Current Overview of Carbon Fiber: Toward Green Sustainable Raw Materials

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Lignin, as a potential precursor of carbon fiber, has the characteristics of abundant reserves, renewable and high carbon content, and its application in the preparation of carbon fibers has substantial cost advantages if some important processing and quality hurdles can be overcome. This paper reviews the preparation process of lignin-based carbon fibers, and moreover, describes the characteristics of carbon fiber prepared by different precursors compared with the presently used precursors. Three preparation methods for lignin-based carbon fibers are introduced: melt spinning, solution spinning, and electrospinning. The applicability, advantages, and disadvantages of the three preparation methods are analyzed from the aspects of process conditions and performance characteristics. Possible directions for future research are considered, with the goal of providing a reference for further study of lignin-based carbon fibers.

Keywords: Lignin; Carbon fiber; Preparation method; Spinning

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INTRODUCTION

Lignin is an abundant natural resource that has an annual production of about 600 billion tons, second only to cellulose (Qian *et al.* 2018). Lignin, cellulose, and hemicellulose constitute the three major components of a plant cell wall (Fechter and Heinze 2019; Tian *et al.* 2019). Currently, cellulose, and hemicellulose are widely used in industry such as papermaking, sugar, and biofuels (Horhammer *et al.* 2011; Mikkonen *et al.* 2019; Singh 2019) (Fig. 1). As a by-product of wood hydrolysate and the paper industry, lignin is present in solution as black liquor (accounting for more than 30% of black liquor solids). Most black liquor is sent to a recovery boiler, where the lignin is incinerated and converted to steam energy, with the recovery of pulping chemicals. The incineration of the lignin to generate steam is a low-value application. It follows that the potential value of lignin as a source for other products is not being fully realized (Lauwaert *et al.* 2019). It is reported that more than 50 megatons of industrial lignin are produced worldwide per year, but only 2% of the lignin is commercialized for value-added purposes (Qian *et al.* 2018). Most lignin is simply used as cheap fuel for combustion, which causes waste of resources, and the high value utilization of macromolecules is still not realized (Liu *et al.* 2017). Therefore, development of relevant technologies for high-value utilization of lignin is of fundamental and practical interest (Qian *et al.* 2014; Zhang *et al.* 2017).

Carbon fibers are excellent materials with many potential applications and have received growing interest due to their fascinating features such as unique thermal properties, high tensile strength, and so on (Gao *et al.* 2015). Currently, more than 90% of commercially marketed carbon fibers in the world are made from polyacrylonitrile (PAN), a non-renewable petroleum-based material (Zhang *et al.* 2014; Zhang *et al.* 2019). Moreover, the price of PAN precursors accounts for 50% of the manufactured cost of carbon fibers (Baker and Rials 2013), making carbon fiber a luxury product. Therefore, finding a renewable environment-friendly precursor (such as lignin) of carbon fiber used in low-value applications has been of great interest in recent years.

Lignin, as a bio-derived alternative, has received growing interest in the production of carbon fiber due to high carbon content of 50% to 71% as well as its availability in large quantities at low cost (Li *et al.* 2017). Although it is currently challenging to replace PAN-based carbon fibers in demanding applications, lignin-based carbon fibers can be considered for general applications. For instance, the properties of lignin-based carbon fibers may be suitable for applications requiring medium mechanical properties, low density, high temperature resistance, low thermal expansion, and thermal conductivity. For such applications, the use of lignin-based carbon fibers may be favored because of their low cost and green reproducibility.

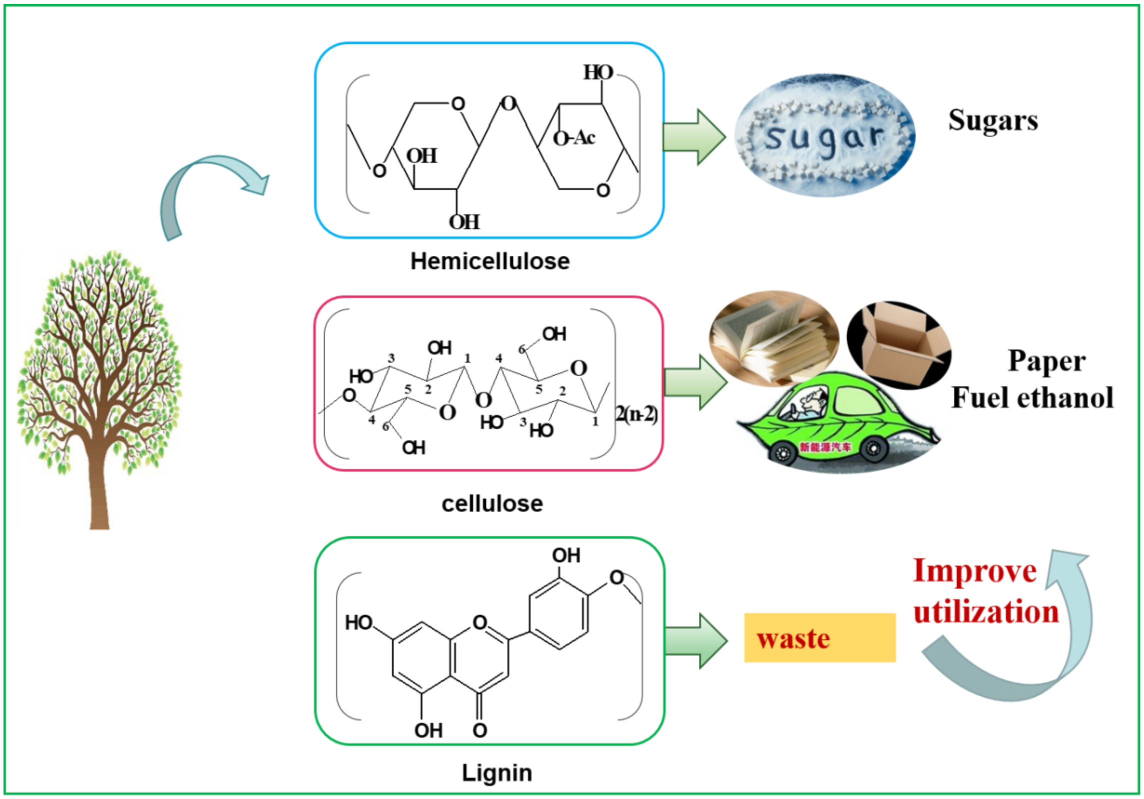

Fig. 1. Applications of three components of plant cell wall

This paper reviews the preparation process of lignin-based carbon fibers and describes the difference between lignin and other precursor raw materials (such as PAN, pitch, and viscose fiber). Three spinning methods for lignin-based carbon fibers: melt spinning, solution spinning, and electrospinning, are highlighted. Moreover, the applicability, advantages, and disadvantages of the three preparation methods are discussed. This paper aims to promote the development of lignin-based carbon fibers.

LIGNIN

Lignin was first discovered by French agronomist P. Payen in 1838. Later, F. Schulze, a German, separated the substance and called it "lignin", which was derived from the Latin "lignum," meaning wood (Souto *et al.* 2018).

Lignin exists in cell wall as a filler and binder, which plays an important role in plant growth. It can strengthen the cell wall by bonding the adjacent cells together, giving the cells and the plant stem great mechanical strength (Lebo, Jr. *et al.* 2000). The content of lignin in lignified plants varies by biomass species. In softwood, lignin content is 25% to 35%, whereas the content is 20% to 25% in hardwood. Gramineae plants have lower lignin content, generally 15% to 25%.

Physical Properties

Unseparated lignin in plant cells is white or nearly colorless, with a molecular weight of several hundred thousand g/mole and insoluble in any solvent. However, the separated lignin has a much lower molecular weight due to degradation, generally ranging from a few hundred to tens of thousands of g/mole. It can be divided into soluble lignin and insoluble lignin.

Lignin is a complex polymer produced by free radical coupling reactions in plant cell walls. Their monomer components and the polymer itself are optically active, that is, they are chiral. Lignin has long been considered to have no optical activity. This is because it is derived from chiral monomers, which seem to be the result of chemical reactions not controlled by enzymes. But there does not seem to be any hard evidence to support that claim. In response to the problem that lignin's optical activity cannot be detected, Ralph *et al.* (1999) proposed that when lignin is being synthesized by plants, there is no direct (regional or three-dimensional) control over the exact process of free-radical coupling events.

Lignin is an amorphous thermoplastic polymer with no stable melting point, exhibiting a high glass transition temperature (Vural *et al.* 2018). Below the glass transition temperature, lignin behaves as a glassy solid. When the temperature is higher than the glass transition point, the molecular chain segments are able to move, resulting in lignin softening and undergoing viscous flow in response to stress. The ability of lignin to cool without forming a crystalline phase, *i.e.* vitrification, is not common in natural macromolecular resources. Lignin exhibits both thermoplastic and vitrification properties. In this respect, lignin resembles certain biobased plastics that are synthesized by microbial fermentation. The thermoplastic and vitrification properties of lignin are not shared by other natural macromolecules such as starch and cellulose. The vitrification temperature varies with species, separation method, molecular weight, and water content (Perez *et al.* 2011; Duval *et al.* 2013; Zhou *et al.* 2016). The softening temperature of absolutely dried lignin is between 127 to 129 ℃. Moreover, the softening points obviously decrease with the increase of moisture content of lignin samples. For example, the softening temperature of periodate lignin decreased from 193 ℃ to 93 ℃ when the moisture content in the sample was increased from 0 to 27.1% (Jafarpour *et al.* 2009).

The mobility of water molecules affects the softening temperature of lignin, indicating that water is a plasticizer for lignin.

Chemical Structure and Properties

Lignin protects plant cells from biological and chemical damage (Terashima 2013). Covalent bonding between lignin and hemicellulose is known to exist. Whether lignin is chemically bonded to cellulose has not been determined. But the combination of lignin and carbohydrate is customarily referred to as the lignin-carbohydrate complex (LCC) (Fig. 2). Because of its complex combination with cellulose and hemicellulose, it is difficult to separate and identify it completely. The effective separation of lignin from cellulose and hemicellulose plays an important role in improving the utilization rate (Harfouche *et al.* 2010; Yu *et al.* 2016). Research on this issue has been conducted for centuries, and many separation methods have been discussed as far back as 105 A.D., when papermaking technology was invented in China. At that point the term "lignin" did not exist. In fact, the fundamental reason for the difficulty in separation lies in the complexity of the sequence of chemical components, the way it is connected, and the three-dimensional structure of lignin (Vicuna 2000; Liitia *et al.* 2003). These questions have aroused extensive interest among scientists. A variety of modern advanced characterization methods have been used to investigate the structure of lignin, and important progress has been made (Lindgren *et al.* 1974).

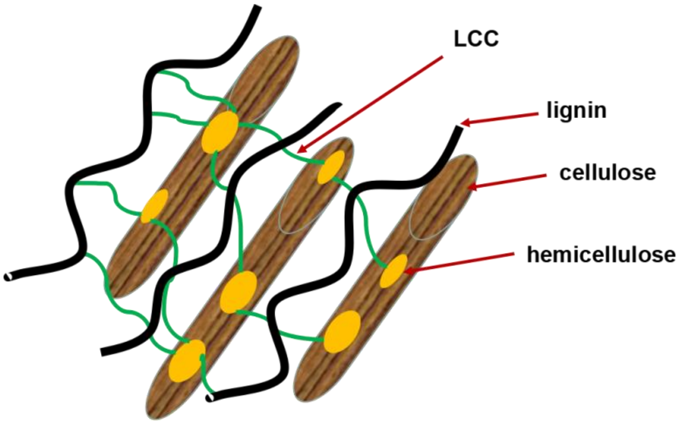

Fig. 2. The connection between lignin, cellulose, and hemicellulose

Phenol-propane units constitute the basic skeleton structure of lignin (Bolker and Brenner 1970), and the units are connected together by ether bonds and carbon-carbon bonds. Recent studies also have found ester bonds between lignin structural units (Li *et al.* 2018). The chemical structure of lignin varies with plant species, so the term "lignin" does not represent a single substance, but a group of substances with common properties in plants.

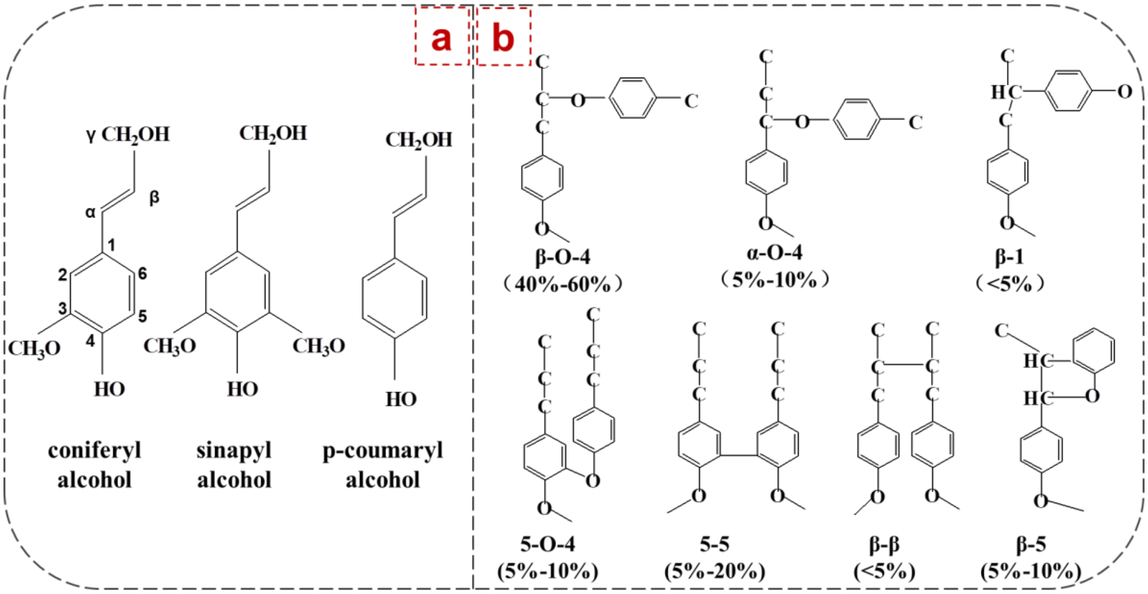

Fig. 3. (a) The basic structural units of lignin; (b) Main linkages between lignin structural units in woody plants

Table 1. Effect of Phenyl Propane Structure on Thermal Behavior

	Softwood Lignin	Hardwood Lignin	Herbaceous Lignin
H : G : S	4 : 95 : 1	1 : 25 : 25	1 : 14: 5
Thermostability	Thermal instability, tends to crosslink due to imbalanced structure in G units	Chemically stable, less likely to crosslink, tends to fuse during stabilization	Seldom used in carbon fiber production

Notes: H: hydroxyphenyl, G: guaiacyl, S: syringyl, the thermostability refer to high-temperature interactions

Studies have shown that lignin structure plays an important role in carbon fiber processing. Lignin is an amorphous aromatic polymer whose physicochemical and thermal properties depend on the biomass source and the lignin separation method. The phenol propane structure of lignin mainly consists of three monolignols, guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) units. They are results of three aromatic alcohol monolignols: coniferyl alcohol, syringyl alcohol, and coumaryl alcohol (Fig. 3a and Table 1) (Nawawi *et al.* 2016; Shioya *et al.* 2017). G units are mainly in softwood lignin, while S units are mainly in hardwood lignin. The major units in gramineae are G and S units (Matsushita *et al.* 2007; Hirayama *et al.* 2019).

The phenol propane structural units of lignin are connected by ether bonds (mainly containing β-O-4, α-O-4, and 5-O-4 linkages) and carbon-carbon bonds (consisting of 5-5, β-1, β-β, and β-5 linkages), with the former generally accounting for 60% to 70% and the latter for 30% to 40% (Fig. 3b) (Beste and Buchanan 2012; Yang *et al.* 2016). Carbon-carbon bonds are highly stable when lignin degrades under the action of chemicals (Murakami and Ishida 2015). In addition, a small amount of ester bonds also exist, especially in grasses.

There are many active functional groups in the molecular structure of lignin, such as benzene ring, phenolic hydroxyl, alcohol hydroxyl, carbonyl, conjugate double bond, *etc*., which enable the lignin to undergo oxidation, reduction, hydrolysis, acid hydrolysis, sulfonation, alkylation, and other chemical reactions (Laurichesse and Averous 2014).

Extracting Lignin from Plants

There are two main methods to separate lignin. The first is to dissolve and remove other components in plants except lignin; such approaches generally separate and extract lignin as an insoluble component. The product prepared by this separation method is mainly hydrolyzed lignin (mainly kraft lignin (KL)). The second type of method dissolves lignin as a soluble component while other components (such as cellulose) are insoluble for the purpose of separation (Yuan *et al.* 2013). Such methods result in the production of alkali lignin (AL), lignin sulfonate (LS), organosolv lignin (OL), and steam explosion lignin (SEL), *etc*. These products are all obtained by the second separation method. Table 2 describes the characteristics of several industrial lignins.

Table 2. Types and Features of Lignin

Type	Features	Application
AL	More hydroxyl groups, strong hydrogen bonding, good or poor water solubility, depending on MW	Synthesized polymers, such as phenolic resin adhesive
OL	High purity, high solvent cost, and complex recovery	Synthesized polymer, such as lignin-based flocculant
KL	Compared with native lignin, phenolic hydroxyl content is higher, methoxyl and alcoholic hydroxyl content are lower, and purity is higher.	Dispersant, such as soil conditioner
LS	A surfactant amphiphilic polymer molecule whose molecular structure is severely damaged during pulping	Polymeric dispersant, such as cement water-reducing agent
SEL	High requirements on equipment, high energy consumption	No commercialization at present
* AL: alkali lignin; OL: organosolv lignin; KL: kraft lignin; LS: lignin sulfonate; SEL: steam explosion lignin		

CARBON FIBERS

Development of Carbon Fiber

Carbon fiber is a multifunctional linear carbon material that can have excellent mechanical properties, and its carbon content can reach 90% to 99% (Liu and Kumar 2012; Lee *et al.* 2014). It has good biocompatibility (Menini *et al.* 2017) and strong physiological adaptability (Usmani *et al.* 2016). Carbon fiber composite is a new implant material with good biocompatibility, stability, and reliability. Jenkins and coworkers (Jenkins *et al.* 1997; Jenkins and McKibbin 1980) demonstrated through animal experiments that carbon fiber implanted into living tissues has good biocompatibility and can stimulate the regeneration ability of surrounding tissues. The resulting collagen fibers function normally. Their preliminary clinical application has also achieved a good result.

The origins of carbon fiber date back to the 1860s. A British man named J. Swan used carbon filament to make light bulbs before the American T. A. Edison. The light bulb designed by J. Swan was not practical because it failed to solve the vacuum problem of the light bulb. However, he was the first to develop carbon silk and inspired the invention of synthetic fiber. Then, T. A. Edson successfully applied carbon filament to incandescent lamps in 1879 and made it practical (Souto *et al.* 2018).

Carbon Fiber Raw Materials

With the growth of carbon fiber demand, many precursors have been considered for the production of carbon fibers, such as polyacrylonitrile (Kim *et al.* 2014), asphalt (Lim *et al.* 2019), viscose fibers (Wang *et al.* 2016a), lignin (Meng *et al.* 2019), polyvinyl alcohol (Mercader *et al.* 2012), polyvinyl chloride (Liu *et al.* 2018a), and so on. Of these, only three main kinds of carbon fiber raw materials have been manufactured at commercial scale: PAN-carbon fiber (Liu *et al.* 2015), viscose-based carbon fiber (Gorina and Cheblakova 2016), and asphalt-based carbon fiber (Li *et al.* 2008).

The PAN-based carbon fibers with poor mechanical properties were first prepared in 1959 in Osaka, Japan, which promoted the development of the carbon fiber industry. Although the TORAY company of Japan has experienced many difficulties in producing high strength and high modulus carbon fiber, the company has achieved the leading levels of performance in this field in the world (Macia-Agullo *et al.* 2007; Jiang *et al.* 2009). The PAN-based carbon fibers are mainly produced in two steps. The first step is to produce polyacrylonitrile precursor, which mainly involves the polymerization of monomers and the preparation of spinning liquid, which is then spun further. This initial step is crucial in the production of carbon fiber because the quality of the precursor determines the performance of the carbon fiber. The second step is pre-oxidation and carbonization of the precursor. Figure 4 shows the preparation process (Yusof and Ismail 2012; Zhang *et al.* 2014).

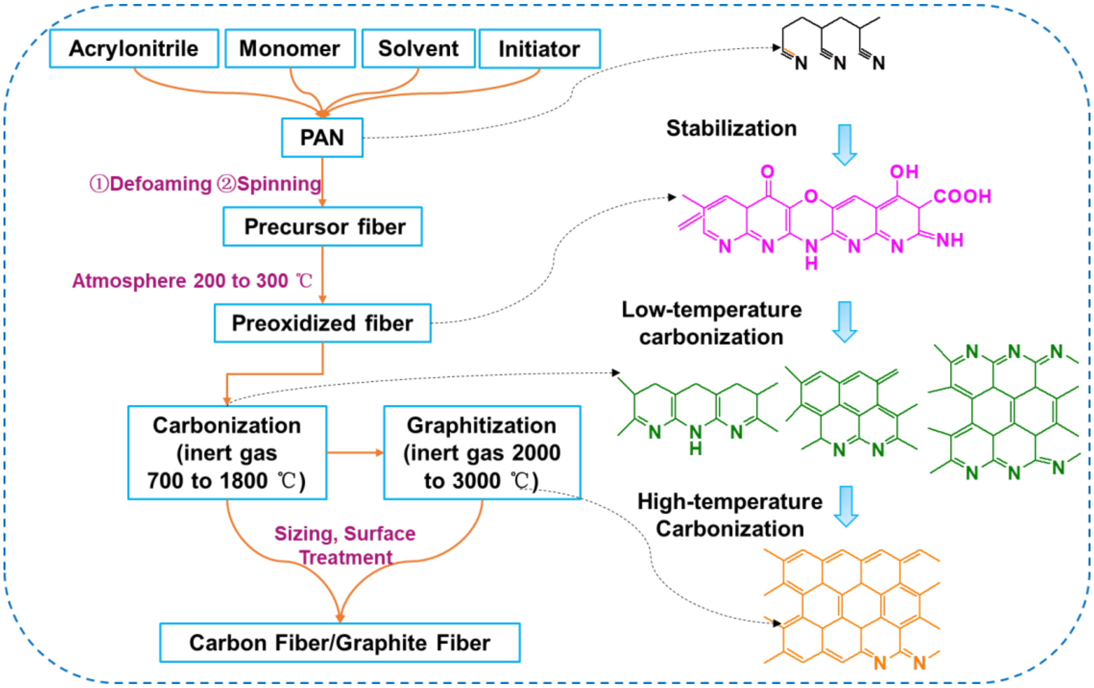

Fig. 4. PAN-based carbon fiber preparation processes

Pitch is second only to PAN as the raw material used to make carbon fiber (Matsumoto *et al.* 1993). There are two kinds of pitch-based carbon fibers. The first kind is general-purpose carbon fibers made from isotropic asphalt. Another type is high-performance carbon fibers made from mesophase pitch (Alway-Cooper *et al.* 2013; Yao *et al.* 2014). Pitch-based carbon fibers have higher thermal conductivity (Lee and Rhee 2019), better thermal expansion (Asano 2017), and more impact resistance (Meehan *et al.* 2010) than PAN-based carbon fibers.

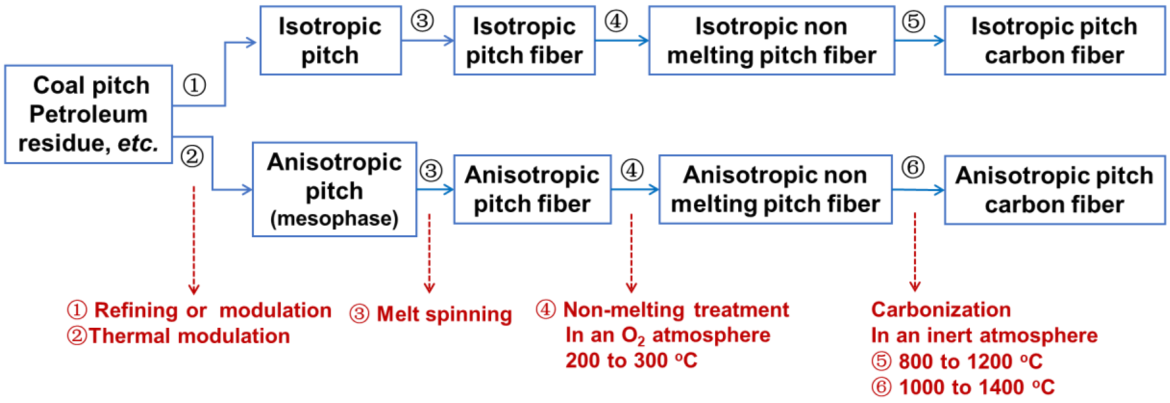

Fig. 5. Pitch-based carbon fiber preparation processes

Mesophase pitch is obtained by pretreatment of pitch or petroleum residue. Then the mesophase pitch is subjected to melt spinning, heat stabilized, and further carbonized to obtain asphaltene-based carbon fiber. It is worth noting that the obtained pitch-based carbon fiber varies with the pretreatment. The isotropic pitch-based carbon fiber is obtained through refining or modulation, while the anisotropic pitch-based carbon fiber is obtained through thermal modulation. The specific preparation conditions are shown in Fig. 5.

Viscose-based carbon fibers were invented in the 1950s. Until today, wood pulp and cotton pulp, mainly composed of cellulose, have been used in the production of viscose-based carbon fibers (Culica *et al.* 2019). The production process needs two more steps than that of PAN-based carbon fibers: washing and impregnating the catalyst, which undoubtedly increases the production cost (Paunonen *et al.* 2019). However, it has no impact on the irreplaceable position of viscose-based carbon fibers in the field of carbon fibers. In addition to thermal insulation and ablative resistance, viscose-based carbon fibers are also used as environmental and medical materials due to their well-developed pore structure and easy regulation (Su and Wang 2007; Gorina and Cheblakova 2016).

Table 3. Comparisons of Four Precursor Fibers

Type	Cost	Preparation Technology	Carbonization Yield (Raw Materials)	Performance	Market Share
PAN	Highest	Simple	40%	High tensile strength (9.03 GPa)	> 90%
Pitch	Low	Complex	85 to 90%	Highest modulus (930 GPa), high thermal conductivity	7%
Viscose	Higher	Complex (need catalysis)	30%	Blation resistance, heat insulation	< 1%
Lignin	Low, renewable	Simple	40 to 50%	High specific capacitance	-

The PAN and pitch precursors are derived from petroleum-based resources (Rhee *et al.* 2017), while carbon fibers from viscose have a high cost and a low yield (Su and Wang 2007; Paunonen *et al.* 2019). Table 3 summarizes the characteristics of four different classes of precursor fibers. With the depletion of fossil fuel resources and the aggravation of environmental pollution, it is urgent to find renewable environment-friendly resources. Lignin, as a kind of abundant renewable resource second only to cellulose, has attracted increased attention in this regard.

Applications of Carbon Fiber

Carbon fiber, when well prepared, has many excellent properties that no other material can surpass, such as high strength, high modulus, low density, high temperature resistance, corrosion resistance, and other excellent functions (Frank *et al.* 2012). In addition, carbon fiber materials have a small thermal expansion coefficient, a good dimensional stability, and a strong adaptability to sudden changes in environmental conditions (Cho *et al.* 2011; Poveda *et al.* 2012). Carbon fiber has good shock-absorbing performance, which allows it to achieve seismic repair and improve fastness in construction applications. Carbon fiber is anisotropic, with large design freedom, good deep processing performance, and strong adaptability to complex structures of equipment (Moskalyuk *et al.* 2015; Tane *et al.* 2019). Carbon fiber is a structural conductive material with inherent electrical and thermal conductivity. As a consequence of these characteristics, during the processing, there will be no excessive heat storage and overheating.

Currently, carbon fiber has formed an important new material system, and has been applied in many fields because of its excellent properties. In terms of overall properties, carbon fiber ranks first among the top five reinforcement materials (carbon fiber, boron fiber, silicon carbide fiber, alumina fiber, and kevlar fiber). It is usually used as a reinforcement material to prepare composite materials together with other materials for improving the properties of composite materials.

With the development of science and technology, the application field of carbon fiber composite materials is also expanding. At present, carbon fiber has become an indispensable new material in aerospace (Yang *et al.* 2014) and military industries (Yang *et al.* 2012). At the same time, it is being used for new applications in the civil industry field (Fitzer 1989), such as transportation, information, and communication, building materials, wind power generation, and so on. With the extensive application of carbon fiber, the social and economic benefits will be more significant.

PREPARATION OF LIGNIN-BASED CARBON FIBER

Research on the preparation of lignin-based carbon fibers was started in the last century. It was first prepared by Otani in Japan in 1965 (Otani 1968). He successfully prepared lignin-based carbon fibers by dry and wet spinning using lignin sulfonate in pulp. However, the mechanical properties were unsatisfactory. The United States and other western countries have made preliminary explorations and found that the internal molecules of lignin-based carbon fiber have no directionality, which is responsible for the performance of lignin-based fibers to be lower than that of pitch-based carbon fibers (Dave *et al.* 1993). Later, the lignin-based fibers were modified by a melt spinning technology, which provides a better method to prepare high-performance lignin-based carbon fibers (Kim *et al.* 2015).

The preparation of lignin-based carbon fibers mainly includes spinning, pre-oxidation, and carbonization. However, a key problem for the preparation is how to process lignin into fibers with a certain linear density and morphology. Furthermore, the mechanical properties of the fibers still needs to be maintained after stabilization and carbonization (Qin *et al.* 2013).

Currently, pretreatment steps, such as organic modification or blending with polymers, are being used to reduce the brittleness of lignin-based fibers and improve their spinnability. Then, the initial fibers are obtained *via* wet spinning, melt spinning, and electrospinning. Finally, the carbon fibers are prepared by post-treatment. The operation process is shown in Fig. 6.

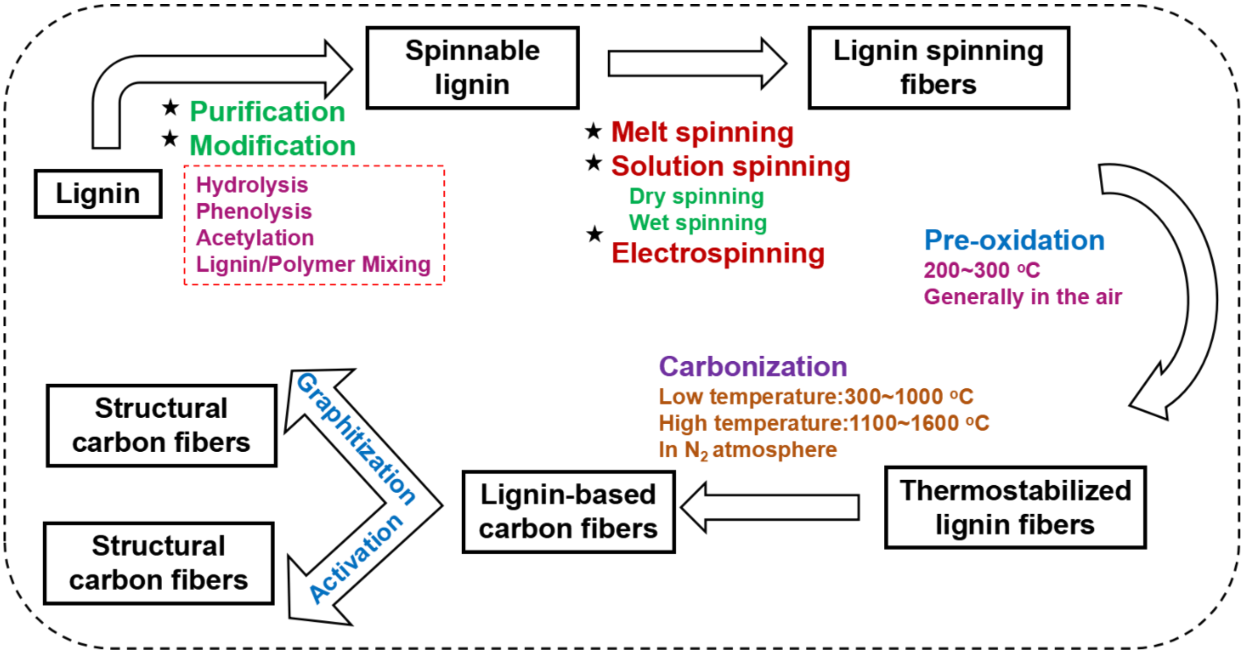

Fig. 6. The process of preparing carbon fiber from lignin

Spinning

Melt spinning

Melt spinning is the most common method of preparing lignin-based carbon fibers. It has the advantages of being a simple process with high material utilization and a small level of environmental pollution (Huang *et al.* 2019). Up to now, only organic lignin has been successfully melt-spun without being treated. However, the time required for stabilization is too long to be realistic (Kadla *et al.* 2002). Generally, hardwood lignin is more easily melt-spun than softwood lignin, while softwood lignin has a faster setting time than hardwood lignin due to the difference in chemical structures. Proper pretreatment, such as organic solvent liquefaction, blending with polymer, and chemical modification, all can contribute to improving the spinnability and efficiency.

For the first time, Kadla *et al.* (2002) used hardwood kraft lignin (HKL) without chemical modification to melt-spin at 200 °C, and they then obtained carbon fiber with a tensile strength of 422 ± 80 MPa and a tensile modulus of 40 ± 11 GPa after simple heat treatment.

Sudo and Shimizu (1992) used SEL to melt-spin at 50 ℃ after hydrocracking in vacuum. However, the viscosity was too low to form a filament after smelting. It was found that the melt spinning property was greatly improved after vacuum concentration at a temperature of 300 to 350 ℃. Then carbon fibers with a diameter of 7.6 μm and a strength of 660 MPa were obtained by pre-oxidation and carbonization. However, the yield of carbon fiber produced by this method was only 15.7% to 17.4%. To further improve the yield of carbon fiber, Sudo *et al.* (1993) treated SEL with phenol to obtain lignin with good fluidity. The spinning fiber was prepared by melt spinning at 95 ℃. Compared to treatment with hydrocracking, the yield of carbon fiber treated with phenolic aldehyde was up to 43.7%. Kadla and Kubo (2003) blended polyethylene oxide (PEO) with HKL for melt spinning, which not only improved the fiber forming performance, but also reduced the spinning temperature (160 to 232 ℃). The final yield of carbon fiber was up to 45% when PEO content was 5%. The content of hydroxyl groups in softwood kraft lignin (SKL) is more than that in HKL, which makes it easier to crosslink and lose melting property during heating. Therefore, SKL is more difficult to obtain spinning fiber under these conditions. Subsequently, Kubo and Kadla (2005) studied the compatibility between SKL and PEO, and the results showed that SKL and PEO have not only strong hydrogen bond interactions, but also relatively weak intermolecular interactions. Based on this theory, they blended PEO with SKL and prepared lignin-based fibers by melting spinning. However, the spinning temperature (220 to 240 ℃) was found to be higher than that of mixing PEO with HKL, and only when the proportion of PEO is higher than 37.5% can continuous spinning be realized. This further indicates that SKL melt spinning is more difficult than HKL.

Kubo *et al.* (1996) also studied the influence of pretreatment on the melt spinning process, including acetylation, saponification, and heat treatment. The results showed that lignin treated with acetylation had the highest spinnability. It was further investigated for the effects of molecular weight and soluble components on the melting properties of softwood lignin (Kubo *et al.* 1998). The results demonstrated that lignin could only be melted when the molecular weight was less than 3200 g·mol^{-1} or when the fusible component accounted for 58.2%.

On the basis of this work, two directions to improve lignin melting properties were proposed by Kubo. One is to reduce the phenolic hydroxyl interaction in lignin molecules through acetylation, thus reducing the hydroxyl dehydration and cross-linking during heating. The other is to increase the proportion of molten lignin by molecular weight fractionation.

However, there are no suitable means to improve the lignin melting property for industrialization. At the same time, only general-grade lignin-based carbon fibers can be prepared by melt spinning, which is not suitable for preparing nano-scale materials and therefore their application scope is limited.

Solution spinning

Solution spinning is a method for preparing lignin-based carbon fibers with higher mechanical properties (Jin and Ogale 2018). It can be divided into wet spinning and dry spinning according to the curing mode. Wet spinning makes it easy to control the diameter of the fibers, and there is little residual solvent in the fibers. Dry spinning, however, is less often used due to the amount of voids and residual solvent in the fibers. Lignin-based carbon fiber with high tensile strength can be prepared by dry spinning. Zhang and Ogale (2014) obtained acetylated lignin, which can dissolve completely in acetone by modifying SKL with acetic anhydride. Then, carbon fibers with tensile strength of 1.04 ± 0.10 GPa were prepared by dry spinning, and this is the highest tensile strength of lignin-based carbon fibers reported up to now. However, the pre-oxidation process took a long time (at a heating rate of 0.01 °C/min), making it an unsuitable material for large-scale production.

Maradur *et al.* (2012) dissolved lignin and acrylonitrile oligomer in dimethyl sulfoxide (DMSO) and then obtained carbon fiber with good tensile properties through wet spinning and subsequent heat treatment. More importantly, the total yield of carbon fiber prepared by this method was up to 56%, which provides a new idea for the preparation of low-cost lignin-based carbon fibers.

Lignin needs to be modified before solution spinning because of its poor solubility in organic solvents. Compared with melt spinning, solution spinning has a relatively high cost and a low efficiency in producing lignin-based carbon fibers. Therefore, there has been relatively little research on this aspect.

Electrospinning

Electrospinning is a special fiber manufacturing technology that has developed rapidly in recent years. When a polymer solution or melt is sprayed and spun in a strong electric field, the droplet at the tip of the needle changes from a sphere to a cone (known as a "Taylor cone") (Wang *et al.* 2016c), then extending from the tip of the cone to form filaments. In this way, polymer filaments with nanoscale diameters can be produced. The schematic diagrams of lignin electrospinning are shown as Fig. 7.

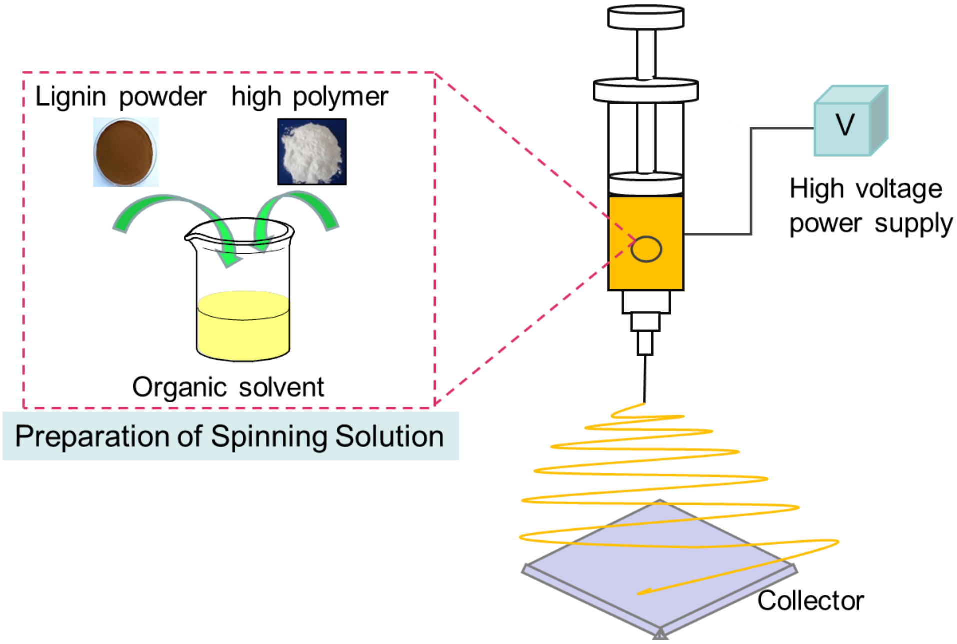

Fig. 7. Schematic diagrams of lignin electrospinning

Lignin is often mixed with polymer for electrostatic spinning, because of its poor conductivity and solubility (there are few solvents that can dissolve lignin). In addition, the pure lignin solution is difficult to form fiber during electrospinning, resulting in electrospray particles formed in this process. This has been demonstrated by relevant research. Dallmeyer *et al.* (2010) dissolved KL in N,N-dimethylformamide (DMF) solution. The spinning liquid could not obtain fibrous material under the action of a high voltage electric field. However, both SKL and HKL could obtain fibers with a smooth surface and micron diameter through electrospinning when PEO was added to the spinning solution. This indicated that the spinnability of lignin could be improved by blending polymer with lignin.

Feng and Aorigele (2009) produced uniform acetic acid lignin/polyvinyl-pyrrolidone (AAL/PVP) blend fibers by electrospinning. However, the solvent volatilizes too fast during spinning, which was not conducive to formation of fibers. Using trifluoroacetic acid as solvent, Svinterikos and Zuburtikudis (2016) prepared a kraft lignin/polyethylene terephthalate (KL/PET) blended carbon fiber mat by electrospinning, which had a nanometer diameter and a carbon content of 94.3%.

The advantage of electrospinning is that carbon fiber can be prepared at the nanoscale level, which is impossible for melt spinning and solution spinning methods. Therefore, electrospinning is often used to produce products with specific performance requirements. At the same time, the method also has shortcomings such as low fiber yield, poor orientation, and low strength (Teo *et al.* 2011; Lu *et al.* 2014). Currently, the preparation of carbon nanofibers based on lignin by electrospinning is mainly in the experimental stage, and it still needs to overcome a difficult problem to realize industrial production.

Pre-oxidation

Pre-oxidation is a subsequent step after obtaining the spinning fiber. Pre-oxidation is one of the most time-consuming and important intermediate processes in carbon fiber production (Dave *et al.* 1993; Newcomb 2016), which not only controls the quality of carbon fiber, but also determines the yield of carbon fiber. The purpose of pre-oxidation is to improve the mechanical properties of the fiber by converting the macromolecular chain of the polymer into a stable structure, so that pre-oxidized fiber will not melt or burn in the subsequent high-temperature carbonization stage and the obtained lignin-based carbon fiber will maintain the fiber morphology as well as thermodynamic stable state (Gupta and Harrison 1997). Lignin spinning fibers are susceptible to bonding and crosslinking at high temperature if carbonized directly. Therefore, it is necessary to carry out pre-oxidation treatment before carbonization (Niu *et al.* 2011; Newcomb 2016).

Pre-oxidation is usually carried out in an oxygen atmosphere at temperatures in the range of 200 to 300 °C. The selection of heating rate directly affects the mechanical properties of carbon fiber (Ji *et al.* 2007; Zhang *et al.* 2018). Incorrect process conditions may lead to insufficient or excessive pre-oxidation, further resulting in structural defects of fibers and low mechanical properties (Liu *et al.* 2018b). Therefore, the optimum pre-oxidation time must be optimized according to the experiment.

The chemical and structural changes caused by heat treatment in the pre-oxidation process are complex. Up to this point, it has not been fully recognized and understood for the following reasons. The first reason is that spinning fiber is composed of two or more monomers. The type and content of the monomers affect thermal stability of the spinning fiber. The second reason is the diversity of physical aggregation structure caused by the processing of spinning fiber, such as diameter, crystal morphology, and orientation. The third reason is that the diffusion and reaction of oxygen are not homogeneous in the process of thermal stabilization.

The pre-oxidation step is where the orientation loss usually occurs. Higher molecular orientation could improve the mechanical properties of the fiber. A critical process parameter for carbon fiber is tension during oxidative-stabilization. Researchers at Clemson University reported studies (Zhang and Ogale 2014) that maintain molecular orientation by applying tension during preoxidation . Using a commercial SKL as raw material, they acetylated the raw fiber to obtain different degrees of substitution. Then the thermal stabilization was carried out under applied tension. The results showed that the fibers had obvious molecular orientation under applied tension. The diameter of the fiber became thinner and the tensile strength increased. During pre-oxidation and carbonation, the tensile strength of fibers treated without tension was only half that of fibers treated with tension. The research group also investigated the effects of the addition of photoinitiators and further UV exposure on the properties of the synthesized PAN and preoxidized fibers (Mrales and Ogale 2013). 1wt % of photogenic agent (4,4'-bis(dilamino)benzophenone) was added to the PAN and 5 minutes of UV irradiation was applied. The results showed that the traditional stabilization time of thermal oxidation can be significantly reduced. This indicates that these two treatments have potential in preparing more molecular-oriented precursors and may shorten the time of thermal oxidation in carbon fiber processing.

Carbonization

The carbonization is an important step in the transformation of the structure and properties of carbon fiber. The purpose is to make the material undergo crosslinking, cracking, condensation, and other chemical reactions by heating under inert gas protection, resulting in the formation of a disordered layer of graphite structure. Finally, carbon fiber with disordered graphite structure is obtained (Wang *et al.* 2016b).

The whole process of carbonization is divided into two stages: low temperature carbonization at 300 to 1000 ℃ and high temperature carbonization at 1100 to 1600 ℃. However, the signature carbonization temperature is 700 ℃ (Hu *et al.* 2017; Salim *et al.* 2018), which is also the boundary temperature between low-temperature and high-temperature carbonization.

Research on the influence of carbonization conditions on the structure and properties of carbon fiber showed that the relative importance of different carbonization conditions was as follows: heating rate > carbonization final temperature > holding time (Ma and Zhao 2011). Within a certain range, the lower the heating rate, the higher the carbonization temperature, and the longer the holding time, the greater the tensile strength and modulus of the obtained carbon fiber (Baker *et al.* 2012). When carbonization temperature exceeds a certain value, the tensile strength of carbon fiber will decrease. The reasons are as follows: On the one hand, with the gradual increase of carbonization temperature, non-carbon heteroatoms (mainly N) become further exited, which enriches elemental carbon and finally forms disordered layer graphite structure. During this process, the tensile strength of carbon fiber increases gradually. When the bulk density of disordered graphite structure is balanced with the preferred orientation of fiber, the tensile strength reaches its maximum value. On the other hand, when the carbonization temperature reaches the optimal temperature, a large amount of N element comes out in the form of N_2, which increases the fiber pores and defects and further leads to the decline of tensile strength.

Table 4 summarizes the preparation of lignin-based carbon fibers by different methods.

Table 4. Summary of Preparation of Lignin-based Carbon Fiber

	Lignin Treatment		Spinning System	Preoxidation/ Carbonization	Result
Melt Spinning	No		HKL	250 °C (12 to 180 °C/h) 1000 °C (180 °C/h)	Carbon fibers with tensile strength (422 MPa), modulus (40 GPa)
	Acetylation		OL	-	Improved spinnability
	Hydrocracking		SEL	210 °C (1-2 °C /min) 1000 °C (5 °C /min)	Low yield
	Phenolics		SEL	210 °C (1 to 2 °C /min) 1000 °C (5 °C /min)	Yield 43.7%, tensile strength 400 MPa
	Mixing with polymers		HKL/ PEO	210 °C	Yield up to 45%
			HKL/ PP	250 °C (18 °C /h) 1000 °C (180 °C /h)	Carbon fiber with void
			KL/PVA	220 °C (0.5 °C /min) 1200 °C (5 °C /min)	Microporous carbon fiber
			HKL/PET	250 °C (12-180 °C /h) 1000 °C (180 °C /h)	Fiber obtained
			SKL/PLA	280°C (0.25 °C /min) 1000 °C (3 °C /min)	High tensile modulus and low tensile strength
Solution Spinning	Dry	Acetylation	SKL	220 °C (0.2 °C /min) 1000 °C (4.5 °C /min)	Sawtooth fibers, highest tensile strength (1.04 GPa)
	Wet		L/PAN	280 °C (1 °C /min) 800 °C (5 °C /min)	Yield up to 56%
Electrospinning	Blending with polymer		L/PAN	250 °C (20 °C /h) 1000 °C (10 °C /h)	Nanofibers obtained
			SKL (or HKL)/PEO	250 °C (5 °C /min) 1000 °C (10 °C /min)	Micron fibers obtained
			AAL/PVP	250 °C (0.5 °C /min) 700 °C (100 °C /h)	Solvent evaporates quickly, poor fibrillation
			KL/PET	260 °C (120 °C /h) 1000 °C (180 °C /h)	Nanofibers obtained

* L: Lignin; PAN: Polyacrylonitrile; HKL: Hardwood kraft lignin; OL: Organosolv lignin; SEL: Steam explosion lignin; PEO: Polyethylene oxide; PP: Polypropylene; PVA: Polyvinyl alcohol; PET: Polyethylene terephthalate; SKL: Softwood kraft lignin; PLA: Polylactic acid; AAL: Acetic acid lignin; PVP: Polyvinylpyrrolidone; KL: Kraft lignin

CURRENT PROBLEMS IN PREPARATION OF CARBON FIBERS FROM LIGNIN

The tensile strength of lignin-based carbon fibers is usually between 350 and 550 MPa (Mainka *et al.* 2015). Micro-nanometer lignin-based carbon fibers can be prepared by electrostatic spinning (Carrott and Carrott 2007), and the smaller the diameter, the greater the mechanical strength. Currently, the mechanical strength of lignin-based carbon fibers is still low due to the material impurities and low molecular weight of lignin, which limits the application of lignin-based carbon fibers.

Among many types of industrial lignin, sulfate lignin has the most single structures and high purity, so it is often used to prepare carbon fiber. There are also reports from research institutions and schools on the preparation of lignin-based carbon fibers from alkali lignin. During pulping and papermaking, the lignin sulfonate substructure is seriously damaged. At the same time, many inorganic salt impurities with complex components remain, which are difficult to remove. Based on this, lignin sulfonate is not suitable for the preparation of lignin-based carbon fibers. Steam blast lignin and organic solvent lignin experience less structural damage and fewer impurities in the process of separation and extraction. However, the requirements of extraction conditions are strict and the cost is high, which makes large-scale production difficult.

TECHNICAL EVALUATION

The lack of a clear molecular orientation of lignin is the main reason why the mechanical properties of lignin-based carbon fibers are lower than those of PAN-based carbon fibers. This deficiency in strength limits the application of lignin-based carbon fibers.

Unfortunately, the paper and pulp industries tend to maximize the extraction of raw lignin without considering the structural protection of lignin macromolecules. The purity and separation methods of lignin determine the quality of recovered lignin to a large extent. These are the factors to be considered in the preparation of carbon fiber from lignin. In addition to the correct heating rate, each material may have an optimum temperature during the heating.

Lignin is a natural, partially oxidized substance that requires strict control of the spinning process. Additionally, the integrity of lignin fibers depends on the crosslinking capability of the fibers during the thermal stabilization of pre-oxidation. Lignin should have a narrow molecular weight distribution (with little difference between glass transition temperature (T_g) and softening temperature (T_s)) to ensure that the molecular weight of lignin increases evenly during thermal stabilization of oxidation. Further, a more uniform carbon fiber structure is provided in the process of the carbonization process.

The T_g of lignin is influenced by the ratios of phenyl propane units (S, G, and H) and molecular weight, of which the influence of the former is more important. Molecular weight measurement is difficult because different lignin may have different properties, such as chemical composition, chemical structure, degree of branching, and relative solubility, *etc*. Based on this, it can be concluded that the T_g of lignin containing more S (hardwood) is lower than that of lignin containing more G (softwood), and then lower than that of lignin containing more G and H (grass).

Research on the pre-oxidation and carbonization optimization of lignin is helpful to improve the strength of lignin-based carbon fibers. It should be noted that in addition to the correct heating rate, each material may have an optimum temperature during the heating process. Currently, the process parameters of lignin filament in the pre-oxidation and carbonization stages refer to those of the preparation process of PAN-based carbon fibers, while the thermochemical mechanism involved in the transformation is completely different.

Moreover, lignin has ultraviolet absorption characteristics. The ultraviolet-visible (UV-vis) test of the lignin fiber film obtained from electrospinning shows that the electrospun lignin fiber film absorbs ultraviolet light. This demonstrates the potential of lignin electrospinning films in ultraviolet applications. Based on this, electrospun lignin fiber film can be directly used in the field of ultraviolet absorption without carbonization.

In addition, taking advantage of the existing characteristics of electrospun fiber in the form of film, carbon fiber is also used as a new power source in the field of supercapacitors, which has the advantage of high weight ratio capacitance. Without the addition of conductive material and binder, it can be used directly as electrode material in the form of film. A novel electrode synthesis method was proposed in Oak Ridge Laboratory (Tenhaeff *et al.* 2014). Lignin-based carbon fiber felt was used as electrode material by scalable melt processing technology. The resulting independent electrode is comparable to commercial carbon-based anodes in material and processing costs. The results showed that carbonized felt can realize reversible cycling in conventional aprotic organic electrolyte, and its coulomb effect exceeds 99.9%. This dual function eliminates the need for large metal current collectors and polymer adhesives in traditional electrode designs. Not only the production process is simple, but it also avoids the problem of rising resistance caused by the use of binder, which shows the application prospect of lignin-based carbon fiber. This is not only conducive to the comprehensive utilization of lignin resources, but also conducive to the development of clean energy.

CONCLUSIONS

1. It is feasible to convert lignin, with abundant reserves and high carbon content, into low-cost carbon fiber. Thus, lignin has great potential and development prospects in the preparation of low-cost carbon fiber.
2. With the continuous progress of science and technology, lignin-based carbon fibers have become a material with good economic attractiveness and environmental sustainability. The research of lignin-based carbon fiber not only broadens the utilization direction of lignin, but it also alleviates the shortage of carbon fiber in the current market, which shows good social and economic benefits.

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