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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称：博士（農学）　　氏　名：ｼﾞｬﾝ　ﾘﾝ（Jian Lin）

学 位 論 文 題 名

Preparation and characterization of softwood lignin-based carbon fibers

(針葉樹リグニンを原料とする炭素繊維の調製とその特性の解明)

Lignin, one of the major cell wall components in higher plants, is the second most abundant biopolymer next to cellulose on the earth. A huge amount of technical lignins are produced as a by-product from pulp and paper-manufacturing processes, and most of them are merely burned for energy recovery. A preparation of carbon fibers (CFs) from technical lignins seems to be one of the promising processes for producing high value-added materials, because CFs are used in a variety of industrial fields, such as aerospace, automotive and sport equipment, due to their high performance. Several types of isolated hardwood lignins have been directly converted to fibers by melt-spinning, followed by CFs, whereas the modification of softwood lignin was required for melt-spinning. Recently, a novel solvolysis pulping with polyethylene glycol (PEG) has been developed to collect wood components and several chemicals. The obtained lignin fraction, termed as PEG-lignin, showed thermally fusibility at elevated temperature because of the chemical modification with PEG through ether bonds.

In this study, I investigated the optimum processes for production of CFs from this PEG-lignin, including melt-spinning, thermostabilization and carbonization, and finally attempted to prepare activated CFs (ACFs) as an environmental purification agent.

1. Carbon fibers and activated carbon fibers from softwood lignin

A thermally fusible PEG-lignin was isolated by a solvolysis pulping of cedar wood chips with a mixture of PEG 400 and sulfuric acid at 160 ^{o}C for 4 h. This lignin showed glass transition temperature (T_g) of 79 ^{o}C and thermal-flow starting temperature (T_f) of 141 ^{o}C, and was easily transformed into fibers with a diameter of 23 to 38 μm by melt-spinning at temperatures ranging from 145 to 172 ^{o}C without any other modification. The lignin fibers were subjected to oxidative thermostabilization under air atmosphere or a stream of oxygen to obtain infusible fibers, but all the oxidatively thermostabilized fibers melted and adhered to each other even at the slowest heating rate of 0.1 ^{o}C/min (> 2 days). Thereby, I developed an alternative thermostabilization process, termed as “Chemical Thermostabilization”. When

PEG-lignin fibers were immersed in concentrated HCl aqueous solution (6 M) at 100 ^{o}C for 2 h, partial PEG moieties were cleaved from the lignin, resulting in the conversion of fusible fibers to infusible ones. However, several defects including split and flabby structure on the surface of fibers were generated by the treatment. The infusible fibers were, in turn, converted to CFs by carbonization at 1000 ^{o}C under a stream of nitrogen. Their tensile strength was 450 MPa, and was not as high as those of other lignin-based CFs. The low performance was attributed to the defects. However, the defects act as advantageous reaction site for production of ACF. The ACFs with the specific BET surface area of more than 2000 m^2/g were easily prepared by steam activation at 900 ^{o}C only for 30 min. By prolonged activation time to 90 min, the BET surface area reached 3060 m^2/g.

2. Improvement of surface morphology and mechanical properties of softwood lignin-based carbon fibers

I assumed that when defect-free thermostabilized fibers are obtained, CFs with high mechanical strength would be prepared. To prepare such defect-free fibers, I attempted two types of chemical curing reactions for the fibers with hexamethylenetetramine (HMTA) as a curing reagent. The first trial was that PEG-lignin powder was mixed with HMTA, and then the mixture was subjected to melt spinning. However, no fiber was obtained by this process. As a second trial, the PEG-lignin fibers were immersed in aqueous HMTA solution at elevated temperatures, and then the resultant fibers were subjected to the general oxidative thermostabilization. As a result, the fibers could not be converted to infusible ones even at a heating rate of 0.5 ^{o}C/min. Finally, the chemical curing of PEG-lignin fibers were successfully carried out by immersing the fibers in an aqueous mixed solution of HMTA (60 g/L) and hydrochloric acid (3 M) at 85 ^{o}C for 1 h followed by the oxidative thermostabilization at a heating rate of 2 ^{o}C/min. As expected, no defect was observed on the surface of the stabilized fibers and the corresponding CFs. The tensile strength of the CFs was increased to around 700 MPa.

General discussion: Softwood lignin derived from Japanese cedar by solvolysis pulping with PEG400, which had been considered to be an unsuitable raw material for CF production before this study, could be directly melt-spun into fibers. The fibers could be converted to infusible fibers by chemical thermostabilization or by a combination of chemical curing and oxidative thermostabilization within 3 h. The thermostabilized fibers were, in turn, successfully transformed into CFs with relatively high tensile strength, and then into ACFs with large specific surface area. Thus, I developed a novel process for CF production from Japanese softwood. This current research, therefore, contributes to the effective conversion of by-product from the pulping of softwood into valuable materials, leading to viable refinery of woody biomass.