

# A New Carbon Fiber from Lignin

K. SUDO\* and K. SHIMIZU

Forestry and Forest Products Research Institute, P.O. Box 16, Tsukuba Norin Kenkyu Danchi-Nai, Ibaraki 305, Japan

## SYNOPSIS

A new carbon fiber was prepared from the lignin (steam-exploded lignin), which was isolated from steam-exploded birch wood (*Betula platyphylla*). The lignin was modified to melt thermally on hydrogenolysis. The chloroform soluble and carbon disulfide insoluble fraction (HL) of the reaction products was heated at 300–350°C for 30 min, giving a molten viscous material (HHL). The HHL had a softening point of 110°C and melted at over 145°C to form viscous liquid. When HHL was subjected to a spinning test, according to a conventional fusion spinning method at a speed over 100 m/min, a fine filament could be continuously formed through a pinhole (diameter: 0.3 mm). After the filaments were heated in air at 1–2°C/min up to 210°C, by which time the filament was converted to have an infusible property, the filaments were carbonized by heating from a room temperature to 1000°C at a heating rate of 5°C/min in a stream of nitrogen. The typical properties of the lignin based carbon fiber were as follows: Fiber diameter =  $7.6 \pm 2.7 \mu$ ; Elongation =  $1.63 \pm 0.29\%$ ; Tensile strength =  $660 \pm 230$  MPa; Modulus of elasticity =  $40.7 \pm 6.3$  GPa. The chemical structure of the precursor was remarkably changed from that of the original lignin, indicating the elimination of aliphatic functional groups implied originally in the starting material.

## INTRODUCTION

Carbon fibers are one of the most important engineering materials in various industrial fields. The properties of carbon fibers are characterized as being light-weight with strong mechanical strength. Carbon fibers have, moreover, excellent properties in heat and reagent resistances, shielding effects against radiated electromagnetic interference, and so on. Therefore, carbon fibers have been applied to material for many kinds of engineering products. In 1959, rayon-based carbon fibers were first produced industrially by Union Carbide Corp., USA. Extensive research work was done to find more suitable raw materials for carbon fibers in the UK and Japan. In 1961, Shindo was successful in converting PAN (polyacrylonitrile) into carbon fibers.<sup>1</sup> The mechanical properties of PAN-based carbon fibers were excellent as compared with those of carbon fibers from rayon. Since then, PAN has occupied the prominent position as a precursor for carbon fibers. However, carbon fibers are still expensive. In order to reduce the cost, extensive work has been carried

out to find new precursors for carbon fibers. A new carbon fiber from the molten pyrolysis product of PVC (polyvinylchloride) was prepared by Ohtani.<sup>2</sup> The method suggested the possibility of utilizing tar pitches from oil refinery and coal pyrolysis processes as a new precursor for carbon fibers. Today, pitch-based carbon fibers have been introduced into the market.

Lignin is the second most abundant organic material, after cellulose, in nature. Since lignin is a phenolic polymer, it has potential as an alternative raw material for petroleum for phenolic resin and chemicals, adhesives, etc. Although a large number of works on conversion of lignin to useful materials have been done on hydrocracking, pyrolysis, and derivatization, there are no lignin products produced commercially except for ligninsulfonate, which can be obtained from sulfite pulping black liquor.

Recently, a steam explosion process has been examined as being one of the most promising pretreatment, not only for an enzymatic saccharification of wood polysaccharides,<sup>3,4</sup> but also for the separation of wood components, cellulose, hemicellulose, and lignin.<sup>5,6</sup> We reported that an appreciable amount of lignin in hardwood becomes soluble in 90% dioxane by steam treatment, and that the exploded lignin

\* To whom correspondence should be addressed.

can be converted more advantageously into useful materials as compared with the conventional lignin sources produced by the pulping process.<sup>7</sup>

This article deals with the conversion method of the steam-exploded lignin into molten viscous material as a precursor for carbon fiber. It also discusses the physical properties of the lignin-based carbon fibers. The chemical structure of the modified lignin is discussed and compared with that of original lignin.

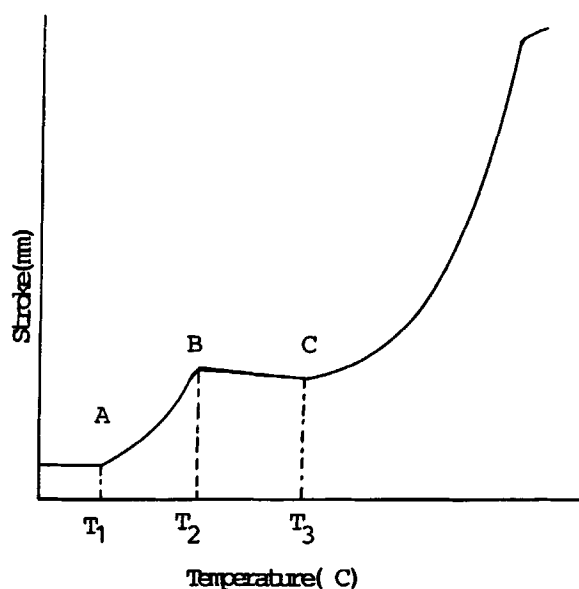
## EXPERIMENTAL

### Preparation of Lignin

The lignin used in this study is a steam-exploded lignin. Birch wood chips were spontaneously flashed into an acceptor after steaming at 203°C (steam pressure: 16 kg/cm<sup>2</sup> in a gauge) for 10 min. The lignin was extracted with methanol from the steam-exploded birch wood and was washed with water to remove the hemicellulose portion. The yield of the extracts was 35.8%, based upon lignin content in the original birch wood.

### Modification of Lignin

The lignin (30 g) was first hydrogenated in the presence of Raney-Ni as a catalyst in 2% NaOH aqueous solution (300 mL) at 250°C for 60 min after



**Figure 1** Typical flow curve of constant heating test. (T1) Starting temperature of softening, (T2) Softening temperature, (T3) Starting temperature of flowing.

introducing H<sub>2</sub> up to 50 kg/cm<sup>2</sup> pressure into a reaction vessel. After cooling, the reaction mixture was filtered to remove the catalyst and was acidified with 2 M HCl. The hydrogenated lignin was extracted with chloroform. In order to remove the low molecular weight of degradation products, the chloroform extracts were subjected to a carbon disulfide extraction at 50°C for 2 hr. The CHCl<sub>3</sub> soluble and CS<sub>2</sub> insoluble fraction of the hydrogenated lignin (HL) was heated to between 300–350°C for 30 min to prepare the precursor in a steam of nitrogen, or under a vacuum.

### Flow Measurement (Viscosity, Rheology Measurement)

The fluidities of lignin and its pitch-like materials were measured using a flow tester (Shimadzu Flow Tester, CFT-500). The flow tester is generally the most common testing machine of a capillary extrusion type for determination of the fluidity of macromolecule materials. A solid sample (1–2 g) is heated in a cell with a pinhole on the bottom, under static load. The molten material, if it has a fluidity, is extruded through the pinhole in capillary form during testing, and a recorder automatically makes a flow curve as shown in Figure 1. In the graph in Figure 1, the axis of the ordinate represents the length (mm) of a piston pushed down by the softening, melting, and extruding of a sample, brought about by heating under loading.

In a flow curve, A, B, and C positions show the points of starting temperature of softening (T1), thermal softening temperature (T2), and starting temperature (T3) of flowing, respectively.

### Spinning of Lignin Pitch (HHL)

An apparatus (Fig. 2) for the spinning of the lignin pitch (HHL) was similar to that used for the spinning test of tar pitch materials by Ohtani.<sup>2</sup> The cell for the melting of the sample has a pinhole (diameter: 0.3 mm) on the bottom. The lignin pitch (HHL) was put into the cell and heated in a stream of nitrogen. The molten HHL was extruded in air through the pinhole as a result of a decrease in viscosity under slight pressure, brought about by a stream of nitrogen; the lignin thread formed was continuously wound on the bobbin (diameter: 10 cm, length: 25 cm) at a speed more than 100 m/min.

### Thermostabilization of Green Fiber

Before carbonization, the fibers were stabilized on heating at a rate of 0.5°C/min to 2.0°C/min to give them an infusible property.

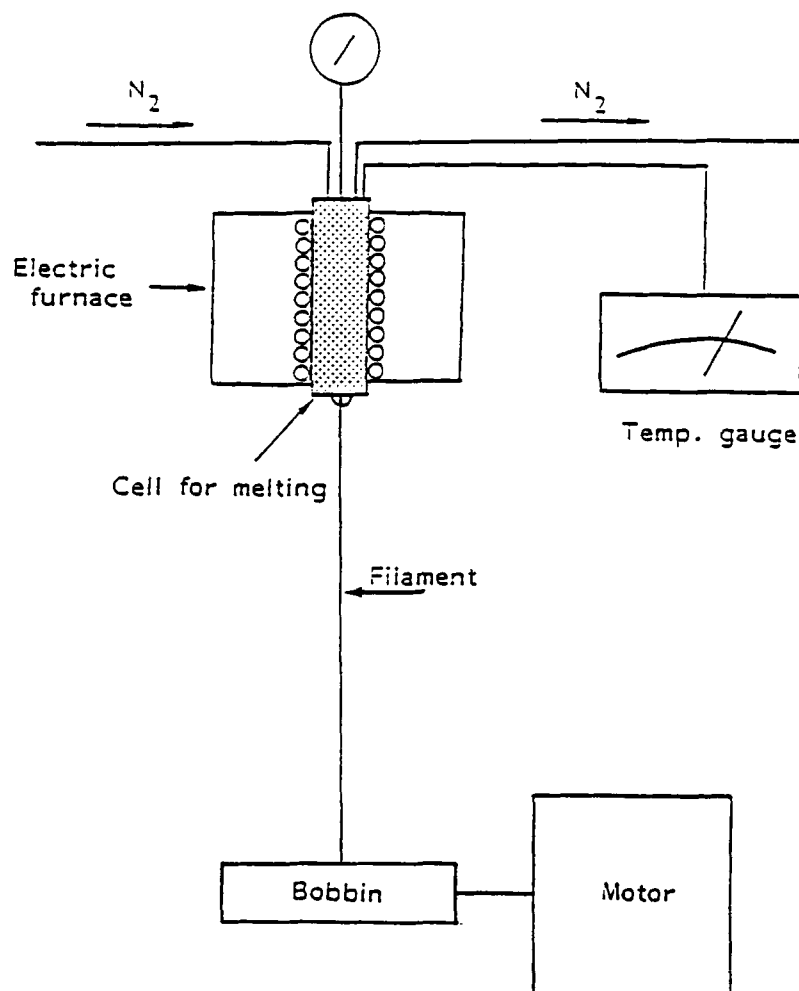


Figure 2 Diagram of an apparatus used for continuous spinning test.

### Carbonization

After the thermostabilization, the fibers were carbonized on heating at a rate of  $5^{\circ}\text{C}/\text{min}$  up to  $1000^{\circ}\text{C}$  in a stream of nitrogen; the maximum temperature was maintained for 20 min. Before heating, air in the electronic furnace was completely replaced with nitrogen.

### Measurement of Thermogravimetric Curve (TG)

A TG run of the lignin pitch was carried out in a temperature range of  $60\text{--}210^{\circ}\text{C}$  at heating rate of  $15^{\circ}\text{C}/\text{h}$  in a stream ( $80\text{ mL}/\text{min}$ ) of air. A Sinko Riko DTG-5000 Differential Micro Thermal Balance was used. The initial weight of the sample was 9–10 mg.

### Measurement of Physical Properties

The mechanical properties of the carbon fibers from the exploded lignin were measured according to the

testing method of carbon fibers (JIS R7601), using a universal tensile testing instrument (Tensilon UTM III-500, Loading capacity: 100 gf, Toyo Baldwin Co., LTD). The diameter of the fiber was measured using an ocular micrometer.

### Gel Permeation Chromatography (GPC)

The GPC experiment was performed on a Toyo Soda HLC-802 LR, equipped with two columns in series, packed with polystyrene gel. The solvent used was tetrahydrofuran (THF). The chromatogram was monitored by a refractometer. The calibration data of molecular weight vs. elution volume was established using polystyrene standards with several kinds of molecular weight.

### NMR Spectroscopy

$^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of modified lignins were recorded at 25.05 MHz on a JEOL FX-100 NMR

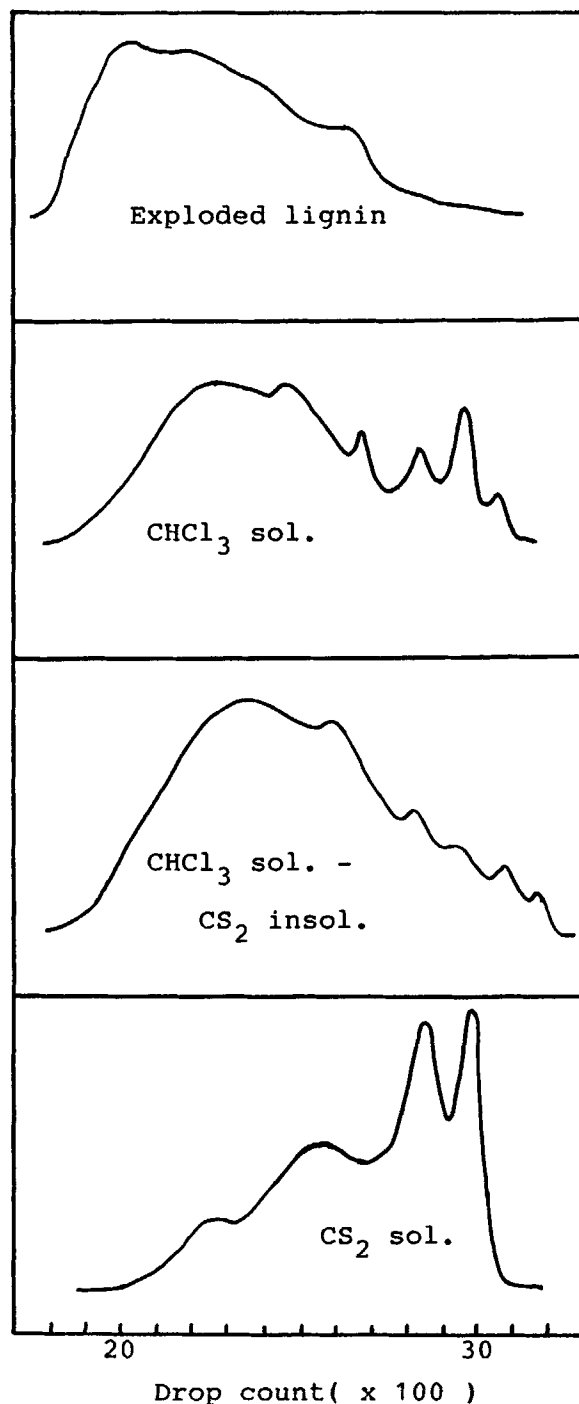
spectrometer at a concentration of 10%, using  $\text{CDCl}_3$  and acetone- $d_6$ / $\text{D}_2\text{O}$  (9 : 1, by volume) as a solvent, respectively.

## RESULTS AND DISCUSSION

The exploded lignin from birch wood (*Betula platyphylla*), steam-exploded at  $203^\circ\text{C}$  for 10 min, was extracted with methanol after removal of the hemicellulose portion by water extraction. The methanol extract was 35.8% based upon Klason lignin in original birch wood. The contents of Klason lignin and acid-soluble lignin in the extract were 81.6% and 6.0%, respectively. The hydrolyzate contained a small amount of xylose: less than 1.0%.

It is well known that lignin is a thermoplastic material. According to Goring's report,<sup>8</sup> the thermal softening temperature of lignin ranges from  $129$ – $193^\circ\text{C}$  in the dry state, depending upon the type of lignin preparation. The thermal properties of the exploded lignin were investigated by means of a flow tester (viscometric, rheological instrument). The lignin started to soften at  $69.1^\circ\text{C}$  and to extrude through a pinhole at  $101.0^\circ\text{C}$  by heating at a heating rate of  $4.0^\circ\text{C}/\text{min}$  under a loading of 10 kgf. The capillary of lignin extruded was, however, extremely brittle. The thermal fluidity of the exploded lignin seems to be brought about by a solvent properties of low molecular weight compounds contained in the methanol extracts. The ether insoluble portion, fractionated according to Bjorkman's method<sup>9</sup> did not show any thermal fluidity, though it started to soften at  $82.0^\circ\text{C}$ . This fact suggests that the low molecular weight of compounds in methanol extracts acts as a solvent for the nonmeltable materials. Therefore, in order to spin the exploded lignin according to the fusion spinning method, the lignin must be modified. In general, a polymer with meltability has a configuration that does not prevent a vigorous molecular rotation to occur by absorbing heat energy. As described above, the lignin essentially does not have any thermal melting property, because lignin is built up by carbon to carbon and alkyl-aryl ether linkages of cinnamic alcohols without any regularity. Therefore, the change of the lignin molecule into the structure with the configuration that allows a molecular rotation, and the removal of functional groups to form cross-linkages with resistance against the occurrence of molecular rotation by absorbing heat energy, would be required. For the above reasons, an alkaline hydrogenolysis was applied to the modification of lignin. It is known that the alkaline hydrogenolysis results in the ex-

tensive cleavage of alkyl-aryl ether bonds and in the formation of ethylene bridges between aromatic nuclei. These results occur because of the reduction of hydroxyl groups and cleavage of hydroxyl methyl groups on the propanoid side chain in the lignin molecule.<sup>10</sup> The hydrogenated lignin, extracted with



**Figure 3** GPC chromatograms of each fraction of hydrogenated lignin separated by solvent fractionation.

**Table I** The Results of Flow Testing of Lignin Pitches

Sample	ST (°C) <sup>a</sup>	SFT (°C) <sup>b</sup>	Viscosity (Poise) <sup>c</sup>
Exploded lignin	69.1	101.0	—
HL	—	70.0	1,444
HHL-300	114.0	145.9	3,899
HHL-330	139.0	170.0	3,899
HHL-340	142.0	173.0	—

(HL) The hydrogenated lignin, (HHL) HL heat-treated.

<sup>a</sup> Softening temperature.

<sup>b</sup> Temperature of the point of thermal flowing.

<sup>c</sup> Viscosity at SFT.

chloroform from the reaction mixture acidified with 2 M HCl, showed a melting point below 50°C. This may have occurred because of the presence of the appreciable amount of the low molecular weight of materials that was newly produced during the hydrogenolysis process. The process can be shown on the GPC curve in Figure 3. The chloroform soluble fraction was extracted with carbon disulfide to remove the low molecular weight of compounds. Hence, the CHCl<sub>3</sub> soluble and the CS<sub>2</sub> insoluble fraction (HL) of the hydrogenated lignin was collected. The yield was 50.9%, based upon starting material. From the calibration data, determined using polystyrene standards with several kinds of molecular weight, it was found that HL has a weight average of molecular weight 950.

In the flow testing, it was observed that HL softened below 50°C and started to draw out continuously to make a fine filament through a pinhole at

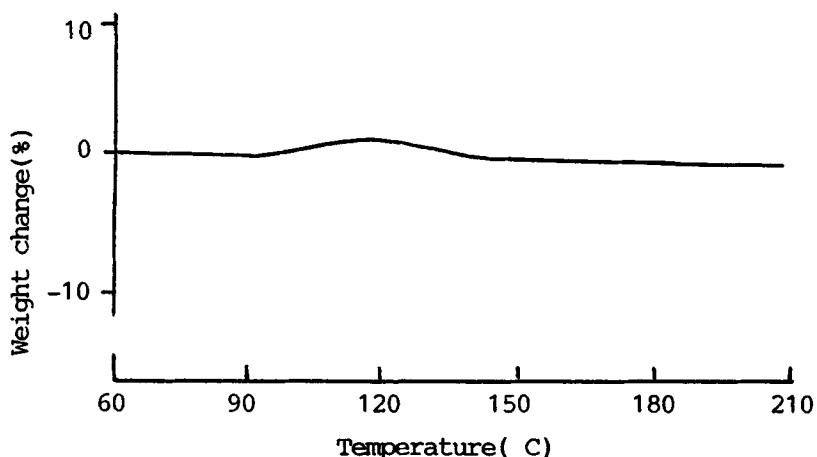
70°C. The extruded, fibrous material solidified immediately in air. The solidified fiber was flexible. However, the HL was difficult to spin continuously into fiber using the fusion spinning method with the apparatus shown in Figure 2. This difficulty is perhaps caused by the low viscosity in the molten state, because the appropriate viscosity of a molten material is required in order to have a stretch and extension, brought about by continuous spinning at a high speed. In addition, the volatile and thermally labile materials, which cause a failure in the successful continuous spinning in molten state because of gasification, must be removed.

To overcome these defects, HL was subjected to a heat treatment at 300–350°C for 30 min in a stream of nitrogen, or under vacuum. The hydrogenated lignin was converted to a pitch-like material (HHL). The HHL was a bright black solid at room temperature.

As shown in Table I, the temperatures of softening and the thermal flow of the lignin pitches increased with increasing temperature in the heat treatment. The yields of lignin pitches prepared at 330°C and 340°C were 77.6% and 77.4%, respectively.

The lignin pitches prepared by heating at 300°C, 330°C, and 340°C spun well into fine filaments at a speed of more than 100 m/min in the temperature range of 155–180°C using the melt-spinning method.

The spinnability of lignin pitches would be given by the increase of the viscosity brought about during the heat treatment. In HHL-300 and HHL-330, their viscosities increased to about 3900 at the starting temperatures of their thermal flowing [from about 1400 in the case of HL (Table I)]. The viscosity of



**Figure 4** Thermogravimetric curve of lignin pitch, HHL-330. Heating rate: 15°C/h, N<sub>2</sub> stream: 80 mL/min.

**Table II Mechanical Properties of Carbon Fiber from Exploded Lignin**

Fiber diameter	$7.6 \pm 2.7 \mu$
Elongation	$1.63 \pm 0.19\%$
Tensile strength	$660 \pm 230 \text{ MPa}$
Modulus of elasticity	$40.7 \pm 6.3 \text{ GPa}$

the molten viscous material must be one of the most important factors of the continuous spinning property. It is interesting that HHL-300 and HHL-330 have the same viscosities at starting temperature of thermal flowing, even though these temperatures are different from each other.

The green fibers from the lignin pitch (HHL) were converted by heating  $60^\circ\text{C}$  to  $210^\circ\text{C}$  at a heating rate of  $1\text{--}2^\circ\text{C}/\text{min}$ , in air, into an infusible fiber. In general, the thermostabilization of green fibers is performed by cross-linkages formed during heating in air. This is an oxidation reaction. According to Ohtani's report,<sup>2</sup> the heat treatment required to give the green filament from PVC molten pyrolysis products an infusible property, which was carried out in oxidizing atmosphere containing ozone, resulted in an increase of 8.6% of the filament by weight. On the contrary, the behavior of the green fibers from HHL was different as shown in the thermogravimetric (TG) curve. As shown in Figure 4, the weight of HHL-330 began to increase at  $70^\circ\text{C}$ , to the maximum increase of 0.8% at  $120^\circ\text{C}$  by weight, then it went back to the starting level of  $140^\circ\text{C}$ . Above  $140^\circ\text{C}$  there was no weight change. This change suggests that at the first stage of the thermostabilization process, the lignin-based green fibers introduce oxygen into the air, though the green fibers contain about 24% oxygen in their molecules themselves. Therefore, both oxygen in air and in the

**Table III Elemental Analysis of Lignin Pitches Prepared by Hydrogenolysis Followed by Heat Treatment**

Sample	Heat Treatment		C (%)	H (%)	H/C
	Temp. ( $^\circ\text{C}$ )	Time (min)			
HL	—	—	65.70	6.28	1.14
A	240	540	70.96	6.16	1.03
B	300	30	69.48	6.26	1.07
C	330	30	69.37	6.20	1.06
D	360	30	69.95	5.72	0.98
E	400	10	73.37	4.85	0.79

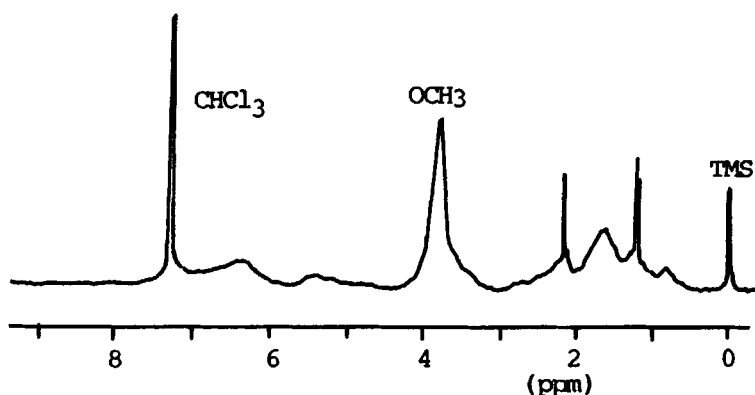
(HL) The lignin hydrogenolyzed in an alkaline solution in the presence of Raney-Ni at  $250^\circ\text{C}$  for 60 min.

molecule seem to contribute to the formation of cross-linkages during thermostabilization.

The thermoset, lignin-based fibers were successfully carbonized by heating from room temperature up to  $1000^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$  heating rate in a stream of nitrogen. The yield was 50–55% based on the stabilized green fiber. Accordingly, the yield of the carbon fiber was 15.8–17.4% based on the starting material, assuming that the yield in the spinning process is 80%. The weight loss during the spinning process is usually about 20%.

As shown in Table II, the tensile strength of the carbon fibers was about 0.66 GPa, indicating that the lignin-based carbon fibers are classified as the so-called "general purpose" grade. The elongation of the fibers was about 1.6%, which means that the carbon fibers are relatively flexible.

It is expected that the chemical structure of the precursor for carbon fibers, produced according to

**Figure 5**  $^1\text{H}$ -NMR spectrum of lignin pitch, HHL-330.

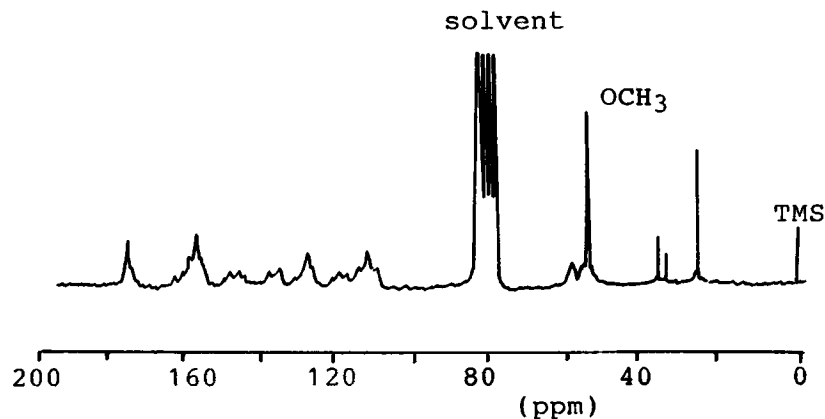


Figure 6  $^{13}\text{C}$ -NMR spectrum of lignin pitch, HHL-330.

the modification reactions, will be remarkably different from that of the original lignin. From the elemental analysis of lignin pitches, which was prepared from the hydrogenated lignin by heat treatment under various conditions, relative amounts of carbon and hydrogen were in the ranges of 69.37–73.37% and 4.85–6.26%, respectively (Table III). These lignin pitches are different from each other in spinnability and in their thermosetting properties in the fibrous form. The lignin pitches A, B, and C could be easily spun at a speed greater than 100 m/min, whereas D and E were difficult to spin continuously. The difficulty of continuously spinning D and E was caused by their high viscosity in the molten state. On the other hand, the fibers from lignin pitches A and C could be converted to infusible property by heat treatment, but not in the fibers from B. Ohtani has reported that the precursor for carbon fibers prepared from tar pitches, which has suitable properties for continuous spinning and thermosetting, would be distinguished in chemical composition so that the atomic ratio of H to C is in the narrow range, 1.06–1.09.<sup>11</sup> The atomic ratio of lignin pitches, H/C, is in the range of 0.79–1.07. The atomic ratios, H/C, of the lignin pitches A and C, which have suitable properties for the spinning and thermosetting of green fibers, were 1.03 and 1.06, respectively (Table III). Therefore, it is considered that the precursor for carbon fiber from the exploded lignin could be distinguished extremely well by the chemical composition.

In the spectrum of  $^1\text{H}$ -NMR of HHL-330 (Fig. 5), it is observed that the relative amount of aromatic hydrogen is much lower than aliphatic hydrogen. From signals in the range of  $\delta$  1.5–3.0 ppm it is indicated that the lignin pitch, HHL-330, contains at least the methyl, methylene, and propane

groups on the benzene ring. It is assumed that some of them exist in the structure as a bridge between aromatic rings, or as a cyclic form attached to aromatic carbon. The presence of phenolic hydroxyl group is clearly indicated in the signal assigned to the methyl protons of the phenolic acetoxy group, but there is no evidence of the presence of the aliphatic hydroxyl group. The presence of aromatic methoxyl group (signal at  $\delta$  3.09 ppm) indicates that the aromatic methoxyl group is extremely stable in the modification reactions. On the other hand, the relative amount of aliphatic carbon is little in comparison with the amount of aromatic carbon, as shown in the  $^{13}\text{C}$ -NMR spectrum of HHL-330 (Fig. 6). The signal pattern in the low magnetic field below 100 ppm, in which signals are assigned to aromatic carbons, is extremely complicated. Therefore, it is assumed that the aromatic rings in HHL-330 are heavily condensed.

## CONCLUSION

A new molten, viscous material, as a precursor for carbon fibers, was prepared from exploded lignin by hydrogenolysis followed by heat treatment. The precursor for carbon fibers was obtained in the yield of about 40% based on the exploded lignin. The carbon fibers, which can be produced in the yield of 15.7–17.4% based on the starting material, is classified to be a so-called “general purpose” grade.

It seems that the structural feature of the lignin pitch would be aromatic polymer, whose benzene rings with the methoxyl and hydroxyl groups are linked to each other by saturated aliphatic groups as a bridge between the aromatic rings and the cyclic form involving aromatic carbons.

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