

Catalytic hydrogenation-assisted preparation of melt spinnable pitches from petroleum residue for making mesophase pitch based carbon fibers

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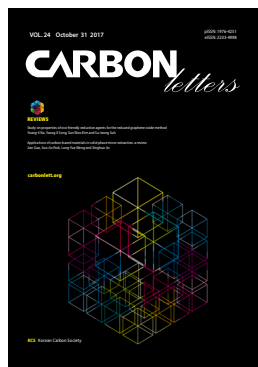
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Abstract

We demonstrated an effective way of preparing melt spinnable mesophase pitches via catalytic hydrogenation of petroleum residue (fluidized catalytic cracking-decant oil) and their subsequent thermal soaking. The mesophase pitches thus obtained were analyzed in terms of their viscosity, elemental composition, solubility, molecular weight, softening point and optical texture. We found that zeolite-induced catalytic hydrogenation under high hydrogen pressure contributed to a large variation in the properties of the pitches. As the hydrogen pressure increased, the C/H ratio decreased, and the solubility in n-hexane increased. The mesophase pitch with entirely anisotropic domains of flow texture exhibited good melt-spinnability. The mesophase carbon fibers obtained from the catalytically hydrogenated petroleum residue showed moderate mechanical properties.

Key words: petroleum residue, hydrogenation, mesophase pitch, spinnability, carbon fiber

1. Introduction

Petroleum is a mixture of a large number of different hydrocarbons in which the most commonly found molecules are paraffins, naphthenes and aromatic compounds. A petroleum refinery is an industrial process plant where crude oil is refined to produce more useful products, such as petroleum naphtha, gasoline, diesel fuel, asphalt, heating oil, kerosene and liquefied petroleum gas [1,2]. In general, petroleum residues are produced as by-products of the petroleum refinery. According to refinery process where they are produced, they are called ethylene bottom oil, fluidized catalytic cracking decant oil (FCC-DO) and asphalt. Typically, petroleum residues are utilized in low value fields, such as low cost fuel, asphalt and bunker C oil. Thus, extensive studies have been carried out to produce high value-added carbon products from petroleum residues. For example, petroleum residues have been examined as good sources of melt spinnable pitch suitable for carbon fiber manufacturing because they have a high carbon content and molecular weight [3-9]. Calculations have shown that the conversion of petroleum residue to carbon fibers increases their value from \$0.6/kg to over \$10/kg [10].

The qualities of the carbon products generally depend on the sources of the petroleum residue. More specifically, the amounts of metals, hetero-atoms, and volatiles within the petroleum residue determine the quality of carbon materials [11]. When petroleum residues are thermally soaked at 400°C under a high flow rate of inert gas, they are transformed to optically anisotropic liquid crystal (or mesophase pitch) [12]. When mesophase pitch is melt spun into a fibrous form, highly ordered structures develop because the mesophase

domains become aligned along the fiber length during the spinning process [13]. Additionally, such alignment is partially enhanced through the carbonization and graphitization steps. The development of a highly ordered structure is directly related to the high modulus, high electrical conductivity and high thermal conductivity of the mesophase pitch carbon fibers. Furthermore, mesophase pitch based carbon fibers exhibit a large variation of cross-sectional textures (e.g., a random structure or a concentric or radial structure), depending on the precursor pitches, their spinning temperature and conditions [13].

Many research groups have developed several ways of synthesizing highly pure, melt-spinnable mesophase pitch to make mesophase carbon fibers at a relatively low cost [14-18]. Mochida et al. [14-16] developed various catalysts, such as HF/BH₃, to synthesize mesophase pitch via catalytic condensation of polycyclic hydrocarbons. Hutchenson et al. [17] developed supercritical fluid extraction as a separation method to improve the reproducibility and quality of the mesophase pitch. Katoh et al. [18] developed a two-step process consisting of heat treatment under high pressure followed by an additional thermal soaking to make mesophase pitch. The properties of mesophase pitch carbon fibers are largely affected by several properties of the pitch (e.g., the content of the mesophase, softening point and degree of hydrogenation). Sato et al. [19] reported a close relationship between the softening point of the pitch and the hydrogen content in the mesophase; as the hydrogen content increases, the softening point decreases, and the thermal stability increases.

It was reported that FCC-DO can form mesophase pitch [20], for which pre-treatment is a critical step to grow the mesophase. Thermal soaking at 400–450°C under hydrogen pressure (7–25 MPa) was developed to thermally crack and catalytically hydrogenate petroleum residues [21,22]. The main function of the hydrogen is to prevent the formation of insoluble coke, thereby suppressing additional side reactions [23]. In addition, the presence of hydrogen under high pressure enhances the fluidity giving much larger domains of mesophase [24]. Thus, it is very important to develop an effective way of producing mesophase pitch with a good spinning ability and high mesophase yield using petroleum residue as a starting material to make a high performance carbon fiber at a relatively low cost.

This study developed an effective way of synthesizing mesophase pitch with an optimized catalytic hydrogenation reaction of petroleum residue (FCC-DO) by adding a zeolite catalyst under various hydrogen gas pressures followed by thermal soaking using a high rate of inert gas. We found that the hydrogenation pressure determined the hydrogen content and rheological properties of the synthesized pitches thereby resulting in the microstructure and properties of the carbon fibers.

2. Experimental

2.1. Hydrogenation of biphenyl

We selected biphenyl (Tokyo Chemical Industry, Japan) as the model compound to examine the catalytic effect of zeolite (Zeolyst CP 787, USA) under hydrogen gas pressure.

2.2. Synthesis of the mesophase pitch

FCC-DO (GS Caltex Co., Korea) was used as a starting material. The synthesis of the mesophase pitch was carried out using a two-step process. First, the catalytic hydrogenation of the petroleum residue (100 g) with the zeolite catalyst (5 g) under various hydrogen gas pressures was achieved in an autoclave. More specifically, the autoclave was thermally heated up to 400°C at a heating rate of 5°C/min and then sustained this temperature for 240 min. Next, the autoclave was cooled to room temperature, and the zeolite was removed by washing with tetrahydrofuran. Second, the reactants in a 500 mL Pyrex flask were thermally soaked up to 400°C at a heating rate of 5°C/min under nitrogen gas at a flow-rate of 800 mL/min.

2.3. Characterizations of the petroleum residue and hydrogenated petroleum residue

The carbon, hydrogen, sulfur and nitrogen contents were determined with a Thermo Fisher Flash 2000 elemental analyzer (USA). The amount of oxygen was obtained using a Thermo Quest EA-1110 elemental analyzer. The viscosities of the residue oils before and after the hydrogenation reaction were measured by the Brookfield viscometer at 150°C. The molecular weights of the residual oils were measured by TOF-Mass spectrometer (JMS-S3000 with 349 nm laser line; JEOL, Japan). The tetrahydrofuran (THF)-soluble fraction was deposited onto a 384 spot target plate. Their solubility was measured using the Soxhlet extraction method. We used n-hexane and toluene as solvents. The hydrogenated sample (2 g) and solvent were placed into the thimble. After the Soxhlet extraction, the thimble was dried in a vacuum oven to remove the solvents completely. The weights of the residues were obtained to calculate the solubility of the hydrogenated residue oil for n-hexane and toluene. Thermogravimetric analysis of the residue oils before and after the hydrogenation reaction was done in a temperature range of 30–600°C at a heating rate of 10°C/min under nitrogen (SDTA 841e-TGA analyzer; Mettler Co., Switzerland).

2.4. Characterization of the synthesized mesophase pitches

The softening point of the synthesized pitches was measured using a Mettler FP 90 according to the ASTM D3104 standard procedure. The pitch was first ground using a bowl. Then, the cell containing the ground pitch was heated up to 350°C at a heating rate of 5°C/min. Thermogravimetric curves of the synthesized pitches were obtained in a temperature range of 30–800°C at a heating rate of 10°C/min under nitrogen. Weight gain was measured at 300°C under ambient conditions. The optical texture of the synthesized pitches was analyzed with a Leica DM750P optical microscope.

2.5. Carbon fiber preparation and characterizations

The melt-spun fibers were obtained using a stainless steel spinneret (0.5×0.5 mm, L/D=1). The spinning temperature was set at 40–50°C higher than the softening point of the synthesized

itches, and the nitrogen extrusion pressure and winding speeds were set to 0.5 bar and 300 m/min, respectively. The melt-spun fibers were air-stabilized in an oven under ambient condition by heating them from room temperature to 300°C at a heating rate of 1°C/min and then maintaining this temperature for 60 min. The air stabilized fibers were carbonized up to 800°C at a heating rate of 5°C/min in a horizontal furnace under a nitrogen atmosphere. The surface structures of the carbon fiber were characterized by a Hitachi S-4700 field-emission scanning electron microscope. The Raman spectra were recorded with an in-Via Raman Microscope (Renishaw plc Co., UK) using a visible (514 nm) laser.

3. Results and Discussion

3.1. The catalytic hydrogenation of the residue oil

Zeolite was used as the hydrogenation catalyst for the petroleum residue to obtain the mesophase pitch with a high yield, good spinning ability and moderate softening point below 360°C. Before applying the zeolite to the petroleum residue, we examined the hydrogenation effect of the zeolite by using biphenyl as a model compound because biphenyl represents one of the cyclic hydrocarbons in petroleum residue. A mixture of biphenyl and zeolite was thermally treated up to 400°C with a heating rate of 5°C/min in an autoclave under hydrogen pressure (38 kgf/cm²), and the mixture was kept at this temperature for 240 min. Then, the effect of catalytic hydrogenation using zeolite on biphenyl was verified with the FT-IR measurement (Fig. S1). The newly appeared bands at 2924 and 2962 cm⁻¹ indicated the formation of aliphatic and naphthenic C-H groups in the catalytically hydrogenated biphenyl [7]. These results show that zeolite is highly effective in the catalytic hydrogenation of cyclic hydrocarbons.

Therefore, the catalytic hydrogenation reaction was carried out by thermally treating the petroleum residue and zeolite in an autoclave up to 400°C with a heating rate of 5°C/min and then kept at this temperature for 240 min. under various hydrogen gas pressures (10, 20, and 30 kgf/cm²). We also carried out the same experiment under nitrogen gas pressure (10 kgf/cm²) for a direct comparison. The atomic composition and viscosities of the residue oil and hydrogenated pitches were compared to examine the effect of the catalytic hydrogenation (Table 1 and

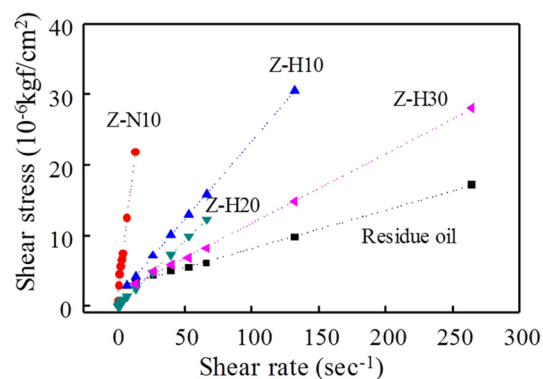


Fig. 1. Shear stress as a function of the shear rate for the pristine residue oil and catalytically hydrogenated pitches using zeolite under high gas pressure. Note that Z indicates the use of zeolite as the hydrogen catalyst; H and N indicate a high hydrogen and nitrogen gas pressure, and the numerical number indicates the pressure of the gas (kgf/cm²).

Fig. 1). We observed a large increase in the C/H mol % of the hydrogenated pitches compared with that of the pristine residue oil indicating that the residue oil experienced chemical reactions under the pressurized thermal treatment. It is interesting to note that the thermally treated pitches under nitrogen gas pressure showed the highest C/H mol % and viscosity compared with those of the hydrogenated pitches. In contrast, with increasing hydrogen gas pressure, we observed a decrease in both the viscosity and C/H mol % in the hydrogenated pitches indicating the effectiveness of the catalytic hydrogenation reaction of the residue oil. To understand in detail the reaction mechanism occurring inside the autoclave, we monitored the inner pressure of the autoclave (Fig. S2). We observed a continuous increase in the internal pressure with the reaction time, which indicated vaporization of the residue oils, i.e., the formation of volatiles. After the reaction of the hydrogenated pitches under hydrogen pressure, the increase in pressure was found to be 6–8 kgf/cm². However, a large increase in the internal pressure (20 kgf/cm²) for the hydrogenated pitches under nitrogen pressure indicated chemical reactions between the residue oils which resulted in the formation of a large amount of gaseous products. This result is quite consistent with the highest viscosity and C/H mol % of the hydrogenated pitch under nitrogen pressure (see Table 1 and Fig. 1).

Table 1. Elemental compositions and viscosities of the pristine residue oil and hydrogenated pitches

Sample	N	C	H	S	O	C/H (mol %)	Viscosity (cP, 150°C)
Residue oil	0.40	86.99	6.55	5.46	0.59	1.11	5.4
Z-N10	0.19	89.81	4.81	2.79	2.40	1.56	153.7
Z-H10	0.60	89.52	5.66	2.63	1.59	1.32	22.1
Z-H20	0.18	89.52	5.72	2.61	1.97	1.30	18.5
Z-H30	0.20	89.35	5.97	3.00	1.49	1.25	9.9

Note that Z indicates catalytic hydrogenation with zeolite. N and H indicate the nitrogen and hydrogen gases, and the numerical value indicates the pressure of the gas (kgf/cm²).

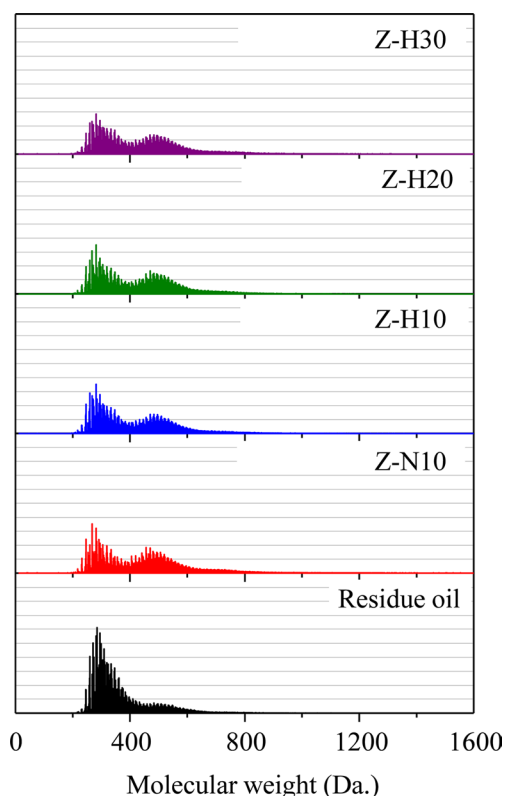


Fig. 2. Time of flight-mass spectra of the pristine residue oil and catalytically hydrogenated pitches using zeolite under high gas pressure. Note that Z indicates the use of zeolite as the hydrogen catalyst; H and N indicate a high hydrogen and nitrogen gas pressure, and the numerical value indicates the pressure of the gas (kgf/cm^2).

To understand the underlying reactions before and after the catalytic hydrogenation reaction, we monitored the change in molecular weight distribution using time of flight (TOP) mass spectrometer (Fig. 2). The pristine residue oil dominantly contained small-sized molecules below 400 Da. However, the catalytic hydrogenation increased the fraction to 400–600 Da indicating that some portion of monomers within the residue oil was chemically changed into dimers or trimers under the pressurized thermal treatment. To examine the change in molecular weight before and after the catalytic hydrogenation, the distribution of the molecular weight was divided into four regions based on the calculated areas, viz. 200 to 400, 400 to 600, 600 to 800 and 800 to 1000 (Table S1). There was no distinctive change in the molecular weight distribution of the hydrogenated pitches when varying the hydrogen pressure. However, the hydrogenated pitch under nitrogen pressure showed relatively higher areas both in the 400–600 and 600–800 regions compared to the hydrogenated one under hydrogen pressure. This result also strongly supports the highest viscosity and C/H mol % of the hydrogenated pitch under nitrogen gas (see Fig. 1 and Table 1). In addition, a solubility test using n-hexane and toluene was carried out to support our claim (Table S2). The residue oil was entirely soluble in hexane. However, we observed a large increase in the hexane insoluble-toluene soluble (HI-TS) portion of the hydrogenated pitches indicating that some of the monomers reacted to form large-

sized molecules under the pressurized thermal treatment. Of note, the hydrogenated pitch under nitrogen pressure showed a higher hexane soluble-toluene insoluble (HS-TI) fraction compared to the hydrogenated pitches under hydrogen pressure. In addition, the hydrogenated pitch under nitrogen pressure contained a toluene insoluble fraction (ca. 17.8%) signifying the largest molecular weight. This result was well-consistent with the results of the molecular weight distribution obtained by TOP-mass spectroscopy (Fig. 2). We also evaluated the change in thermal stability of the residue oil before and after the catalytic hydrogenation using thermogravimetric analysis (Fig. S3). All the samples showed a dominant weight around 300°C. The catalytic hydrogenation substantially decreased the weight loss of the hydrogenated pitches at 400°C compared with that of the pristine residue oil. This result also supports the substantial increase in molecular weight caused by the pressurized thermal treatment. Interestingly, the smallest weight loss at 400°C for the hydrogenated pitch under hydrogen gas of 20 kgf/cm^2 (Z-H20) indicates that the hydrogen pressure should be optimized to control the reactivity of cyclic hydrocarbon within the residue oil under the pressurized thermal treatment.

3.2. The synthesis of mesophase pitch

The synthesis of melt-spinnable mesophase pitch suitable for carbon fiber fabrication was achieved by thermally soaking the hydrogenated pitches to 400°C at a heating rate of 5°C/min and then holding at this temperature for 240 min. under a nitrogen flow. Here, the use of a high flow rate of nitrogen gas (800 mL/min) is critical to remove the low molecular weight species and consequently to commence the formation of the mesophase. As summarized in Table 2, the high yield of the mesophase pitch is critical to reduce the fiber-production cost [14–17] whereas the softening point is closely related with the melt-spinning ability [13]. The mesophase pitches prepared under hydrogen pressure showed a decrease in both the yield and softening point compared with those of the mesophase pitch prepared under nitrogen pressure. However, with increasing hydrogen gas pressure, we observed a large decrease in the softening point. While considering the melt-spinning of the mesophase pitch, it is very important to synthesize a melt-spin mesophase pitch with a softening point below 360°C. This is because in some cases, we observed coke formation from the mesophase pitch with a softening point above 360°C, while in an extreme case, melt spinning of the mesophase pitch with a softening point above 400°C was not possible at all. Even though the mesophase pitch prepared under nitrogen gas showed the highest yield of mesophase pitch (36.4%), its high softening point did not enable us to carry out stable melt-spinning. In contrast, the mesophase pitches prepared under hydrogen pressure had a moderate softening point below 340°C but exhibited a high yield of mesophase up to ca. 30%.

To explain the variation in the softening points of the synthesized mesophase pitches, we measured the molecular weight distributions of the THF-soluble fractions of the mesophase pitches using TOP-mass spectrometer (Fig. 3). It was interesting to note that the fraction of molecular weight below 400 effectively disappeared with the thermal soaking process using a high flow-rate of nitrogen gas. This

result also indicates the importance of low molecular species in the formation of the mesophase pitch. To identify the formation of the mesophase pitch, we obtained polarizing microscope images of the thermally soaked pitches (Fig. 4). For the mesophase pitch prepared under nitrogen gas (Fig.

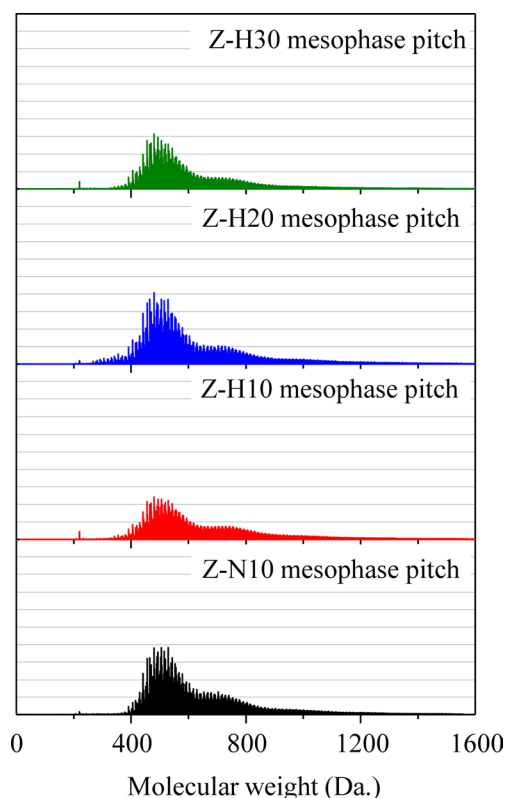


Fig. 3. Time of flight-mass spectra of the thermally soaked mesophase pitches. Note that Z indicates the use of zeolite as the hydrogen catalyst; H and N indicate a high hydrogen and nitrogen gas pressure, and the numerical number indicates the pressure of the gas (kgf/cm^2).

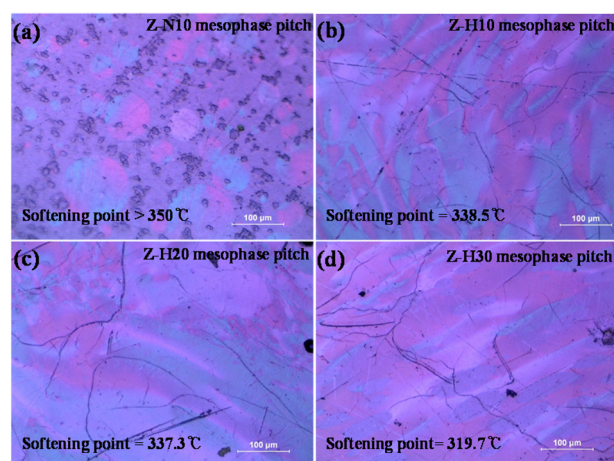


Fig. 4. Polarized optical microscopic images of the mesophase pitches. Note that Z indicates the use of zeolite as the hydrogen catalyst; H and N indicate a high hydrogen and nitrogen gas pressure, and the numerical number indicates the pressure of the gas (kgf/cm^2).

4a), we observed anisotropic spherical droplets with a high degree of molecular order within the isotropic matrix. It was expected that the insufficient fluidity caused by the high molecular weight distribution that originated from excessive polymerization and condensation reactions would perturb the coalescence of anisotropic spherical droplets leading to the formation of the bulk sized anisotropic region in the thermal soaking process. Therefore, we observed a coarse fibrous texture from the mesophase pitches prepared under hydrogen pressure, which indicates their good fluidity related with their low softening points (see Table 2) [25].

3.3. Melt-spun mesophase pitch carbon fibers

With respect to the spinning ability, stable melt spinning of mesophase pitch prepared under nitrogen pressure was very difficult due to its high softening point (see Table 2). Therefore, the mesophase pitches prepared under hydrogen were selected as the melt-spinning dope because of their moderate softening points (ca. 340°C) and completely anisotropic texture. They were successfully melt-spun into fibers using a stainless steel spinneret (0.5×0.5 mm, $L/D=1$) in which the spinning temperature was kept $40\text{--}50^\circ\text{C}$ higher than their softening points, and the nitrogen extrusion pressure and winding speeds were 0.5 bar and 300 m/min, respectively. The good spinning abilities of the mesophase pitches under hydrogen were verified by the formation of a continuous fiber formation [13]. Generally, melt-spun pitch based fibers are highly brittle and difficult to handle. Thus, the melt-spun fibers were air-stabilized in an oven under ambient condition by heating them from room temperature to 300°C at a heating rate of $1^\circ\text{C}/\text{min}$ and then maintaining this temperature for 60 min. Finally, the air-stabilized fibers were carbonized by heating up to 800°C at a heating rate of $5^\circ\text{C}/\text{min}$ in an inert atmosphere. The mass change of the melt spun fibers was monitored in the stabilization and carbonization steps. We observed a large weight gain in the air-stabilized fibers (ca. 8 %) because oxygen atoms diffused into the fibers to induce thermosetting properties [26]. In contrast, a large weight loss of the carbonized fibers at 800°C (ca. 20 %) indicated an increase in the carbon content due to the elimination of non-carbon atoms [26].

Scanning electron microscopic (SEM) studies were also done to observe the macro-morphology of the carbonized fibers obtained from the melt-spinning of the mesophase pitches prepared under hydrogen pressure (Fig. 5). All the

Table 2. The yield and softening point of the mesophase pitches

I.D.	Yield (%)	Softening point ($^\circ\text{C}$)
Z-N10 mesophase pitch	36.4	>350.0
Z-H10 mesophase pitch	30.0	338.5
Z-H20 mesophase pitch	31.0	337.3
Z-H30 mesophase pitch	25.0	319.7

Note that the hydrogenated pitches were thermally soaked at 400°C under a high rate of nitrogen gas flow to develop the mesophase domains.

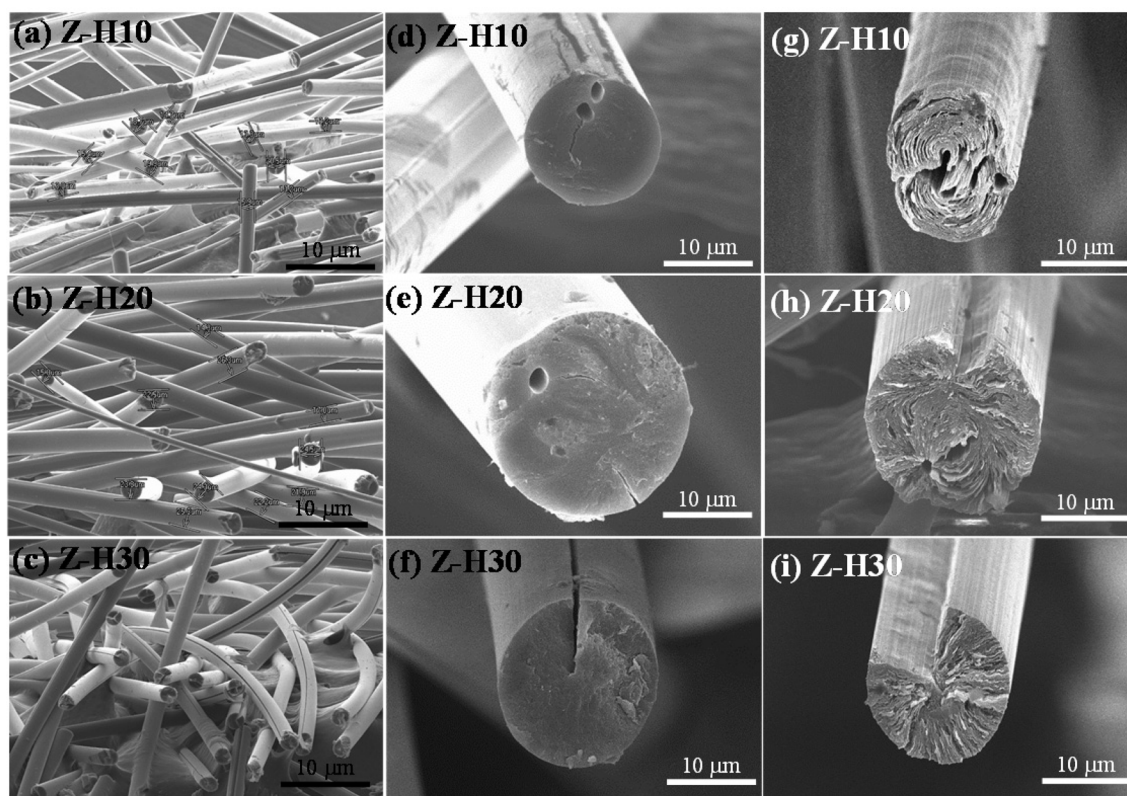


Fig. 5. (a-c) Low resolution and (d-f) cross-sectional scanning electron microscopic images of the carbonized fibers and (g-i) their corresponding graphitized fibers at 2800°C. Note that Z indicates the use of zeolite as the hydrogen catalyst; H and N indicate a high hydrogen and nitrogen gas pressure, and the numerical number indicates the pressure of the gas (kgf/cm²).

mesophase pitch carbon fibers contained a round morphology and exhibited a wide range of diameters from 13 to 26 μm. There were no distinctive defects on the surface of the carbon fibers when observed by the naked eye (Fig. 5a and b). However, cross-sectional SEM micrographs showed large sized holes, which were believed to be formed due to the drastic evaporation of volatiles and also to the presence of entrapped impurities. We also observed long cracks along the fiber diameter direction for the carbon fiber made from the mesophase pitch prepared under a hydrogen gas pressure of 30 kgf/cm² (Fig. 5c). Such cracks can be explained by the anisotropic structural developments in the carbonization step accompanied with densification. To intensify the anisotropic development of the carbonized mesophase pitch carbon fibers, we carried out graphitization at 2800°C using a graphite furnace in an inert gas atmosphere. As shown in Fig. 5d-f, a consecutive change in textures from onion to random to pancake can be explained by the improved molecular mobility with increasing hydrogen pressures.

Finally, we evaluated the mechanical strength of the carbonized mesophase pitch carbon fibers obtained from the mesophase pitch prepared under a hydrogen gas pressure of 10 and 20 kgf/cm². The tensile strengths of the carbon fibers were widely distributed in the range of 400–1000 MPa depending on both the fiber diameter and the entrapped amount of the voids (or cracks) (Fig. 6). With a higher winding speed, we produced carbon fibers with smaller diameters due to the elongation effect

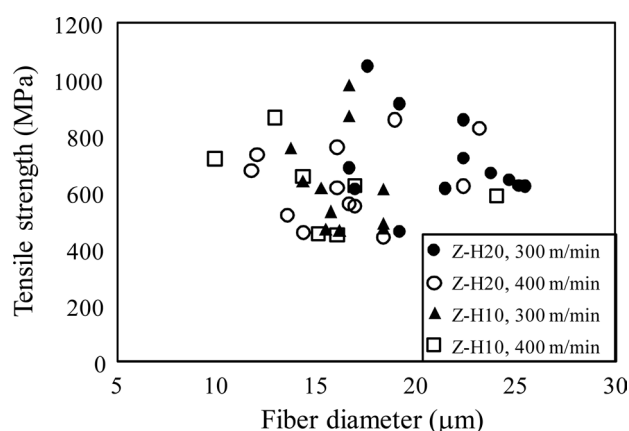


Fig. 6. The distribution of the tensile strength of the carbon fibers prepared at 800°C. Note that Z indicates the use of zeolite as the hydrogen catalyst; H and N indicate the hydrogen and nitrogen gas pressure, and the numerical number indicates the pressure of the gas (kgf/cm²). We used two different winding speeds to obtain the carbon fibers.

along the fiber length direction. Thus, we achieved the best mechanical properties of the mesophase pitch carbon fiber using the mesophase pitch prepared under a hydrogen pressure of 20 kgf/cm² (tensile strength, 1051 MPa; tensile modulus, 104.2 GPa; elongation at break, 0.88). However, the relatively lower mechanical properties of our mesophase pitch carbon fibers

than those of commercially available ones suggest that there would exist a large potential for the thermal conductivity of our mesophase pitch carbon fibers to increase by the optimization of the melt-spinning conditions.

4. Conclusions

In this study, we demonstrated the ability of synthesizing mesophase pitch through the catalytic hydrogenation of petroleum residue with the help of zeolite under a high hydrogen gas pressure and subsequent thermal soaking using a high rate of nitrogen flow. We found that the catalytic hydrogenation suppressed the formation of large-sized molecules, which was essential to synthesize mesophase pitches with a low C/H mol % and high solubility in hexane. Additional thermal soaking using a high flow rate of nitrogen enabled us to prepare the mesophase pitch with flow domains in the optical texture and a moderate softening point (ca. 340°C). Interestingly, the yield of the mesophase pitch was high enough (30%) to reduce the cost of fiber production. In addition, we observed a good spinning ability of our mesophase pitch in a stainless steel spinneret for which the spinning temperature was set at 40–50°C above their softening points due to its moderate softening point as well as its flow-like optical texture. Even though large sized holes in the cross-sectional SEM images and long cracks along fiber length were observed, the mechanical properties of the mesophase pitch carbon fibers we fabricated had a tensile strength and tensile modulus of 1.05 and 104.2 GPa and an elongation at the break of 0.88%, respectively.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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References

- [1] Gary JH, Handwerk GE. Petroleum Refining Technology and Economics, 2nd ed., Marcel Dekker, New York, 31 (1984).
- [2] Leffler WL. Petroleum Refining for the Nontechnical Person, 2nd ed., PennWell Corp., Tulsa, 13 (1985).
- [3] Maeda T, Zeng SM, Tokumitsu K, Mondori J, Mochida I. Preparation of isotropic pitch precursors for general purpose carbon fibers (GPCF) by air blowing: I. preparation of spinnable isotropic pitch precursor from coal tar by air blowing. Carbon, **31**, 407 (1993). [https://doi.org/10.1016/0008-6223\(93\)90127-V](https://doi.org/10.1016/0008-6223(93)90127-V).
- [4] Zeng SM, Maeda T, Tokumitsu K, Mondori J, Mochida I. Preparation of isotropic pitch precursors for general purpose carbon fibers (GPCF) by air blowing: II. air blowing of coal tar, hydrogenated coal tar, and petroleum pitches. Carbon, **31**, 413 (1993). [https://doi.org/10.1016/0008-6223\(93\)90128-W](https://doi.org/10.1016/0008-6223(93)90128-W).
- [5] Park SH, Yang KS, Soh SY. Preparation of partial mesophase pitch-based carbon fiber from FCC-DO. Carbon Sci, **2**, 99 (2001).
- [6] Watanabe F, Ishida S, Korai Y, Mochida I, Kato I, Sakai Y, Kamatsu M. Pitch-based carbon fiber of high compressive strength prepared from synthetic isotropic pitch containing mesophase spheres. Carbon, **37**, 961 (1999). [https://doi.org/10.1016/S0008-6223\(98\)00251-6](https://doi.org/10.1016/S0008-6223(98)00251-6).
- [7] Mochida I, Toshima H, Korai Y, Varga T. Comparative evaluation of mesophase pitches derived from coal tar and FCC-DO. J Mater Sci, **25**, 3484 (1990).
- [8] Mora E, Blanco C, Santamaría R, Granda M, Menéndez R. A novel method to obtain a petroleum-derived mesophase pitch suitable as carbon fibre precursor. Carbon, **41**, 445 (2003). [https://doi.org/10.1016/S0008-6223\(02\)00354-8](https://doi.org/10.1016/S0008-6223(02)00354-8).
- [9] Kim BJ, Kotegawa T, Eom Y, An J, Hong IP, Kato O, Nakabayashi K, Miyawaki J, Kim BC, Mochida I, Yoon SH. Enhancing the tensile strength of isotropic pitch-based carbon fibers by improving the stabilization and carbonization properties of precursor pitch. Carbon, **99**, 649 (2016). <https://doi.org/10.1016/j.carbon.2015.12.082>.
- [10] Yang KS, Kim BH, Yoon SH. Pitch based carbon fibers for automotive body and electrodes. Carbon Lett, **15**, 162 (2014). <https://doi.org/10.5714/CL.2014.15.3.162>.
- [11] Braga CP, Dutra CHMC, Depine de Castro L, Andrade CT. Influence of heat and pressure treatment on the rheological behavior of petroleum pitches. Fuel, **88**, 853 (2009). <https://doi.org/10.1016/j.fuel.2008.10.029>.
- [12] Brooks JD, Taylor GH. The Formation of Some Graphitizing Carbons. In: Walker PI Jr, ed. Chemistry and Physics of Carbon, Vol. 4, Marcel Dekker, New York, 243 (1968).
- [13] Edie DD. The effect of processing on the structure and properties of carbon fibers. Carbon, **36**, 345 (1998). [https://doi.org/10.1016/S0008-6223\(97\)00185-1](https://doi.org/10.1016/S0008-6223(97)00185-1).
- [14] Mochida I, Nakamura EI, Maeda K, Takeshita K. Carbonization of aromatic hydrocarbons: III. carbonization catalyzed by alkali metals. Carbon, **13**, 489 (1975). [https://doi.org/10.1016/0008-6223\(75\)90050-0](https://doi.org/10.1016/0008-6223(75)90050-0).
- [15] Mochida I, Shimizu K, Korai Y, Otsuka H, Sakai Y, Fujiyama S. Preparation of mesophase pitch from aromatic hydrocarbons by the aid of HFBF₃. Carbon, **28**, 311 (1990). [https://doi.org/10.1016/0008-6223\(90\)90005-J](https://doi.org/10.1016/0008-6223(90)90005-J).
- [16] Korai Y, Nakamura M, Mochida I, Sakai Y, Fujiyama S. Mesophase pitches prepared from methylnaphthalene by the aid of HFBF₃. Carbon, **29**, 561 (1991). [https://doi.org/10.1016/0008-6223\(91\)90121-X](https://doi.org/10.1016/0008-6223(91)90121-X).
- [17] Hutchenson KW, Roebbers JR, Thies MC. Fractionation of petroleum pitch by supercritical fluid extraction. Carbon, **29**, 215 (1991). [https://doi.org/10.1016/0008-6223\(91\)90072-Q](https://doi.org/10.1016/0008-6223(91)90072-Q).
- [18] Katoh O, Uemura S, Korai Y, Mochida I. Preparation of mesophase pitch and high performance carbon fiber from decant oil. J Jpn Pet

- Inst, **47**, 100 (2004).
- [19] Sato K, Sato F, Tomioka T. Recent trend of carbon fiber technology from mesophase pitch. *Tanso*, **157**, 107 (1993). <https://doi.org/10.7209/tanso.1993.107>.
- [20] Bagheri SR, Bazyleva A, Gray MR, McCaffrey WC, Shaw JM. Observation of liquid crystals in heavy petroleum fractions. *Energy Fuels*, **24**, 4327 (2010). <https://doi.org/10.1021/ef100376t>.
- [21] Rana MS, Sámano V, Ancheyta J, Diaz JAI. A review of recent advances on process technologies for upgrading of heavy oils and residua. *Fuel*, **86**, 1216 (2007). <https://doi.org/10.1016/j.fuel.2006.08.004>.
- [22] Gray MR. *Upgrading Petroleum Residues and Heavy Oils*, Marcel Dekker, New York, 237 (1994).
- [23] Gray MR, McCaffrey WC. Role of chain reactions and olefin formation in cracking, hydroconversion, and coking of petroleum and bitumen fractions. *Energy Fuels*, **16**, 756 (2002). <https://doi.org/10.1021/ef010243s>.
- [24] Perrotta AJ, McCullough JP, Beuther H. Pressure-temperature microscopy of petroleum-derived hydrocarbons. *Carbon*, **22**, 208 (1984).
- [25] White JL, Price RJ. The formation of mesophase microstructures during the pyrolysis of selected coker feedstocks. *Carbon*, **12**, 321 (1974). [https://doi.org/10.1016/0008-6223\(74\)90073-6](https://doi.org/10.1016/0008-6223(74)90073-6).
- [26] Donnet JB, Bansal RC. *Carbon Fibers*, Marcel Dekker, New York, 55 (1990).