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本科毕业论文

Preparation and Properties of Carbon Fibers Based on Lignin

基于木质素的碳纤维的制备与性质

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Content

Abstract

Lignin is one of the main components of plant fiber materials, and its stock in nature only inferior to cellulose. Lignin can be used as a carbon fiber materials owing to its high carbon content (usually 55% ~ 66%).

Generally, lignin is a by-product of pulping process without recycling, which causes a big problem in environment protection and materials utilization. In this paper, formic acid lignin was extracted from black liquor, and nano-carbon fiber was prepared from formic acid lignin. Firstly, formic acid lignin carbon fibers coming up through electro spinning, and then treated by pre-oxidation and carbonization to obtain the final lignin based nano-carbon fibers.

Key words: lignin; electro spinning; nano-fibers; carbon nano-fibers

摘 要

木质素是植物纤维中的主要成分之一，在自然界中的蕴藏量很大，仅次于纤维素。因为木质素中碳元素含量较高（大约 55%～66%），所以木质素可以作为制备碳纤维的原料进行利用。

木质素是造纸产业中制浆的副产物，如果不经回收，则不利于环境保护以及废物利用。在本文中，从黑液中提取的甲酸木质素最终被制备成纳米碳纤维素。首先，甲酸木质素进过静电纺丝得到碳纤维，经过预氧、高温碳化，最终得到纳米碳纤维素。

关键词：木质素；静电纺丝；纳米纤维素；碳纳米纤维素

Chapter 1　Introduction

1.1 Lignin

Lignin is the second rich aromatic material in nature, its stock only inferior to cellulose in amount. It has natural aromatic macromolecules with the three - dimensional network structure. Bonding with cellulose and hemicellulose, they three form the key section of the plant skeleton, serving as a characteristic adhesive polysaccharide to increase the mechanical strength of wood.[1]

1.2 The structure of lignin

Lignin has an extraordinary complex structure so that there are varied views about its structure, but the currently accepted one is that phenyl propane is the primary unit which has three major monomers -- guaiacyl (G), lilac (S) and P-hydroxyphenyl (H).[2] The basic structures are shown in figure 1-2.

According to the different plants species, lignin could be classed into three categories: softwood lignin, broadleaf lignin and herbs Figure 1-2lignin. The structure of lignin differs in various plants species, it is not the same even in different parts of the exactly same plant. Lignin is chemically unstable, chemical reaction occurs easily when the temperature and acidity changed, even in the more moderate conditions, there will be condensation. Until today, no natural lignin extraction method has been found, which make it difficult for the research.

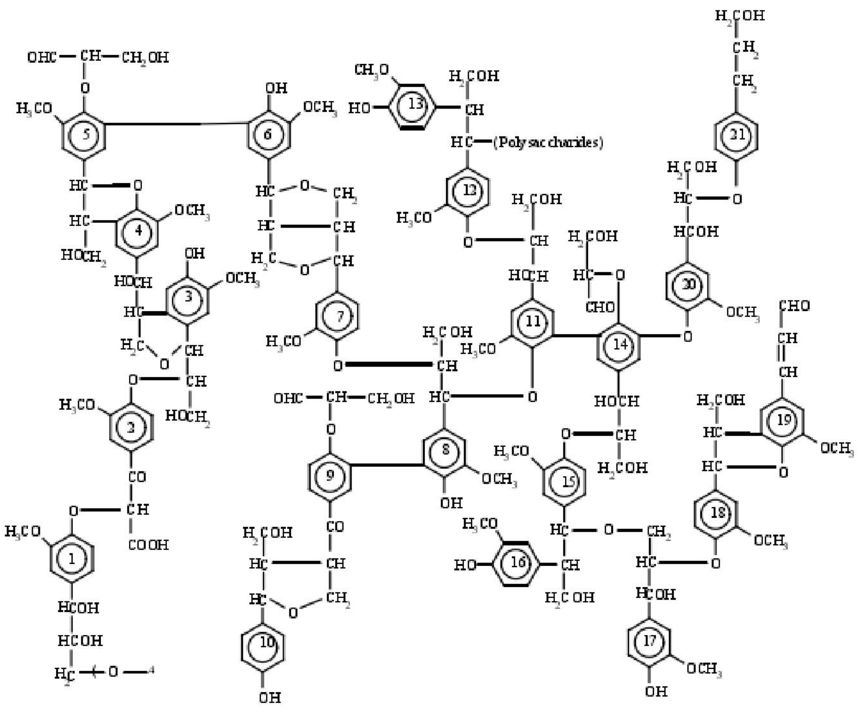
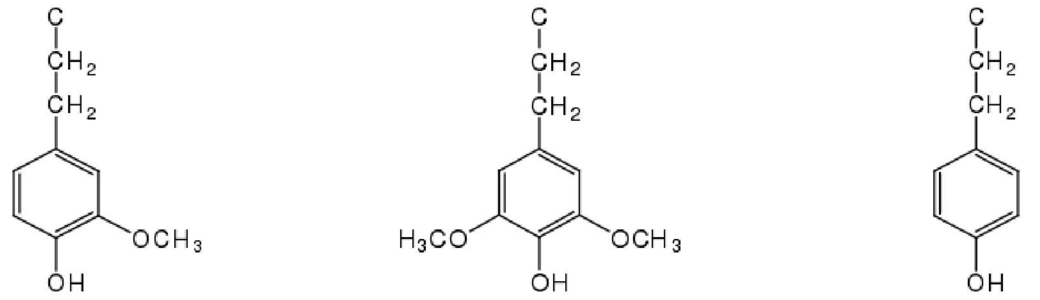


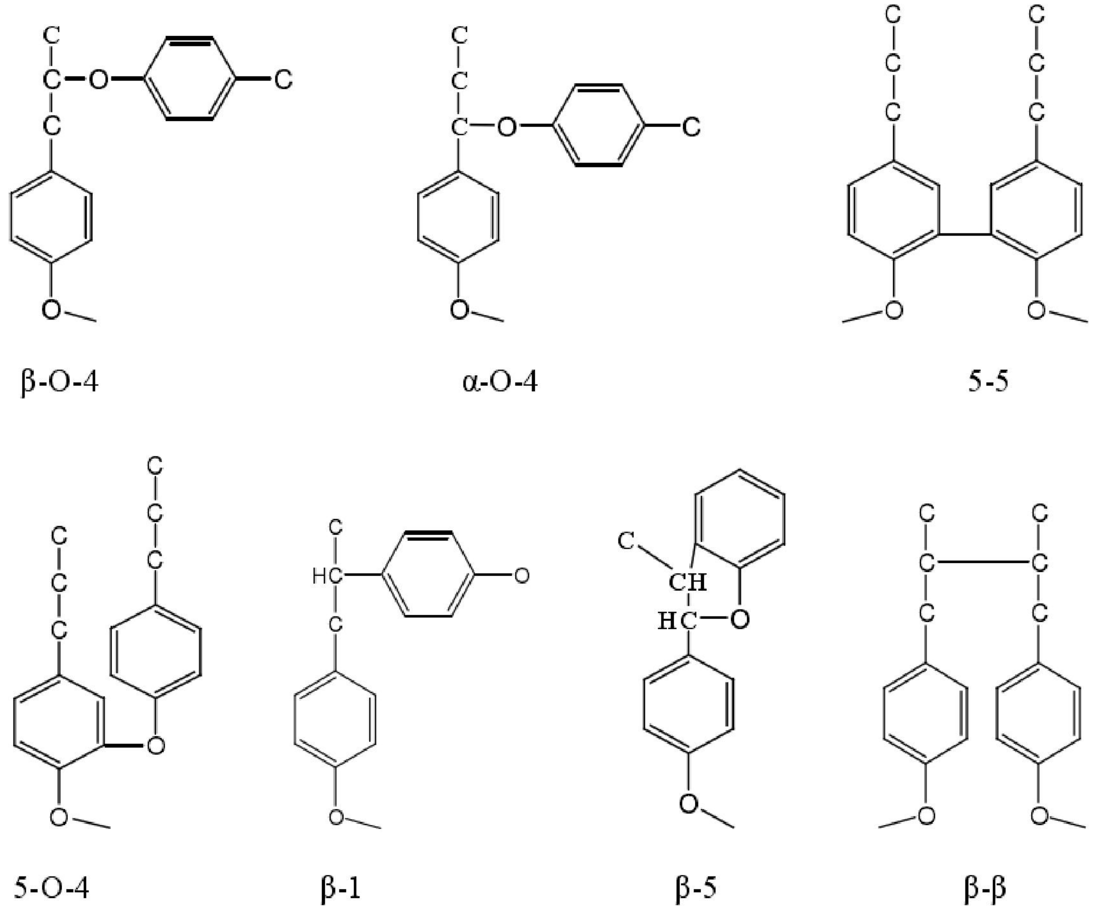
Figure 1-1 The structure of lignin



guaiacyl (G) lilac (S) P-hydroxyphenyl (H)

Figure 1-2

The main connection type between these three lignin structural units above are mainly through C-C and C-O-C connection, there are many kinds of connection, they could be divided into: β -O-4 connection, α -O-4 connection, 5-5 connection, 5-O-4 connection, β -1 connection, β -5 connection and β -βconnection.(As shown in figure 1-3)



β-O-4 α-O-4 5-5

5-O-4 β-1 β-5 β-β

Figure 1-3 kinds of connection

1.3 The property of lignin

1.3.1 The physical property of lignin

The property of the lignin varies greatly depending on the different plant species, the preparation method, and also the separation method. The molecule weight of lignin is in the range of several hundred to several hundred thousand, the molecular weight of lignin generally reduced due to degradation and condensation reaction in the separation process. On the other hand, natural lignin and extracted lignin differs to each other because of the denaturation in the solution.

Most lignin is insoluble into water, having good flame retardant ability, solvent resistance and excellent thermal stability. Lignin is a compound with no certain structure and no fixed melting point, so its glass transition temperature is between 127 and 190 degree Celsius which varies based on the lignin structure formula and the water content.

The lignin in plant fibers is nearly colorless and exhibits different colors with different extraction method. The lignin burning value is so high, and lignin is an aromatic compound with stable molecular structure and high thermal stability. Lignin is an aromatic compound that reflects the aromatic nature and does not have optical properties.

There are a variety of functional groups in the lignin molecule, such as hydroxyl, carbonyl, carboxyl, aryl, methoxyl and so on, so it has the ability to occur nucleophilic, electrophilic substitution, oxidation, color and other reactions.

1.3.2.1 Electrocene Substitution Reaction of Lignin

On the benzene ring, there are the connection of hydroxyl, methoxyl and other electron donor groups, which give the activation to benzene ring, so the electron cloud density get increased, and easier reacts with electrophilic reagents, resulting in electrophilic substitution reactions.

Among the reactions of electrophilic reagents, the most significant two are the halogenation reaction and the nitration reaction, which are characterized by that positive halide ions, n-nitro ions and others reacted on the benzene ring, through a transition state, the hydrogen atoms are replaced, chlorinated lignin and nitrifying lignin formed afterly. The electrophilic substitution reaction of lignin is often accompanied with the lignin oxidation, degradation reaction.

The electrophilic reagent inserting position at the benzene ring of lignin structure generally follows the localization roles of substitution reaction of benzene. As the methoxyl, hydroxyl and other groups on the lignin benzene ring are belonging to ortho or para position groups, So that when the electrophilic group in the reagent reacts with the lignin, the main reaction occurs in the presence of methoxy the ortho or para position of the base hydroxyl.

1.3.2.2 The oxidation reaction of lignin

The oxidation reaction of lignin is the main reaction of pulp bleaching, since the pulp bleach mainly using oxidants. Lignin could occur oxidation reaction with hypochlorite, chlorine dioxide and oxygen.

Hypochlorite is a traditional bleach reagent, the reaction of hypochlorite bleach is mainly oxidation reaction, but also chlorination reaction, and sometimes occurring free radical reaction. Benzene ring benzoquinone structure and side chain conjugated double bond are mainly attacked in hypochlorite and lignin oxidation reaction.

Chlorine dioxide is a free radical, it is easy to attack the phenolic hydroxyl of lignin make it into a free radical, and then undergoing a series of oxidation reactions, and finally form a myristic acid derivative product and chemicals with o- or p-benzoquinone structure. Molecular oxygen, as an oxidant, mainly use molecular oxygen two electrons on the organic matter with a strong reaction tendency, resulting in free radical reaction. The reaction of molecular oxygen with lignin is actually a free radical reaction. In the alkaline medium, the molecular oxygen causes the automatic oxidation of the urinary phenol type and the enol type lignin unit which provides the pre-condition for the electrophilic attack of negative ions.

1.4 The separation method of lignin

Commonly used lignin is separated or extracted from the plant fiber or papermaking residue black liquor, and there are two main ways applied currently. One method is to retain lignin dissolving other components of the plant fiber, therefore lignin could be filtered as an insoluble component; the other is to dissolve the lignin retaining the other components, and lignin is separated as a soluble ingredient.

1.5 Analysis method of lignin structure

Lignin is a polymer compound with a complex structure. The current analysis of lignin structure is mainly through the measurement that the functional groups contained in the lignin molecules, and the connections between the structural units. The main functional groups are listed as follows: alcoholic hydroxyl, phenolic hydroxyl, carbon double bond, carboxyl, carbonyl, methoxyl and so on.

At present, the commonly used lignin structure detection means include the following: infrared absorption spectrum, ultraviolet spectrum, nucleus magnetic resonance, liquid chromatography, meteorological chromatography, GC / MS and gel permeation chromatography.

1.5.1 Infrared absorption spectroscopy

Infrared absorption spectroscopy is a common means of qualitative analysis of lignin, the operation is quite simple, less amount of test sample and there is no need to do the dissolving work. From the infrared absorption spectrum, we can be easily tell the strength of the absorption peak of each functional group. Infrared absorption light spectra can not only qualitatively analyze the types of functional groups inside the lignin, but also quantify the content of functional groups. When estimating the content of each functional group in lignin, the absorption peak area of 1515 cm^{-1} is usually selected as the benchmark of infrared absorption peak for lignin.

Because the area of 1515cm^{-1} is generally considered as the vibration absorption peak of the benzene ring skeleton, which is constant in the infrared spectrum of lignin, so the relative absorption intensity of this region is recorded as 1.000. Combined with the absorption intensity of each region, we can calculate the relative absorption intensity of each region, so there is a way to estimate the content of lignin in the functional groups.

1.6 Lignin based carbon fiber and nano-carbon fiber

1.6.1 Lignin based carbon fiber and its research progress

Carbon fiber is a specific fiber made from polyacrylonitrile (PAN), asphalt and viscose, after pre-oxidation and carbonation, got a structure with high strength, high modulus and high temperature resistance, and its carbon content is more than 90 percent. The density of carbon fiber is 1.8 g / cm^3, its fine and soft fiber, easy to conduct, hard to be corroded, furthermore, adaptable to the organism. Carbon fiber is mainly used as a reinforcement in composite materials. At present, in addition to the traditional aerospace and sports entertainment products, carbon fiber is also playing an important role in the civil construction and transportation fields.

There are three major commercial precursor materials: asphalt (oil or coal), rayon and polyacrylonitrile (PAN). Among these three, polyacrylonitrile (PAN) has been widely used in commercial production, it is commonly admitted excellent precursor material. Nearly 80% of commercial carbon fibers are made from polyacrylonitrile. However, the current polyacrylonitrile carbon fiber is quite expensive, which limits its applications towards low-cost general-purpose carbon fiber field.[5] Supported by scholar papers, low-cost and readily available recycled petrochemical polymers, fibers, renewable cellulose and lignin, they all might be the potential raw materials for general-purpose carbon fibers.

1.6.2 Nano - carbon fiber and its application

Nano-carbon fiber is a new type of carbon material, with excellent physical and mechanical properties and chemical stability, such as large specific surface area, high mechanical strength and Young's modulus. These properties contribute that nano-carbon fiber has the better conductive, thermal and thermal stability when compared with the graphite. Owing to the dense structure of carbon nanofibers, its strength is usually higher than general carbon fiber.

Nano carbon fiber has been utilized in some productions such as the electrode material, catalyst carrier, filter material, storage materials and high efficiency adsorbent productions and so forth. The problem of static dissipation could be properly solved if a small amount of nano-carbon fiber was added in the chip. As a mechanical properties enhancer, the nano-carbon fiber can achieve the same effect of continuous carbon fiber enhancement. Besides, it also can be applied in electromagnetic shielding field.

1.6.3 Preparation of nano - carbon fiber

There are three preparatio[9]n methods of nano-carbon fiber, the traditional Vapor Phase growth method (VG), Plasma Enhanced Chemical Vapor Deposition (PE-CVD) and electro-spinning method.

In the gas phase growth method metal particles are served as a catalyst, so that hydrocarbons such as benzene, methanol and other compounds could be decomposed at the temperature with a range of 700 ~ 1200 ° C in the hydrogen environment, and then carbon particles accumulate into carbon fiber with the previous deposition including seed catalytic gas phase growth and flow catalytic gas phase growth.

Since 2000, plenty of researches have been focused on the study of the certain directional growth of nanofibers, and it is called Plasma Enhancement Chemical Vapor Deposition Method.[9] In final, it shows that the nanocarbon fibers can be aligned in a regular order,having a good characteristic of electron field emission which enables its potential applications in the field emission field. The PE-CVD method can be used to fabricate nanocarbon fiber in a decided orientation, but we are facing some problems such as its cost is higher, the production efficiency is lower and the process is not easy to control.

The nano-polyacrylonitrile (PAN) precursor prepared by electric spinning, can be transferred into nano carbon fiber after carbonization and carbonization. The electric spinning process is simple with a low cost is, which is one of the best methods to prepare nano carbon fiber and it is also the only approach to produce carbon nano-fibers continuously.

Electric field spinning is defined as that treated by high voltage DC power (several thousand volts or tens of thousands of volts), the polymer solution or melted stuff overcomes the surface tension, forming of jet fine, ultimately get fibers of which diameter between tens of nanometers and several microns of on the collector owing to the jet was constantly being stretched mainly because of the static electricity effect, jet splitting happens sometimes.[14] Compared with nano-carbon fiber by the PE-CVD, the one prepared by electric spinning has the advantages of continuous production, uniform diameter and good strength, in addition, purification process is not needed.

1.6.4 Study on lignin based nano-carbon fibers

With the increasing shortage of fossil oil, the shortage of chemicals based on fossil oil are coming up as well. Therefore, producing petroleum-based polymer materials from biomass-based chemicals is becoming more and more significant and popular. Moreover, it is the key problem really needed to be solved that how to effectively use the renewable resources with a high carbon content to prepare carbon fiber or nano-carbon fiber.

In the Chinese patent application No.200710043185.4, Shen Qing proposed a preparation method of lignin nano-carbon fiber. In that patent, the lignin and the synthetic polymer were blended in a mass ratio of 25/75, sliced, and then dried in vacuum to melt the fibers to obtain fibers having a diameter between 50 to 300 nm and the length from 1 to 20 μm. After that, heating them up to do its pre-oxidation in the open air with the temperature from 100 to 350 ℃, and then the carbonation section is completed in the protective atmosphere in the temperature range of 800-2000℃.[3]

The claims of the invention did not mention what kind of raw material is used and the separation means either, but one thing is clear that the used lignin is alkaline lignin pointed in the technical program. As the ordinary alkaline lignin, especially non-wood alkaline lignin contains a lot inorganic salt, the fibers are mixed into lignin during the spinning and are ultimately present in the carbon nanofibers, affecting the purity of the nanocarbon fibers and its dielectric constant, resulting in the use of performance degradation.

Lallave M made the ethanol lignin (Alcell lignin) dissolved in ethanol, the lignin fiber with a diameter of 400 nm to 2μm was prepared by using high-voltage electrospinning. The fibers were stabilized at 200℃ for 24 hours, and then carbonized at 900 ℃, finally got the carbon fiber with a diameter in micron and nano-scale. Due to the lignin- ethanol solution viscosity is very large, in the spray from the nozzle when the evaporation of ethanol lead to the formation of solid solution on the solid surface, coupled with the so-called "Taylor cone" effect, resulting in curing after the formation may not be fiber, but tapered lignin particles.[15] In order to prevent this situation, they used a coaxial electrospinning technology, that is, the central spray nozzle is also sprayed solvent to compensate for solvent evaporation caused by premature solution and poor fiber formation of the consequences of poor. However, the spinneret used in this method is complicated and prone to clogging.

1.7 Preparation of Nano-fibers

There are many methods could be used for the preparation of nano-fibers, such as stretching, template polymerization, phase separation, self-organization, and electrospinning and so forth. The stretching process is similar to the dry spinning in the fiber industry, which produces the long single nanometers fiber filament. But there is one thing need to optimize that only viscoelastic material able to stand the huge stress traction deformation can be stretched into nano-fibers. For the template polymerization method, nano-porous membrane is used as a template to prepare nano-fibers or hollow nanofibers.

The main advantage of this method is that it could be used to spin different materials, such as conductive polymers, semiconductors, metals, carbon nanotubes, and fibrils. The disadvantage is that it cannot be used to prepare continuous nanometer long fibers. The phase separation process involves the process of dissolving, gelling, extracting, condensing and drying to obtain nanoporous foams. The use of this method takes a long time to convert the polymer into a nanoporous foam. Self-organization is a process that spontaneously assembling already existing components into a desired pattern and function. The self-assembly process is also quite time consuming. Compared with these methods, electrospinning is the only way to realize the direct and continuous preparation of polymer nano-fibers.

1.8 Electrostatic Spinning Technology

1.8.1 Principle of Electrostatic Spinning Technology

Electrostatic spinning device mainly consists high-pressure generator, a tube with small nozzle and the receiving device. In the electrospinning process, the high pressure generates the polymer solution or melted to be ejected from the spinneret forming charged jet. Before reaching the receiving device, the charged jets are solidified and form polymer fibers due to the volatilization of the solvent, and finally deposited on the receiving device. The anode derived from the high voltage electrostatic generator is inserted into the polymer solution or the melting.

The other electrode is connected to the receiving device. The general receiving device is grounded. When no voltage is applied, the polymer is stored in the capillary due to the surface tension. With the electric field is turning up, owing to the role of the electric field, the fluid surface produces a large amount of electrostatic charge. When the applied voltage is small, the electric field force is not sufficient to cause the charged portion of the solution to be ejected from the solution.[16] With the increase in voltage, the top of the capillary droplets are gradually elongated to form a charged cone, also known as Taylor cone.[10] When the electric field strength increases to a specific critical value, the charge surface of the fluid charge is greater than the surface tension, charged cone will convert into a charged jet. The charged polymer jet flows through an unsteady elongation process to make the jet stream longer and thinner while the solvent evaporates the fibers and is arranged in a disordered manner on the collection device forming a fibrous web or film.

1.8.2 The main factors affecting the electrostatic fiber morphology

The study of the electrospinning process is aimed at completing the specific spinning objects and cater for the certain diameter and morphology requirements, in order to find out the best spinning process experiment conditions, electrospinning factors must be studied thoroughly. The influencing factors include the nature of the solution (solution concentration and viscosity, conductivity, etc.), operating factors (voltage, distance between the capillary port and the receiving screen, etc.) and environmental factors (ambient temperature, humidity). But the most important factor is the nature of the solution, the voltage and the distance between the capillary port and the receiving screen.[4]

1.8.2.1 Effect of polymer solution concentration and viscosity on fiber

Fong found that the viscosity of the solution is small and so the viscous resistance is when the mass fraction is low, which cannot stand the tensile force of the electric field and the repulsive effect of the Coulomb force, resulting in the fracture of the jet, at this point, the broken jet shrink into a spherical shape in the receiver plate to form into a discrete bead structure due to the role of the surface tension.

When the mass fraction increases, the viscosity of the solution also increases, the viscoelastic force of the jet gradually becomes larger, and the jet will not be pulled off at this time, so the state of the transition on the fiber is formed.[17] With the increase of the mass fraction, When the viscous force is large enough, the pearl knuckles gradually disappear, but when the mass fraction reaching 9%, both the spinning solution viscosity and the viscosity resistance are large enough, which decreasing its rheology, and the spinning process becomes more difficult.

Researchers have found that increasing the concentration of the solution and viscosity under the range of the viscosity of the spun bond can optimize the fiber shape in the spinning process. Megelski also pointed out that uniform and slippery fibers could be got if increasing the viscosity. After a series of studies, Mit-upatham came out the above conclusions.

1.8.2.2 Effect of Electrostatic Voltage on Fiber Morphology

Theorically, as the voltage increasing, the diameter of the resulting fiber decreases, and some researchers test the results repeatedly also proved this one. This conclusion draws the other sum that the diameter of the fiber decreases with increasing voltage. However, in some experiments, they found that the diameter of the fiber increases with the increasing in voltage, or even no significant changes.[18] Demir reported that the diameter of the fiber increases with increasing voltage. However, Reneker was studying polyoxyethylene electrospinning behavior results in a spinning voltage that has no significant effect on the diameter of the fiber.

Krishnappa's study shows that raising the voltage increases the density of the beads, but when the voltage increases to a certain extent, will form a larger diameter of the beads-like fiber. Zhao point out that the speed of fiber spray is higher with the voltage increasing, thereby reducing the jet duration time. This means that the fibers will have been deposited before the polymer molecules are aligned, and the polymer macromolecules do not have enough time for the regular arrangement. Therefore, sufficient discharge time is a key element for enhancing the crystallinity of the fiber at high voltage.

1.8.2.3 Effect of Reception Plate Distance on Fiber Morphology

The effect of the distance on the fiber diameter has two factors, on one hand, the increase in the distance makes the jet have more stretching and whipping, so that the diameter of the fiber becomes smaller; on the other hand, the electric field force decreases with the increase of the receiving distance, therefore the acceleration of the fiber becomes smaller and the coarse fiber is obtained.[19] The effect of the distance received on the fiber diameter is the result of these two factors.

1.9 The purpose and significance of this study

Lignin, as a natural macromolecular compound, mainly distributed in plants, its amount in nature only inferior to cellulose. The amount of lignin produced by the earth each year from photosynthesis is about 150 billion tons. On the other hand, millions of tons lignin waste were produced in the paper-making industry annually. Because lignin is a macromolecule polymer with a complex structure, pretty hard to be solved down, resulting in a huge environmental pollution. The study found that lignin could be transferred into carbon fiber material when it is modified under certain conditions. If the conversion of lignin waste into high performance carbon fibers is achieved, it is of great significance to reduce pollution and more importantly, to master a new energy source.

Chapter 2 Preparation of formic acid lignin

Due to the varied chemical treatment types and molecule length, lignin is different from each other in terms of molecular weight, functional groups, concentration, the cross-link types and so forth. So there is a problem when preparing nano-carbon fiber by electro spinning using lignin as raw material to produce all kinds of chemical products. People usually produce the chemical products by sulfonate and alkali lignin (containing sulphate lignin) which are the by-products in pulp and paper industry.

In the separation process, a part of lignin is oxidized into small molecules, some of them have secondary condensation, and the condensation is quite hard, which resulting in that the linking between lignin structural units is complicated, the relative molecular mass distribution is wide, and reducing the solubility of lignin in organic solvents. In short, it is tough to electro spinning.[20] Considering the inherent deficiencies of the presence of raw materials, it is necessary to change the lignin separation method to obtain a lignin with better solubility in the organic solvents and the appropriate relative molecular mass. In this chapter, organic lignin was treated with organic solvent and special method to prepare lignin which make it easy to electro spinning.

2.1 Experimental materials and instruments

2.1.1 Raw materials and reagents

Formic black liquor, paper-making laboratory of Qilu University of Technology

2.1.2 Instruments

Electronic balance
Oil bath pan
Water bath pan
Centrifugal machine
Drying oven
Thermometer

2.2 Experimental method

2.2.1 Preparation of formic acid lignin

Black liquor contains organic substances from the cooking liquor that lignin, hemicellulose and cellulose degradation products and organic acids eluted from the plant fiber raw materials. In the caustic soda method, the sulphate pulping process, about 50% of the fiber raw material dissolved in the cooking liquor, because of its deep color, known as black liquor.

Usually, there are some substances insoluble in black liquor, it is necessary to clear the liquor roughly at the beginning. Centrifuging the acid black liquor three times and take the upper liquid until there is no more precipitation at the bottom of the centrifuge tube. The centrifuged liquor has been transferred into a larger flask, and 200g black liquor was took as a sample. On top of that, distillation process was going on and the devices are shown in the figure 2-1.

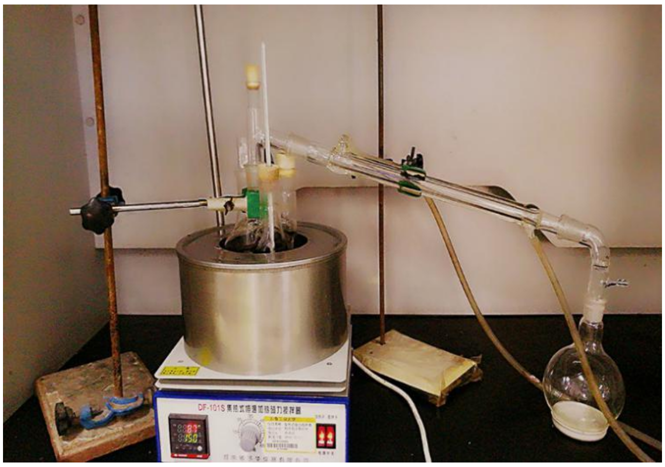


Figure 2-1

There has not any beads until the temperature of the oil is up to 130℃ although the boiling point of formic acid is 100.8℃, and the distillation process is quite slow. After plenty of trying, we found that the distillation is going fluently when the set temperature is 150℃, which is the applied temperature in whole distillation experiments.

Moreover, 200g black liquor sample was heated at the temperature of 150℃ keeping 2 hours until there is no more beads coming out. The evaporated liquid is mainly the mixture of water and formic acid which is stored in the blown bottles. The distillate residue in the three-necked flask was rinsed with 50 degree warm water and transferred to a beaker and stirred by magnetic stirrer for around 10 minutes. After stirring, the mixture was transferred to a centrifuge tube and centrifuged three times until the supernatant was clear. The precipitate of the centrifuge tube was taken out and dried to obtain crude lignin (as shown in picture 2-2), and the yield was calculated then.[21]

We get an average value of the weight of gained crude lignin solid from each sample, it is 4.23g, so the yield is calculated like this:

$$\text{Yield} = \frac{weight\ of\ crude\ lignin}{weight\ of\ black\ liquor} \times 100\% = \frac{4.23}{200.00} \times 100\% = 2.12\%$$

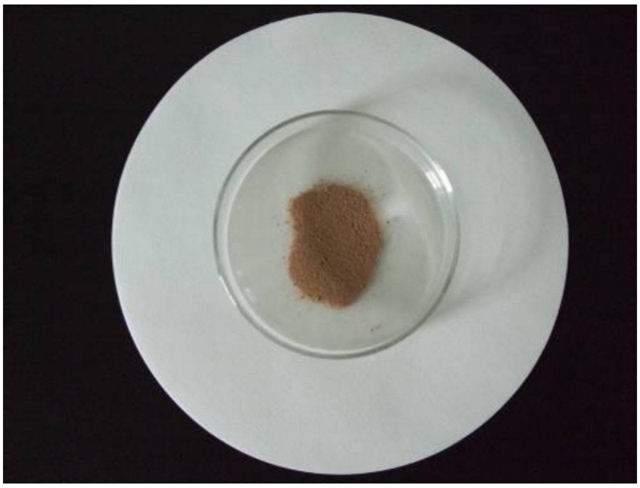


Figure 2-2 The lignin obtained

2.2.2 The Gel Permeation Chromatography analysis

Gel Permeation Chromatography is a technical means used to detect the molecular weight of polymer compounds. The separation principle is different from that of general chromatography. The stationary phase in the chromatographic column is a porous silica gel with a certain void or an inert cross-linked polymer gel used in series according to its size. After the molecular weight of the polymer is injected into the column, the solute particles flows down as well as the solvent, due to the large radius, the molecules with large molecular weight cannot enter the pores of the porous gel. And they flow down from the gap between the gel particles, were eluted through the column firstly.

Molecules with smaller molecular weight can penetrate into the voids of the partial gels and then diffuse out and stay relatively longer time in the column. Molecules with the smallest molecular weight can penetrate into the voids of all gels and could repeated in and out of the gel, the longest staying time in the column until it is finally eluted. The polymer is separated according to the molecular weight to obtain a change curve of the molecular weight, so the average molecular weight and the mass average molecular weight can be calculated.

The relative molecular weight distribution of lignin is mainly to understand whether the lignin molecules are homogeneous and can achieve the homogeneity of the properties of synthetic materials.[22] Figure 2-4 shows the GPC spectra of formic acid lignin. The abscissa is the logarithm of the relative molecular weight and the ordinate is the percentage. Table 2-3 shows the relative molecular mass of lignin.

After analysis of the GPC graph, the peak molecular weight of formic acid lignin is 4993, the molecular weight (Mw) is 8618, and the average molecular weight (Mn) is 5027, so its polydispersity (Mw / Mn) is 1.71.

Chapter 3 Preparation of formic acid lignin Nano-carbon fiber

In order to study the properties of electro spinning formic acid lignin, the different proportions of lignin (FAL) and polyvinyl pyrrolidone (PVP) were mixed into a solution for electro spinning, it is found that when the proportion of PVP up to 90%, the electro spinning still works. After electro spinning, lignin nano-carbon fiber was got in final through the pre-oxidation and carbonation process. This chapter explored the appropriate conditions for both peroxidation and carbonation.

3.1 Experimental materials and instruments

3.1.1 Raw materials and reagents

FAL (formic acid lignin)
Polyvinylpyrrolidone
Tetrahydrofuran, analytical grade
N, N-dimethylformamide, analytically pure
Glacial acetic acid, analytical grade

3.1.2 Instruments

magnetic stirrer
high voltage electrostatic generator
muffle stove
scanning electron microscope

3.2 Experimental steps

3.2.1 Preparation of electro spinning solution

After a series trying experiments to test the PVP solution with different concentration, it is found that the PVP solution works the best when it has a mass fraction of 40%. And then, electro spinning solution using water as a solvent, and 4 g of PVP powder was dissolved in 6g water to prepare a PVP solution having a mass fraction of 40%. 0.2g of FAL was dissolved therein, and the prepared solution was shaken on a magnetic stirrer to mix evenly.

3.2.2 Electro spinning

Using the high-voltage electro spinning device shown in figure 3-1, where the positive and negative electrodes are connected to the spinneret 3 and the collecting plate 4, the spinneret 3 and the collecting plate 4 are located in the constant temperature and humidity container 5. The distance between electro spinning device 3 and the ground collecting plate 4 is 15 cm, and the diameter of the spinneret 3 is 0.1 mm, the high voltage electrostatic generator 6 has a voltage of 30 kV.[23]

The prepared spinning solution was placed in a liquid storage container 2 of a high-pressure electro spinning apparatus, and the infusion pump 1 is extruded from the vessel at a flow rate of 0.1 m L / h and then ejected from the nozzle port 3, and the discharged spinning liquid is solidified to form nano-fibers, arranged in a disordered manner on the collecting plate 4 to form a fibrous film similar to that of the nonwoven fabric.[11]

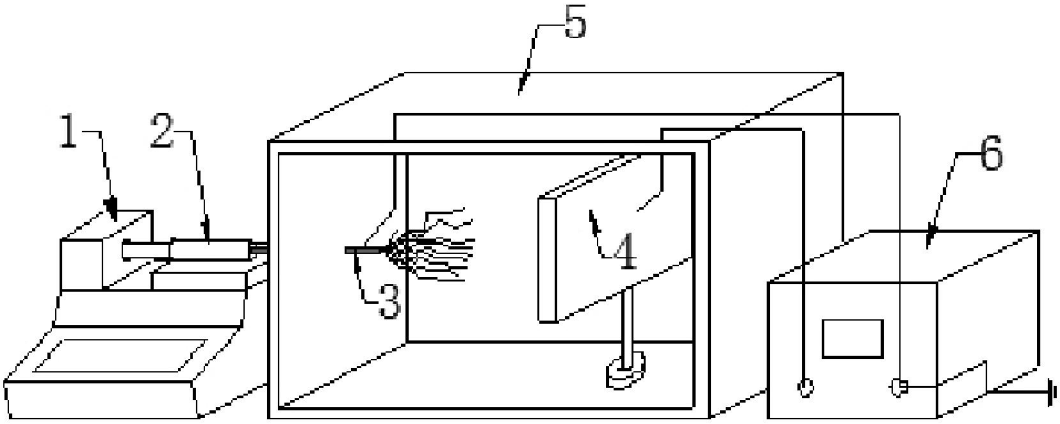


Fig 3-1 schematic diagram of electrospinning

1 syringe pump 2 syringe 3 needle 4 collector 5 humidity box 6 power supply

3.3 Preoxidation

The nanofibers obtained by electrospinning FAL and PVP solution were preoxidized in muffle furnace with a temperature of 300° C.

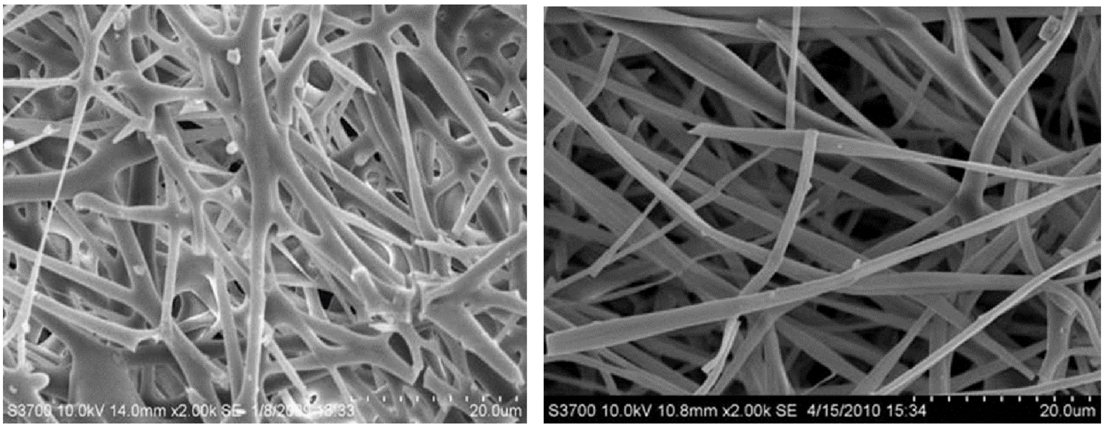
3.4 Carbonization

The original wire is placed in a stretched state before it is placed in the carbonization furnace and applied to its longitudinal fixed tension. This allows the carbon fiber molecules to crystallize along the longitudinal direction, which helps to maintain the shape of the carbon fiber, and also improve the physical properties of carbon fiber. The carbon fiber precursor in the stretched state was placed in a carbonization furnace, nitrogen was introduced, heated to 700 ° C at a specific heating rate of 100° C per hour, and carbonized at that temperature for 1 hour.[12]After the carbonization is completed, the carbon fiber is naturally cooled to room temperature.

3.5 Analysis and characterization

3.5.1 The impact of heating to diameter and morphology of fiber

It can be seen from the figure 3-2, after pre-oxidation and carbonization, FAL retained the intact fiber morphology. The average diameter of fibers after carbonation at 700 ° C, Lignin fibrils and pre-oxidized fibers are shown in Table 3-3. As can be seen from the table, in the pre-oxidation and carbonation process, the fiber diameter decreased. The fiber has a certain amount of bending shrinkage deformation. The decrease in fiber diameter is due to that carbonization causes changes in fiber structure and weight loss.



(A) thermostabilized nano-fibers (B) 700℃ carbonized nano-fibers

Figure 3-2 SEM images of FAL nano-fibers

State	Lignin fiber	thermostabilized nano-fibers	700℃ carbonized nano-fibers
Diameter/ μ m	1.6	1.5	1.4

Figure 3-3 The average diameters of lignin fibers during heat treatment

3.5.2 Analysis of Surface Element Content of FAL Nano-carbon Fibers

The XPS surface element analysis of FAL nano-fibers is shown in Figure 3-4. It can be seen from the figure that the carbon content in the carbon fiber is 86.7% and the oxygen content was 13.3%.[24] The organic polymer goes through a complex thermal decomposition process during the production, non-carbon atoms are excluded, leaving the adjacent molecules in the chain of carbon atoms combined to form a hexagonal sheet. Carbon content in the carbonation process gradually increased (the general carbon fiber carbon content of 75% -95%, 2500 ℃ above the graphitization, the carbon content up to 98% or even more). The carbon content is relatively less owing to it is exactly in the carbonation stage.

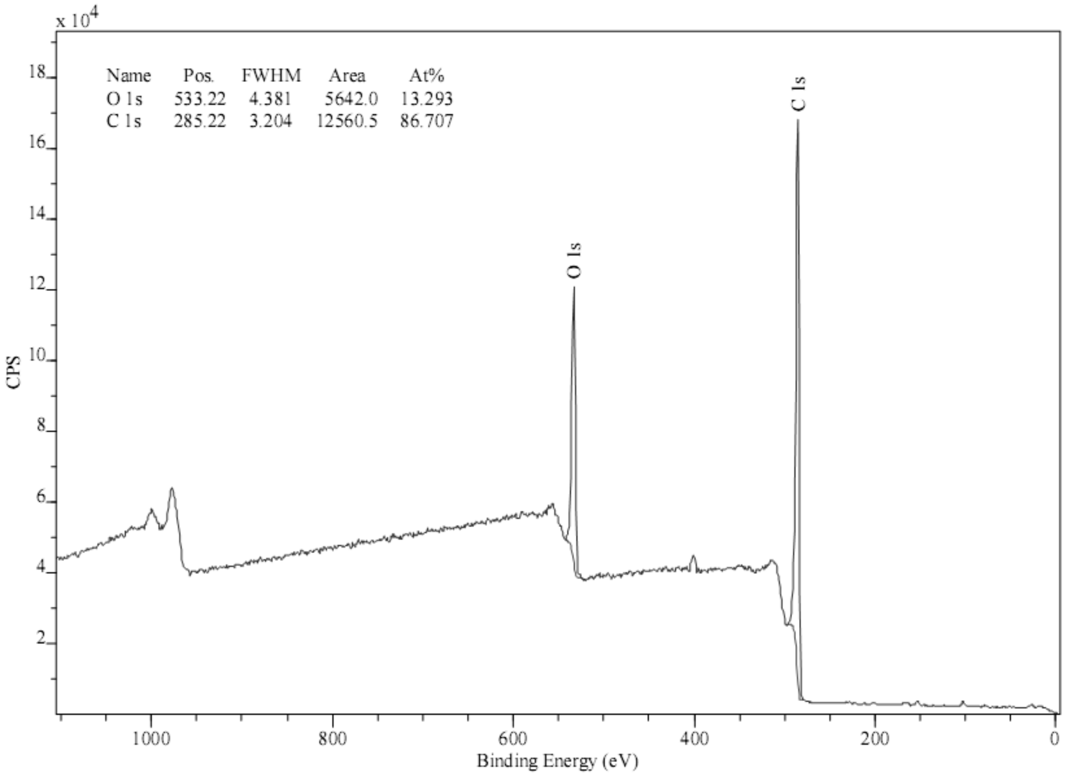


Figure 3-4 XPS of FAL carbon fibers

Chapter 4 Discussion

FAL and PVP blends together to prepare mixed nano-fibers, and the diameter of fiber is around 200nm. When the fAL ratio is high up to 90% could be still electros pined, increasing the FAL ratio would not affect morphology and diameter of fiber significantly. In order to retain the fiber morphology, it is necessary to pre-oxidize the fibrils. The pre-oxidation treatment of FAL nano-fibers needs to be carried out at an elevated rate of less than 1 ° C / min in an air atmosphere. When the rate of rising temperature is high, the fibers will be melted. Correct FAL fiber carbonization treatment at a fixed heating rate of 100 ℃ / h conditions, the fiber will be burned when the carbonation temperature is higher than 700 ℃.

According to GPC graph of FAL, the peak molecular weight of formic acid lignin is 4993, the molecular weight (Mw) is 8618, and the average molecular weight (Mn) is 5027, so its polydispersity (Mw / Mn) is 1.71.

FAL Nano-carbon Fibers goes through a complex thermal decomposition process during the production, non-carbon atoms are excluded, leaving the adjacent molecules in the chain of carbon atoms combined to form a hexagonal sheet. Carbon content in the carbonation process gradually increased.

After pre-oxidation and carbonization, FAL retained the intact fiber morphology. The average diameter of fibers after carbonation at 700 ° C, Lignin fibrils and pre-oxidized fibers, in the pre-oxidation and carbonation process, the fiber diameter decreased. The fiber has a certain amount of bending shrinkage deformation. The decrease in fiber diameter is due to that carbonization causes changes in fiber structure and weight loss.

References

[1] Liu X A. The contribution of different fractions of fines to pulp drainage in mechanical pulps [J]. Cellulose Chem Technol, 2001, 27(4): 139-143

[2] John F. Kadla.in: Chemical modification, properties, and usage of lignin, edited by

Thomas Q. Hu. New York: Kluwer Academic/Plenum Publishers, 2002, p.121-127.

[3] Shofner M L, Rodriguez-Macias F J, Vaidyanathan R, et al. Single wall nanotube and vapor grown carbon fiber reinforced polymers processed by extrusion freedom fabrication [J]. Composites: Part A-Applied science and manufacturing, 2003, 34: 1207-1217

[4] Ko F, Gogotsi Y, Ali A, et al. Electro spinning of continuous carbon nanotube-filled nano-fiber yarns[J]. Advanced Materials, 2003, 15(14): 1161-1165

[5]Yoshida C，Okabe K，Yao T，et al. Preparation of carbon fibers from biomass-based phenol-formaldehyde resin [J]. Journal of Materials science, 2005, 40(2):335-339.

[6] Endo M, Takeuchi K, Igarashi S, et al. The production and structure of pyrolytic carbon nanotubes[J]. Journal of Physics and Chemistry of Solids, 1993, 54(12): 1841-1848.

[7] Collins S, Brydson R, Rand B. Structural analysis of carbon nano-fibres grown by the floating catalyst method [J]. Carbon, 2002, 40: 1089-1100.

[8] Merkulov V I, Melechko A V, Guillorn M A, et al. Controlled alignment of carbon nano-fibers in a large-scale synthesis process[J]. Applied Physics Letters, 2002, 80(25): 4816- 4818

[9] Wang Y, Santiago-Aviles J J, Furlan R, et al. Pyrolysis temperature and time dependence of electrical conductivity evolution for electrostatically generated carbon nano-fibers[J]. IEEE Transactions on Nanotechnology , 2003, 2(1): 39-43

[10] Wang Y, Serrano S, Santiago-Aviles J J. Raman characterization of carbon nanofibers prepared using electro- spinning[J]. Synthetic Metals, 2003, 138: 423-427

[11] Park S H, Kim C, Choi Y O, Yang K S. Preparations of pitch-based CF/ACF webs by electro spinning[J]. Carbon, 2003, 41: 2655-2657

[12] Guillorn M A, Melechko A V, Merkulov V I, et al. Operation of a gated field emitter using an individual carbon nanofiber cathode[J]. Appl Phys Lett, 2001, 79(21): 3506-3508

[13] Guillorn M A, Mcknight T E, Melechko A, et al. Individually

addressable vertically aligned carbon nanofiber-based electrochemical probes[J]. Journal of Applied Physics, 2002, 91(6): 3824-3828

[14] Chun I, Reneker D H, Fong H, et al. Carbon nanofibers from Polyacrylonitrile and mesophase pitch[J]. J of Adv Mater, 1999, 31: 36-41

[15] Park S H, Kim C, Yang K S. Preparation of carbonized fiber web from electrospinning of isotropic pitch[J]. Synthetic Metals, 2004, 143(2): 175-179

[16] Lallave M B J, Ruiz-Rosas R, Rodriguez-Mirasol J, Cordero T, Otero J C, Marquez M, Barrero A, Loscertales I G. Filled and hollow carbon nanofibers by coaxial electrospinning of Alcell lignin without binder polymers[J]. Advanced Materials, 2007, 19(23): 4292–4296

[17] Ondarcuhu T, Joachim C. Drawing a single nanofibre over hundreds of microns[J]. Europhysics Letters, 1998, 42(2): 215-220

[18] Ma P X, Zhang R Y. Synthetic nano-scale fibrous extracellular matrix[J]. Journal of Biomedical Materials Research.1999, 46(1): 60-72

[19] Deitzel J M, Kleinmeyer J, Hirvonen J K,et al. Controlled deposition of electrospun poly(ethylene oxide) fibers[J]. Polymer, 2001, 42: 8163-8170

[20] Ohkawa K, Cha D I, Kim H, et a1. Electrospinning of chitosan[J]. Macromolecular Rapid Communications, 2004, 25(18): 1600-1605

[21] Fong H, Chun I. Reneker D H. Beaded nanofibers formed during electrospinning[J]. Polymer, 1999, 40(4): 4585-4592

[22] Doshi J, Reneker D H. Electrospinning process and applications of electrospun fibers[J].

Journal of Electrostatics, 1995, 35(2): l51-160

[23] Megelski S, Stephens J S, et al. Micro and nanostructured surface morphology on electrospun polymer fibers[J]. Macromolecules, 2002, 35(22): 8456-8466

[24] Mit-uppatham C, Nithitanakul M, Supaphol P. Ultrafme electrospun polyarnide-6 fibers: Effect of solution conditions on morphology and average fiber

diameter[J]. Macromolecular Chemistry and Physics, 2004, 205(17): 2327-2338

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