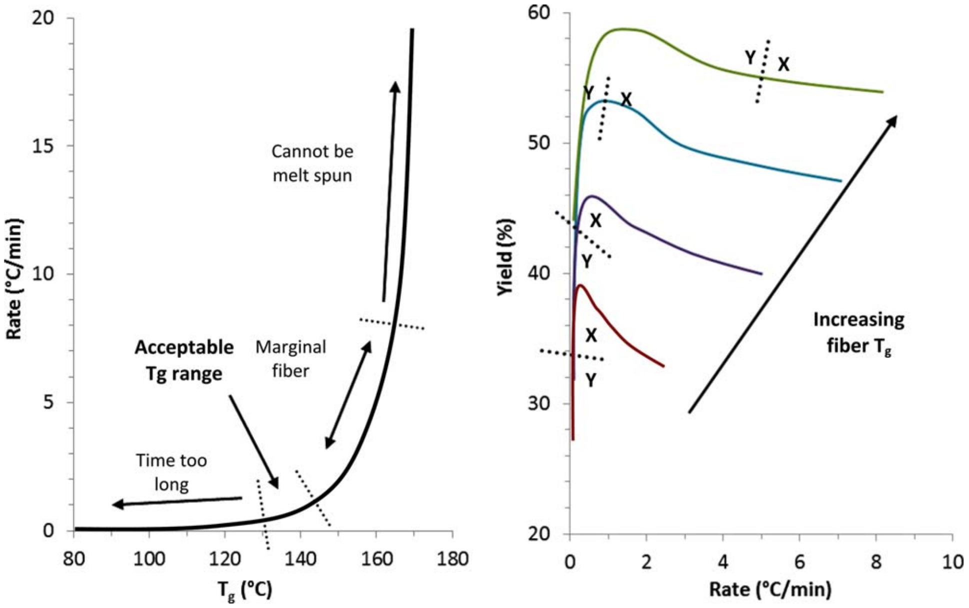

Figure 5. Representation of the relationship between (a) potential fiber T_g and maximum permissible rate of oxidative stabilization without fusion/adhesion; and (b) carbon fiber yield and rate of oxidative stabilization of lignin fibers (Y denotes region of fully infusible fiber formed; X denotes fusible region). Both relationships are lignin specific but all lignins studied have similar trends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

using the Lignoboost process, both with (SKLP, HKLP) and without (SKL, HKL) prior treatment by ultrafiltration to reduce polydispersity. Each lignin was assessed for melt-spinning capability and it was found that the permeate lignins, HKLP (T_g 114°C) and SKLP (T_g 146°C), could be spun into continuous filaments while the non-permeate HKL (T_g 139°C) could not easily be spun and SKL (T_g 150°C) could not be melt spun into fiber. Comparison of the molecular weight data given for SKLP and SKL suggests that while their T_gs are similar, the molecular weight is almost double for the latter. This implies the presence of substantial infusible components in the lignins that were solubilized when acetylated for SEC measurement; and this is observed in the diminished magnitude T_g of SKL relative to the permeate lignins. The authors also provided information regarding the use of low T_g permeate lignins to plasticize high T_g parent lignins, and the resulting effects observed in T_g measurements and improved fiber spinning. Norberg[81] continued in further describing the utility of SKL, SKLP and HKLP for making carbon fiber and described the oxidative thermostabilization profiles of several fibers and the changes in lignin chemistry that resulted during conversion. Most significantly, processing rates of 15°C/min were reported to achieve thermoset fibers, furthermore, studies were done that bypassed oxidative thermostabilization allowing direct carbonization to take place.

Brodin[82] also reported the oxidative stabilization of kraft lignins using powders, including spruce, birch and eucalyptus, and used an experimental design to elucidate the effects of various parameters on yields of stabilization and carbonization. The input factors were feedstock, oxidative thermostabilization temperature, isothermal time, and heating rate; the responses were oxidative stabilization yield, carbonization yield, and T_g (if detectable). They demonstrated that the carbon yield of lignin increases with the severity of oxidative thermostabilization conditions used for both birch and eucalyptus, but not for pine lignin which exhibited an optimum condition. Under the conditions used for stabilization, almost all of the lignin powders exhibited a T_g and thus few were completely thermostabilized during treatment. In contrast to this, Baker[83] showed that there was an optimum rate of oxidative thermostabilization for improving carbon fiber yields, below which carbon yield was reduced because the balance of oxidation versus degradation became in favor of the latter, and above which lignin volatilization predominated over oxidation and crosslinking. Brodin et al., however, provided XPS data to suggest a mechanism by which lignin oxidative thermostabilization occurred, and demonstrated differences in lignin functionality across the fiber diameter that revealed air diffusion dependence. This is similar in concept to the accepted sheath-core differences in structure observed for both polyacrylonitrile and mesophase pitch carbon fibers that cause the interior of fiber cross sections to be of lower strength. Similarly, Baker[83] melt spun lignins to give fibers of differing diameter and converted them to carbon fiber using identical conditions. It was found that while the cross sectional area was doubled, strengths were reduced by only 15% and the modulus by 8%, suggesting that although there is a diameter diffusion dependence, it is much reduced compared with other precursors,[84] and that is because lignin is already highly oxidized. It is this inherent oxygen fuctionality that allowed Norberg et al. to directly carbonize lignin fibers.[81]

Lignins recovered from other delignification processes have also been suggested as precursors for carbon fiber. Luo et al.[85]

described the recovery of lignins from the green liquor process, which has become a popular process directed towards biorefinery implementation. Lin et al.[86] described the manufacture of carbon fiber from lignins obtained by the polyethylene glycol solvolysis of wood,[87] which gave carbon fiber with diameters as low as 10.2 μm and tensile strengths of up to 0.457 GPa (66.3 ksi; 46.6 kg-f/mm^2).

While most of the work so far described lignins from more traditional delignification techniques, other lignin precursors have also been considered. Prauchner[88] described the use of a lignin-rich pitch precursor derived from the slow pyrolysis of eucalyptus used to manufacture charcoal in Brazil. Condensation of the volatiles released during treatment gave a tar which was distilled to give a crude pitch residue. Thermal treatment of the lignin pitch increased its softening temperature from 76.1°C to 134°C that could be melt spun at 175–180°C to give single filaments of around 40μm diameter. Oxidative thermostabilization of the filaments proceeded at 0.08°C/min to 180°C and carbonization at 2.0°C/min to 1000°C, giving carbon fiber of 0.129 GPa (18.7 ksi; 13.2 kg-f/mm^2) average strength. Qiao[89] used lignin-rich mixed hardwood tars and bamboo tars that were polymerized using an aqueous solution of formaldehyde catalyzed by oxalic acid and hydrochloric acid to increase softening temperatures. The resulting pitches were melt spun at 130°C and 180°C for those derived from hardwood and bamboo, respectively. The fibers were then rendered infusible by treatment to 200°C at up to 0.3°C/min, and carbonized at rates of up to 2°C/min to 1000°C, resulting in carbon fibers with diameters as low as 13.4 μm, tensile strengths of up to 632 MPa (91.7 ksi; 64.4 kg-f/mm^2), and moduli of 44 GPa (6.38 Msi; 4.49×10^3 kg-f/mm^2).

Qin[90] described a process by which a pyrolytic lignin was recovered[91] from bio-oil obtained as a product of the pyrolysis of mixed hardwood sawdust. The pyrolytic lignin had a T_g of 70°C and was thermally treated under varying conditions to give lignins with T_gs of up to 111°C. The author presented the effects of the treatments on pyrolytic lignin in terms of NMR, elemental composition, molecular weight, fiber spinning performance, oxidative thermostabilization response, and ultimately, carbon fiber strength. The lignin with the best melt-spinning performance (T_g of 89.1°C) was selected for conversion giving 49 μm diameter carbon fibers with an average strength of 0.370 GPa (53.7 ksi; 37.7 kg-f/mm^2) and a modulus of 36 GPa (5.22 Msi; 3.67×10^3 kg-f/mm^2); the yield with reference to the spun fiber was high at 52%. The pyrolytic lignin based carbon fibers were found to be comparable with those prepared from the kraft hardwood lignin and Alcell lignin used for comparison in the same study.

In recent years there have been several patent applications and patents issued. Berlin[92] obtained a patent providing specification for features within lignins which could be suitable for carbon fiber manufacture. They stated that increased alkoxy contents and/or carbon contents provide for improved lignin-based carbon fibers, although no examples of lignin fiber or carbon fiber manufacture are provided. The particular properties of the so-called derivatives of native lignin do not appear to be particular to the fractionation process used, and therefore perhaps apply to any lignin that could be manufactured. In general the specifications state that the carbon content of a lignin for carbon fiber manufacture should be greater than 64.5%, and/or the alkoxy content greater than 0.45 mmol/g for hardwood derived lignins, 0.35 mmol/g for softwoods, and 0.25 mmol/g for annual fiber lignins. Yang[93] obtained a patent for the provision of lignin precursors based on lignin mixtures comprising two or more of softwood lignin, hardwood lignin, and pitch. Kim[94] described a method for manufacturing lignin with high melt processibility. Wohlmann[95] patented a specification for lignins having a T_g in the range 90–160°C, a polydispersity of less than 28, an ash content of less than 1% (wt), and a volatiles content of less than 1% (wt). Sjoholm[96] described methods for making fractionated softwood and hardwood alkali lignins, mixtures of the same, and mixtures with parent lignins, and the extrusion properties of the materials formed.

Carbon Fiber from Blends and Chemically Modified Lignins

Kadla, Kubo[71] et al. proposed a method by which a kraft hardwood lignin of high softening temperature could be plasticized using polyethylene oxide (PEO) to improve fiber spinning performance and handling during subsequent conversion steps. The blends were formulated with PEO from 5 up to 25 wt %, causing a reduction in single filament fiber spinning temperatures of up to 45°C, and an improvement in spinning performance. However, oxidative thermostabilization proceeded much more slowly. The amount of PEO added to the kraft lignin was then reduced to less than 5 wt % and it was found that not only could spinning performance be improved, but the strength and thermostabilization rates could be retained in comparison to the kraft lignin itself. Furthermore, the mechanical properties of the blend-derived carbon fibers appeared to reach an optimum with the addition of 3% PEO, and this could be further improved by using PEO with an increased molecular weight to increase tensile strength by 10% and the modulus by 20%. Kubo and Kadla reported further examinations of the effects of kraft lignin structure on PEO miscibility,[97] and the relationship between thermal properties, structure, and organosolv lignin/PEO blend behavior.[98] In a similar study they reported the use of polypropylene instead of PEO, and although it was found that polypropylene was largely immiscible with the lignin, it was used to assist in the manufacture of hollow core carbon fibers,[99] and later,[100] carbon fibers with high macroporosity but relatively low mesoporosity. Further to this, Kubo and Kadla reported[101] the effects of blending a hardwood kraft lignin with poly (ethylene terephthalate) and various polypropylenes on fiber spinning efficacy and fiber thermal properties. Most notably, they report that oxidative thermostabilization of a 75/25 w/w lignin/PET blend proceeded more rapidly (2°C/min to 250°C) than lignin fibers alone (0.2°C/min to 250°C). The mechanical properties of the carbon fibers prepared from the blends were improved compared with neat lignin analogues; they reported that the maximum single fiber strengths tested were 0.605 GPa (87.7 ksi; 61.7 kg-f/mm^2), with a modulus of 61 GPa (8.85 Msi; 6.22×10^3 kg-f/mm^2) for 100% lignin; and 0.703 GPa (102 ksi; 71.7 kg-f/mm^2), with a modulus of 94 GPa (13.6 Msi; 9.59×10^3 kg-f/mm^2) for the 75/25 blend (plots appear to give average fiber properties of approximately three fifths of these values). Similarly, the patent literature reveals a current interest in carbon fiber from lignin/polymer blends.[102,103]

Another polymer of interest for coextrusion is PAN, however the literature has focused on using lignin as an extender for PAN rather than PAN as a potential polymer to improve both the processing of lignin fiber into carbon fiber, and the mechanical properties of the resulting carbon fibers. In 2011, Zoltek and Weyerhaeuser[104,105] entered into a partnership to develop the technology with DOE funding until 2014. Pilot-scale carbon fibers have been produced containing up to 45 wt % lignin, although the wet-spinning performance of the blends decreased significantly above 35 wt % lignin. Furthermore, the porosity of the spun fibers increased substantially above 15 wt % addition, which resulted in micron sized voids that were elongated along the fiber axis. Although the voids were attributed to low solution viscosities, it may be that the particular lignin used, separates from the PAN as it phase inverts during coagulation, resulting in the lignin leaving with the solvent. To remedy this, the team is investigating higher molecular weight PANs. However, using a lignin loading of 35 wt %, they report carbon fiber strengths of 244 ksi (1.68 GPa; 172 kg-f/mm^2) and moduli of 29.2 Msi (201 GPa; 20.5×10^3 kg-f/mm^2), and this essentially meets DOE automotive targets. Patents have been obtained.[106] Other investigators have reported lignin/PAN blends and their thermal conversion chemistry.[106–110]

More recently, there has been a growing interest in preparing carbon fiber from lignin nanocomposite fibers. Sevastyanova et al.[111] described the incorporation of two types of modified montmorillonite organoclays into an organosolv lignin, and reported the extrusion properties of the composite materials at various levels of inclusion. They concluded that the addition of the materials improved fiber spinning efficacy and that the strength of the resulting lignin fiber was almost doubled. Qin and Kadla[112] continued the work using a pyrolytic lignin isolated from bio-oil,[113] which was thermally treated to increase its molecular weight and glass transition temperature prior to compounding and fiber spinning. X-ray diffraction data showed that the clays were well intercalated and remained so throughout thermal conversion to carbon fiber. However, in this case, the addition of the organoclays did not substantially improve the strengths of the lignin fibers as they had for the organosolv lignin, but an optimum level of addition of around 1% wt. was found. Similarly, the resulting carbon fibers also exhibited a maximum improvement at a concentration of 1% wt. The authors concluded that the decrease in strength observed at levels above 1% wt. was attributed to increased fiber diameter, a lack of preferred orientation of the clay platelets along the fiber axis, and the presence of micro-voids in the carbon fibers produced. However, this author suggests that the diameter dependence of oxidative thermostabilization for lignin is low and that the addition of nondiffusive nanomaterials to lignin at higher levels could reduce the oxidative thermostabilization rate of lignin fibers as they provide a significant barrier to air diffusion.

Baker et al.[114] explored the possibility of using carbon nanotubes to enhance the strength, modulus, electrical conductivity and thermal conductivity, of various lignins used to manufacture carbon fiber; possibly the most expensive lignin-carbon fibers made so far. Investigations using an organosolv lignin, a purified hardwood kraft lignin, and a blend comprising a softwood kraft lignin and the purified hardwood lignin, revealed that the carbon nanotubes (multiwall) could be added in quantities as high as 15 wt % before fibers could not be melt-spun. In many cases, i.e., at an optimal level of CNTs, the nanotubes enhanced the fiber spinning process via the increased heat capacity of the composite, which allowed the fiber to remain molten a greater distance on the spin-line, therefore allowing increased stretching and more fine diameter fibers to be spun. The lignin composite fibers were also found to be much stronger than fibers prepared using lignin alone. However, after oxidative thermostabilization and subsequent carbonization, the resulting carbon fibers exhibited only a 20% increase in tensile strength and a 50% increase in modulus in comparison to the neat lignin based carbon fibers. The reason for this poor increase in strength was attributed to low interfacial adhesion between the nonfunctionalized CNTs and the lignin carbons (Figure 6).

While much has been done to modify lignin properties and their carbon fibers by coextrusion, some work describes the use of chemically modified lignins. Although chemically modified lignins are well known,[116] and in fact acetylation is a common route to molecular weight assessment, their application towards carbon fiber manufacture is not commonly applied. Eckert and Abdullah[117] described a process for the limited acetylation of kraft softwood lignins to improve melt spinning performance. Wohlmann et al.[118] reported processes by which lignins are derivatized through their free hydroxyl groups to give plasticizing derivatives attached via ester, ether and/or urethane functions. Shen et al. suggested[119] a method of preparing activated carbon fibers using phenol-formaldehyde resin technology. Maradur et al.[120] reported the preparation of carbon fibers from a lignin-acrylonitrile copolymer; this is highly significant since a large portion of PAN-based carbon fiber cost is from acrylonitrile itself. In this respect the authors hope to manufacture a hybrid polymer that has lower cost and improved spinnability, thermal processing characteristics, and strength over lignin-based carbon fibers. Copolymerization was achieved using a two-step radical polymerization process in which the first step involved the oligomerization of acrylonitrile and the second the addition of peroxide activated lignin to the acrylonitrile oligomers (Figure 7). The product, containing up to 50 wt % lignin, could be spun from a 16% copolymer DMSO solution into fine fibers of around 15 μm diameter. Oxidative thermostabilization was done isothermally at 280°C, and carbonization proceeded at 5°C/min to 800°C without fiber fusion, giving carbon fibers of around 10 μm diameter. The authors described details concerning the synthesis, some characteristics of the copolymer, fiber spinning and conversion. Further work is reported to be in progress to make improvements to the process and characterize the resulting carbon fibers.[121]

Others have examined the possibility of lignocellulosic[122] and liquid wood precursors.[123] Although not strictly lignin-based carbon fibers, they represent an interesting class of material, as they could provide a way to low-cost carbon fiber through the use of low-value lignocellulosic streams (e.g., municipal waste, forest brush, rice straw), potential biorefinery waste streams

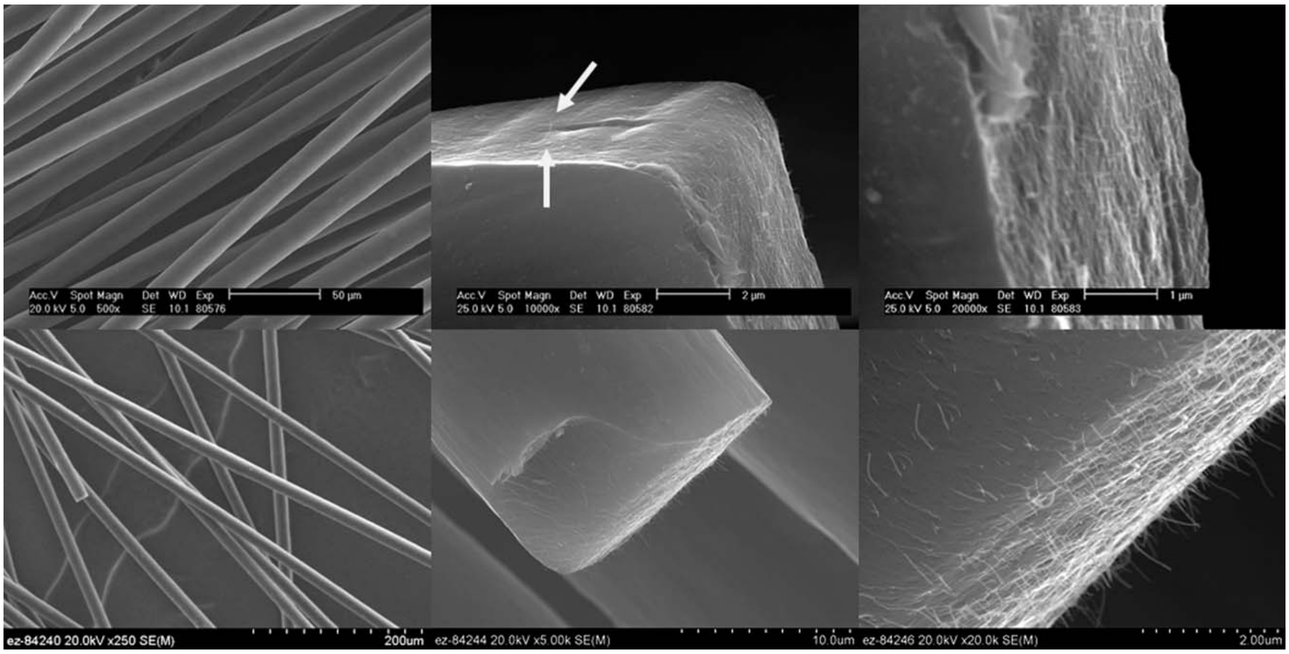

Figure 6. 1% (upper) and 2.5% (lower) CNT composite lignin-based carbon fibers illustrating the good alignment of CNTs along the fiber axis but low interfacial adhesion. The arrows point to a CNT which "pealed" from the lignin during a fracture along the carbon fiber axis (fiber treated to 1000°C).[16,114,115]

(streams from biorefineries that use pretreatment rather than fractionation technologies), and/or sawdust. Ma and Zhao[124] suggested a process by which powdered wood is first mixed in phenol to which phosphoric acid has been added at 160°C for 2.5 h. The liquid wood is then polymerized by the addition of hexamethylenetetramine (5 wt %) and heated to cause cross-linking. The solution is then spun and fiber stabilization is effected by soaking the fibers in a solution containing formaldehyde and hydrochloric acid at 90°C for 2 h. The authors presented much analytical data for the process,[125,126] including tensile strengths and moduli that approach 1.7GPa (247 ksi; 173 kg-f/mm^2) and 176 GPa (25.5 Msi; 17.9×10^3 kg-f/mm^2), respectively. Lin et al.[127] report similar syntheses as do others.[128,129] However, it is unclear if these processes could be economically or environmentally attractive. A potentially more desirable route to lignocellulosic-based carbon fiber has been suggested by Lehmann et al.[122] whereby differing levels of lignin additive are added to a polymer solution of a cellulose or cellulose derivative that is solution spun into a coagulation bath to form spooled continuous fibers. The solution forming solvents are noted to be ionic liquids, N-methylmorpholine-N-oxide, and other solvents common to cellulose and cellulose derivative dissolution.

Submicron Carbon Fiber

The rediscovery of electrostatic spinning late in the last century caused much interest in the manufacture of nanofibers (technically submicron fibers in many cases) from many polymers.[130–133] In part this has been due to the ease with which electrospinning equipment can be implemented and its very low cost. More recently the process has been applied to manufacture carbon nanofibers. Carbon nanofibers have great potential for use in separation,[134,135] energy storage,[136,137] and structural composite applications.[138,139] This is due to their relatively high strengths, high

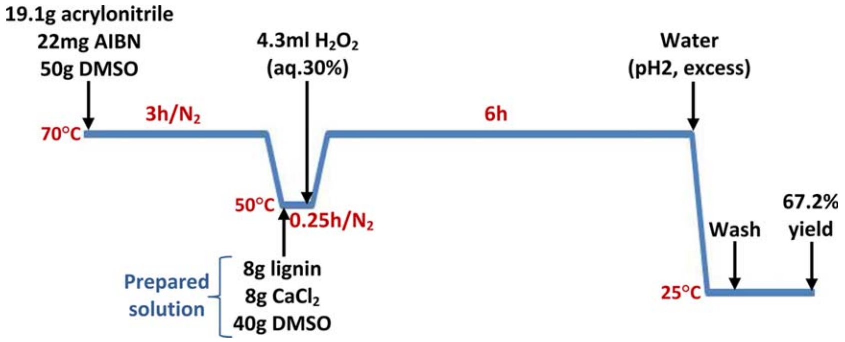

Figure 7. Method of preparation of poly (acrylonitrile-*co*-lignin).[120] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

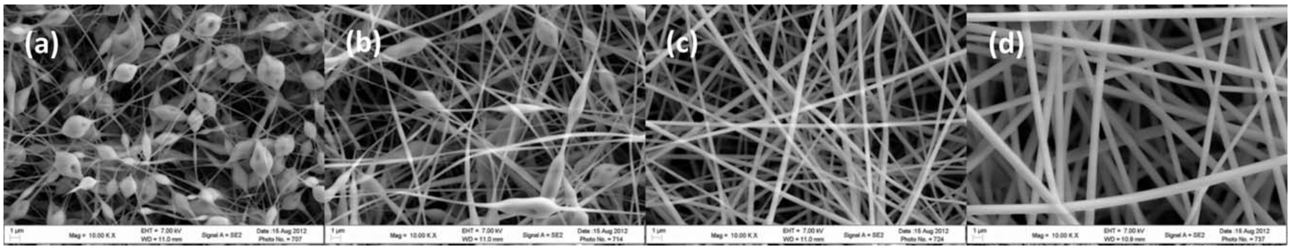

Figure 8. Effect of increasing lignin concentration ((a) to (d)) on fiber morphology.

specific surface areas, and the ease of imparting morphological and chemical functionality. Commercialization could be achieved provided that they are manufactured efficiently and with low material cost. Currently, they are generally made from polyacrylonitrile via electrostatic spinning, and therefore potential problems exist in their commercial manufacture due to high precursor and solvent recovery costs, evolved gas handling, and the slow intricate temperature control required during nanofiber conversion to carbon nanofibers. Conversely, lignin is a low-cost material, it is highly soluble in volatile solvents, does not evolve noxious gases during conversion, and has the potential for a very rapid conversion from electrospun thermoplastic lignin nanofibers to thermoset, and consequently to carbon nanofibers.

Lallave et al. were the first to report the manufacture of carbon nanofibers from lignin.[140] They formulated a method by which an organosolv lignin (Alcell) dissolved in ethanol at ratios around 1 : 1 w/w could be coaxially electrospun to give lignin fibers in the range of 400 nm to 2 μm diameter. Difficulties caused by the evaporation of ethanol from the highly concentrated solution led to the use of a coaxial spinneret whereby ethanol was passed through an outer sheath to prevent Taylor Cone[141] solidification. Oxidative thermostabilization of the thermoplastic lignin fibers was brought about by a heat treatment consisting of a ramp phase to 200°C at 0.25°C/min, and an isothermal phase of 24 h (36 h), while carbonization to 900°C was achieved at 10°C/min. Carbon nanofibers were recovered in 31.6% yield (based on electrospun lignin fiber), were reported to have diameters of 200 nm, and had surface areas of up to 1200 m^2/g (BET, N_2). Further to this, the use of a tri-axial spinneret, which added a center hole through which glycerin could be pumped, led to the preparation of lignin nanotubes, which could be oxidatively thermostabilized at a rate of 0.05°C/min to 200°C, and carbonized at a rate of 10°C/min to 900°C, to give carbon tubes of ~400 nm diameter. Using similar electrospinning techniques and fiber conversion profiles, the same authors followed up[142] with a more in-depth article where they described the formation of both lignin-based and platinum-containing carbon nanofibers while measuring the loss of small molecules during thermal conversion treatments to provide some mechanistic insights. Elemental composition, functional groups, and adsorption/desorption isotherms were characterized as a function of conversion ordinate and platinum contents.

Dallmeyer et al.[143] reported the electrospinning of seven differing technical lignins (including organosolv, kraft, pyrolytic lignins) by the less complicated, and commercially more attractive, single orifice method and reported that none could be electrospun without substantial bead formation unless a small amount of poly(ethylene oxide) was added. The addition of just 1% (w/w) PEO enabled the continuous electrospinning of micron-sized fibers, and further adjustments of lignin concentration enabled the production of submicron diameter fibers from each lignin. However, the conversion properties of the lignin fibers have not yet been reported. Similarly, Seo et al. reported the electrospinning of PAN/lignin (alkali type) composite submicron fibers.[144] Solutions comprising between 100 : 0 and 80 : 20 w/w PAN/lignin were electrospun under identical conditions to give fibrous mats of varying morphology. In this case oxidative thermostabilization was brought about by electron beam irradiation rather than by thermal ramping, and carbonization was effected by thermal treatment to 1000°C at a rate of 10°C/min, to give fairly uniform fibers of 300nm average diameter. The authors monitored the tensile strength of the spun fiber mats during stabilization as a function of irradiation dose to determine appropriate irradiation levels. The best performing carbon fiber mats were produced using a 50 : 50 PAN/lignin solution, 15kV, and with a target distance of 100mm to manufacture the fiber mat; and a radiation dose of 2000 kGy to render the fibers infusible prior to carbonization. The latter process could have potential significance if applied to the conversion of melt-spun low-T_g lignin fiber to carbon fiber.

Hosseinaei and Baker,[145,146] based on prior lignin purification and glass transition manipulation studies,[147] described a concept by which a commercial lignin can be purified and prepared by solvent extraction to give a high T_g lignin (185°C) that can be electrospun, rapidly oxidatively thermostabilized and carbonized. The refined softwood kraft lignin could be electrospun using concentrations of between 35% and 50% w/w in 75/25 DMF/methanol (v/v) to give fibers with varied morphology; the finest and most uniform were those spun from a 41.7% w/w solution which ultimately gave carbon nanofibers with an average of 300 nm diameter; it was noted that fiber diameter was very sensitive to solution concentration compared with other polymers used for electrospinning (Figure 8). The high T_g of the lignin allowed conversion to carbon nanofibers to proceed very quickly since the oxidative thermostabilization step could be accomplished at rates in excess of 20°C/min without fiber fusion, although for many applications, such as energy storage devices, fusion would be desirable.

TECHNICAL COMMENTS

Lignins are complex polymers[148,149] containing three main monomer units, (syringyl (S), guaiacyl (G) and p-hydroxyphenyl (H)), that are recovered as waste products during the manufacture of carbohydrates for paper, sugars, and for biofuels production. Consequently, lignins are not considered a single polymer, but are a wide ranging class of polymeric materials, the properties of which depend on their S, G, & H monomer proportions (i.e., alkoxy content),[150] molecular weights,[151,152] shape,[153] degree of branching, inclusion of infusible/insoluble components, other functionalities, and purity.[154] The nature of the lignin contained within biomass, and the method used to separate it, largely define the recovered lignin properties and the course of action required to both purify and recover the lignin components most suitable for carbon fiber manufacture.

Structure and Thermal Properties

It is clear that lignins required to manufacture carbon fiber of greater strengths via melt extrusion should be prepared to not only have high purity, but also have T_ss well below the anaerobic decomposition/crosslinking temperature of the lignin, so that their rheology is such that fine fibers can be obtained. Their T_gs should be sufficiently high to allow the lignin fibers to undergo oxidative thermostabilization at a commercially acceptable rate. Furthermore, the lignin should have a narrow molecular weight distribution (indicated by a small difference between T_g and T_s) to ensure uniform increases in molecular weight throughout the material during oxidative thermostabilization, and to provide for a more uniform structure during carbonization.

With respect to the selection of lignins and therefore to enable the choice of fiber spinning method, the author has noted that the T_g of a lignin is affected more by S, G, and H contents than by molecular weight. Given the difficulties associated with lignin molecular weight measurements, it may be suffice to conclude that lignins containing more S (hardwoods) will have a lower T_g than those with more G (softwoods), and then lower than those with more G and H (grasses). If three lignins, hardwood (a), softwood (b), grass (c) were to have the same molecular weight and distribution, the T_g would have the order $a < b < c$. Similarly, if they had the same T_g, the molecular weight would be $a > b > c$. The rationale being due to the additional free volume, and therefore plasticization, been provided by the additional methoxy groups. The observation is, of course, general as there are several other contributing factors to consider. Furthermore, the author has spun lignin fiber from both hardwood kraft lignin and softwood kraft lignin with similar T_g and T_s and found the hardwood lignin was able to be oxidatively thermostabilized far more rapidly than the softwood. This suggests perhaps that the softwood lignin had a lower molecular weight, even when accounting for differences in oxygen contents which would change relative oxidation rates.

One particular difficulty in arriving at scientific conclusions with respect to polymeric lignin products almost certainly resides in molecular weight measurements. The differing chemical compositions, chemical structures, shapes, degree of branching, relative solubilities, and any associative properties differing lignins may possess, must render comparison of differing lignins almost impossible, at least by SEC, since these will all contribute to the measurement. Of course, SEC is the preferred route of measurement as it also offers molecular weight distribution which is critical for lignin to carbon fiber conversion, and which, for the author, is implied by the difference in T_g and T_s, so that a higher difference implies increased polydispersity, as does the difference between the onset and offset of T_g. To further illustrate difficulties in the molecular weight determination of lignins, several studies have been reported.[155–157]

Glass Transition Measurement

There are also potential difficulties to be found in T_g measurements as they are generally measured using Differential Thermal Analysis (DTA, single heavy furnace design) and at low speeds (1–10°C/min) so that measurement quality is improved. Several studies, including round-robin, of T_g have been done.[158–162] However, once lignins with T_g offsets that exceed ~185°C are measured, crosslinking/reactions within the lignin occur and therefore measurement becomes inaccurate or impossible at DTA rates. Since this author has been examining high T_g lignins (up to 240°C offset) for fiber spinning, experiments have been performed to evaluate the utility of increased rates of measurement of up to 500°C/min (by DSC, dual low-mass furnace). It was found that good measurements could be made using rates of up to 200°C/min for lignins with little impact due to time-transition delay. Furthermore, the thermal history of lignins often needs to be erased so that a more accurate measurement of T_g can be made for extrusion purposes whereby the lignin will be homogenized (pelletized) prior to thermal extrusion. Erasure of lignin thermal history is done by heating it through T_s and then by cooling rapidly; the T_g is measured during the second measurement. The ability to heat and cool rapidly is therefore useful to prevent chemical changes in the lignin and therefore the use of low mass dual-cell DSC instrumentation is of additional value, although other preparative methods can be used to circumvent the problem of quenching.

In this respect the author has found an appropriate method was to first measure the T_g at a rate of 100°C/min to obtain an initial rough measurement; a second dried sample would then be used for the actual T_g measurement. The second sample would then be run at 500°C/min to 120°C, held isothermally to remove any potential moisture, ramped at 500°C/min to around 20–40°C above the T_g offset measured for the first sample, and then cooled rapidly. This allows the sample to be quenched while preventing lignin volatilization (for low T_g, or high polydispersity lignins) or substantial crosslinking/degradation to occur (for high T_g lignins). The T_g could then be measured at a rate of 100°C/min. Comparison of the T_g measurements of lower T_g lignins recorded at 10°C/min and 100°C/min differed by less than 1°C which indicated a small time-transition delay, while higher T_g lignins gave improved measurements (i.e., lower temperature of T_g, greater magnitude, and more narrow in range) at the increased rate.

Extrusion and Oxidative Thermostabilization

Many studies, by necessity, have used single filament devices to melt-spin lignin fiber, which is then oxidatively thermostabilized and carbonized. A potential problem therefore arises in transition to larger scale extrusion operations which will operate at high pressure, with high shear (at the die) and with much

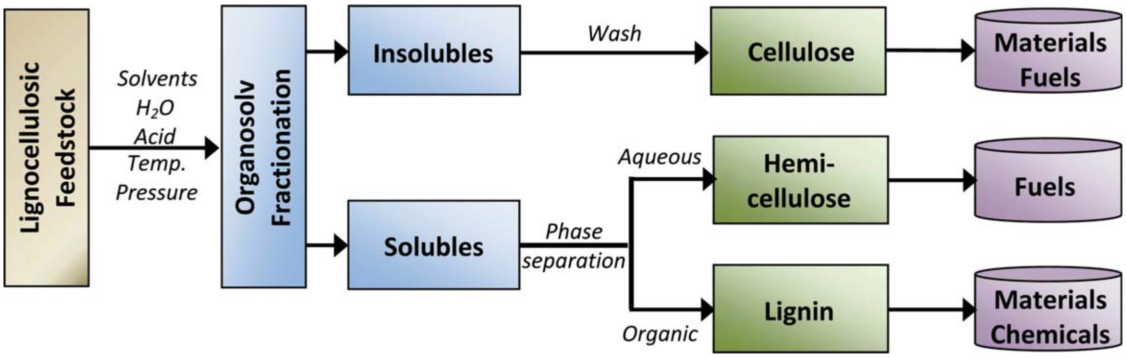

Figure 9. The organosolv fractionation process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

longer residence times at the melt temperatures used; some material might even remain in the extruder for longer times due to admixing. Therefore a process that appears to perform well at the bench-scale may not scale well when using pilot multifilament fiber extrusion equipment. The reason for this is undoubtedly the reactive chemistry of lignin which will cause some level of polymerization during thermal extrusion and this becomes more critical as the T_g, T_s, and therefore melt extrusion temperature is increased. However, because a higher T_g is needed to efficiently oxidatively thermostabilize lignin fibers prior to carbonization, low residence times are preferable. In this respect, other larger-scale spinning technologies ought to be considered, such as those that have low residence times (melt-blowing; centrifugal spinning; short barrel extrusion) or low heat (electrospinning; phase inversion extrusion). If traditional melt-spinning is preferable due to cost and the ability to get continuous filaments for composite manufacture then transient melt-rheological measurements are recommended to assess longer-term (1–2 h) lignin thermal stability at the melt-spinning temperature prior to extrusion.

Further to this, differences in permissible oxidative thermostabilization rates for single filament experiments and for fiber tow experiments have been observed in comparisons that have used identical lignins, particularly when fiber integrity used as a measure of the completion of thermoplastic to thermoset conversion. In this respect, single filaments appear to undergo oxidative thermostabilization at least one order of magnitude more rapidly than fiber tows, and this can be explained by the effect of inter-fiber adhesion. In the former case a single fiber (or a well-dispersed fiber sample) will maintain its shape due to high viscosity in a near molten (or tacky) state at much higher rates of thermal treatment, because there are few external stresses and limited opportunities for adhesion. In contrast, fiber tows that are typically manufactured in bundles of 2–80 K continuous fibers, and sometimes under controlled tension, have a much greater opportunity for adhesion if they are allowed to be slightly tacky since each fiber will be in contact with others almost continuously along its length. Therefore, to investigate the potential scaling of a particular lignin from single filament to multi-filament spinning trials, the complete thermoset conversion of single filament lignin fibers should be checked so that oxidative thermostabilization profiles are similarly applied.

FUTURE DIRECTIONS

Lignin required to manufacture carbon fiber of greater strengths should not only be of high purity, but it should also have a narrow molecular weight distribution (small difference between T_g and T_s). There are many difficulties in providing lignins suitable for carbon fiber manufacture, in fact, no demonstration has yet been made of suitable lignins being processed into carbon fiber that satisfy both strength requirements and cost objectives. This is due to the unavailability of lignins with suitable properties so that they are: (A) able to be melt spun into fiber; (B) converted rapidly to carbon fiber; and (C) at low cost. Unfortunately, (A) requires a low T_g lignin to be melt spun, (B) requires a high T_g lignin to assure low cost, and (C) requires minimal processing cost of the lignin prior to fiber spinning; for a melt spinning process, (D) may therefore be high.

The potential to realize cost reductions could therefore be achieved by way of alternative fiber spinning methods that are not bound by the stringent technical requirements needed for the traditional melt-spinning of fibers. However the provision of improved or refined lignins[146,147,150] may yet provide the necessary lignin performance qualities required for traditional melt spinning, or indeed the use of any fiber forming method to give higher strength carbon fiber. In consideration of the methods used to manufacture lignin (organosolv, kraft, green liquor, various pretreatments…), lignin products will all require purification and refining to be suitable for carbon fiber manufacture. This has been found to be true for even an advanced organosolv process (Figure 9) which provides high purity, well-defined lignins directly and with much more appropriate T_g and T_s properties than competing organosolv technologies.[163,164] In the context of lignocellulosic biorefining towards advanced fuels[21] the application of organosolv processes has been shown to be cost competitive with pretreatment and other fractionation technologies[25,36,48,165,166] and with the added provision of relatively pure lignins.[167] However, in order to direct particular pretreatment, fractionation, or lignin refining techniques towards obtaining specific lignins for carbon fiber manufacture, a much improved understanding of lignin as a polymer and its conversion to materials is needed, and in that respect there is a fundamental lack of knowledge.

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