Properties of Precursor Pitch Derived from Petroleum Residue

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Hai Il, Ryu* · Gyu Dong, Lee** · Young Bae, Kwon***

ABSTRACT

Properties of precursor pitch derived from petroleum residue were studied physical and chemical analysis method for investigation of production of pitch fiber. For preparing of those precursor pitches it was carried out a temperature and time variation experiment in reactor. It was demonstrated the precursor pitch prepared in this study to have a similar properties to Ashland precursor pitch capable of bulk mesophase formation from the results of the basic analysis, that is, molecular weight distribution, coking yield, carbon content, chemical composition, etc.

1. Introduction

The use of carbon fibers, such as graphite fibers, in reinforcing plastic and metal matrices has gained considerable commercial acceptance where the exceptional properties of the reinforced composite materials clearly offset the generally high cost associated with preparing them. These carbon fibers have been produced from organic polymer fibers processing is associated with hight cost. If the cost associated with the formation of the fibers could be substantially

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reduced, it is generally accepted that long-scale use of carbon fibers as a reinforcing material would gain even greater acceptance in the market place.

Because of those reasons, the formation of carbon fibers from relatively inexpensive pitches has received considerable attention in recent years. But, those pitches, that is, carbonaceous raw materials, such as petroleum pitch, coal tar pitch, oil-bottom residues are consisted of a variety of different molecular species. It could be broadly classified into four different categories known as saturates, naphthenaromatics, polar aromatics and asphaltenes.

Therefore, in order to produce a carbon fiber that has the requisite stiffness characteristics, the pitches is necessary to thermally transform the carbonaceous raw materials to liquid crystal or the so-called mesophase state during the long period of time, and fractionate by organic solvents. So, use of relatively inexpensive pitch material has not substantially reduced the cost of the formation of carbon fibers.

Recently, there has been discovered a process for forming optically an isotropic pitch in exceedingly short periods of time. For example, Union Carbide Corporation has developed a process for making high modulus carbon fibers from low-cost commercial pitches, that is, A240 pitch, without additional hot-stretching at high temperatures.

The process is based on the new concept that the liquid crystalline phase, produced in aromatic pitches by proper heat-treatment can be oriented by the shear forces which occur during spinning and drawing such pitch into filaments.

In this study, for preparing of precursor pitch capable of making a mesophase pitch, it was carried out a temperature and time variation experiment in large reactor designed specially. Also, carbon contents, coking yields, molecular weight distributions, and chemical compositions of some precursor pitches derived from petroleum residue were investigated with A240 pitroleum pitch.

2. Experimental

The material used in this study was petroleum residue which is a product of Yukong Ltd. Thermal treatment apparatus was especially designed through the data of the small-scale experiment process. The reactor volume is about 20 liters. The thermal treatment was controlled by means of a programmable temperature controller.

The sulfur content and the carbon content in precursor pitch was measured by the use of a sulfur analyzer and a elemental analyzer.

The coking yield and the content of volatile matter was determined by means of a ASTM-(D271-40) method and conradson method, respectively. QI value was determined by the quinoline extraction method.

Molecular weight distributions were determined at room temperature with a Gel Permeation Chromatography equipped with styrachel columns, 100Å-500Å-10³Å-10⁴Å-10⁶Å and a differential refractometer detector. For comparison of molecular weights, polystyren standards obtained
Waters Associates Company and standard pitch were utilized.  

3. Results and Discussion

For relative carbon content, sulfur content, volatile matter, coking yield, QI value, and softening point comparison with A 240 petroleum precursor pitch, the data of G4, G7, G12, and G14 precursor pitch which was made of petroleum residue are shown in table 1.

Table 1. The basic analysis of precursor pitches.

<table>
<thead>
<tr>
<th>Precursor pitch</th>
<th>Carbon content (wt%)</th>
<th>Sulfur content (wt%)</th>
<th>Volatile matter (wt%)</th>
<th>Coking Yield (wt%)</th>
<th>Q I (wt%)</th>
<th>softening point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G 4</td>
<td>91.4</td>
<td>0.24</td>
<td>43.26</td>
<td>48.85</td>
<td>0.62</td>
<td>97</td>
</tr>
<tr>
<td>G 7</td>
<td>92.3</td>
<td>0.20</td>
<td>39.06</td>
<td>50.49</td>
<td>1.13</td>
<td>97</td>
</tr>
<tr>
<td>G 12</td>
<td>91.5</td>
<td>0.18</td>
<td>35.52</td>
<td>55.07</td>
<td>0.55</td>
<td>155</td>
</tr>
<tr>
<td>G 14</td>
<td>93.9</td>
<td>0.20</td>
<td>32.00</td>
<td>53.45</td>
<td>0.35</td>
<td>178</td>
</tr>
<tr>
<td>A 240</td>
<td>93.3</td>
<td>2.19</td>
<td>36.30</td>
<td>55.10</td>
<td>0.10</td>
<td>112</td>
</tr>
</tbody>
</table>

These carbonaceous materials contain a large amount of carbon content, which are similar to the carbon content of A240 petroleum pitch.

G4, G7, G12, and G14 precursor pitch have about 0.24wt%, 0.20wt%, 0.18wt% and 0.20 wt% in each sulfur content. These values represent less than that of A240 petroleum pitch, especially A240 petroleum pitch appears to about 2.19wt% of sulfur content.

The content of volatile matter represents near 36wt% in all the pitches, also the coking yield appears about 53wt% in all the pitches. QI value of G7 precursor pitch is 1.13wt% and other precursor pitches have below 0.6wt%. Softening point depends greatly upon the content of isotropic phase and anisotropic phase in precursor pitch that thermally heat-treated. Herein, softening point of G4 and G7 precursor pitch have the same value and G14 precursor pitch have the most value among the precursor pitches.

It is important to investigate the chemical composition and molecular weight distribution in precursor pitch. For such work G7 precursor pitch among the four kinds of precursor pitches was selected. In Fig. 1, extraction stages and solubilities were represented with block diagram form.

Both A-series extraction stage and B-series extraction stage have a high solubility in the first stage when the solubilities are compared with one another. On the other hand, from the second stage to the fifth stage represent less solubilities as was seen in Fig. 1. The A₁ fraction and B₁ fraction will contain compounds with low molecular weights because of doing by the sequential extraction method. And the A₅ fraction and B₅ fraction will contain high molecular weights.

Generally, their fractions differ from one another mainly in terms of their molecular weight.
Properties of Precursor Pitch Derived from Petroleum Residue

<table>
<thead>
<tr>
<th></th>
<th>Solubility</th>
<th>A series</th>
<th>B series</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>48%</td>
<td>$A_4$ fraction</td>
<td>$B_1$ fraction</td>
<td>44%</td>
</tr>
<tr>
<td>Solubility</td>
<td>5.2%</td>
<td>$A_5$ fraction</td>
<td>$B_2$ fraction</td>
<td>10.2%</td>
</tr>
<tr>
<td>Solubility</td>
<td>1.5%</td>
<td>$A_5$ fraction</td>
<td>$B_3$ fraction</td>
<td>6.1%</td>
</tr>
<tr>
<td>Solubility</td>
<td>9.4%</td>
<td>$A_4$ fraction</td>
<td>$B_4$ fraction</td>
<td>5.4%</td>
</tr>
<tr>
<td>Solubility</td>
<td>4.5%</td>
<td>$A_6$ fraction</td>
<td>$B_5$ fraction</td>
<td>2.2%</td>
</tr>
<tr>
<td>final Insoluble</td>
<td>31.4%</td>
<td></td>
<td>final Insoluble</td>
<td>32.1%</td>
</tr>
</tbody>
</table>

Fig. 1 Solubilities and sequential extraction steps for G7 precursor pitch

and degree of aromatic character. Saturates, for example, are paraffinic compounds, while naphthenic material is composed largely of cyclized paraffines. On the other hand, polararomatics are made up of lower molecular weight substituted by polynuclear aromatics and heterocyclics. While the asphaltenes are higher molecular weight, highly aromatic compounds of carbonaceous materials.

We can determine directly molecular weight distributions on the concentration of solute in each fraction of A-series and B-series by means of Gel Permeation Chromatography. That is, the differential signal intensities and elution volume values obtained on a given fraction, together with previously determined molecular weight data relating to the various chromatographic fractions of standard pitch can be processed by a computer. Also, since the magnitude of these differences in signal intensity is linearly related to the concentration by weight of solute molecu-
cules present, the relative concentration by weight of molecules in each fraction can be determined by dividing the differential signal intensity for that fraction by the total integrated differential signal intensity of all the fractions.

This relative concentration may be graphically depicted by a plot of the differential signal

Fig. 2 Molecular weight distributions for A-fractions of G7 precursor pitch determined by Gel Permeation Chromatography

Fig. 3 Molecular weight distributions for B-fractions of G7 precursor pitch determined by Gel Permeation Chromatography
intensity for each fraction against the accumulative elution volume of the fraction. By this procedure, complete printouts are routinely provided of number average molecular weight, $\bar{M}_n$, and weight average molecular weight, $\bar{M}_w$.

Chromatograms for A-fractions are shown in Fig. 2. In figure 3, it was shown chromatograms for B-fractions of G7 precursor pitch. As we can see in Fig. 2, in the direction from the $A_1$ fraction to the $A_5$ fraction molecular weight represented the high molecular weight distributions. Number of average molecular weight, $\bar{M}_n$, calculated is 831 g/mole in the $A_1$ fraction, 872 g/mole in the $A_2$ fraction, 935 g/mole in the $A_3$ fractions, 1232 g/mole in the $A_4$ fraction, and 1322 g/mole in the $A_5$ fraction.

In the case of the B-series fractions, it was observed to have the lower content of carbonaceous material than the A-series fractions over all of the chromatograms from the $B_1$-fraction through the $B_5$ fraction.

The size of molecular weight indicates the amount of the concentrated high molecular weight. Number average molecular weight, $\bar{M}_n$, of the $B_1$-fraction is 704 g/mole, the $B_2$-fraction 889 g/mole, $B_3$-fraction 983 g/mole, the $B_4$-fraction 958 g/mole, and the $B_5$-fraction 1083 g/mole, respectively.

Table 2. Molecular weight analysis of precursor pitches derived from petroleum residue.

<table>
<thead>
<tr>
<th>precursor pitch</th>
<th>data</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>dispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>4</td>
<td>510</td>
<td>512</td>
<td>1.00</td>
</tr>
<tr>
<td>G</td>
<td>7</td>
<td>545</td>
<td>562</td>
<td>1.03</td>
</tr>
<tr>
<td>G</td>
<td>12</td>
<td>557</td>
<td>581</td>
<td>1.04</td>
</tr>
<tr>
<td>G</td>
<td>14</td>
<td>267</td>
<td>320</td>
<td>1.20</td>
</tr>
<tr>
<td>A</td>
<td>240</td>
<td>585</td>
<td>739</td>
<td>1.26</td>
</tr>
</tbody>
</table>

In table 2, it was shown the molecular weights and dispersities of precursor pitches derived from Korean petroleum residue with A-240 petroleum pitch. As we were discussed above, for separation the carbonaceous material into suitable molecular weight distribution it is suggested that the A-series fraction method is better than the B-series fraction method. Also the A-series fractions have narrow molecular weight distributions than the B-series fractions.

The chemical composition of the A-series fractions were also examined by Infrared Spectrophotometer, and the infrared spectra are shown in Fig. 4, and for comparison the A-series fractions with spectrum of a pure aromatic compound is illustrated on the bottom of fig. 4.

The spectra are almost the same for all types of the A-series fractions. In the case of the $A_1$ fraction, the absorbance of the absorption band at 2920cm$^{-1}$ corresponding to the aliphatic C-H band is larger than that of the absorption at 3030cm$^{-1}$ assigned to the aromatic C-H band. 3) But, in the case of the $A_5$ fraction, that of the absorption at 3030cm$^{-1}$ is larger than that of the absorption band at 2920cm$^{-1}$. Also, the absorption bands at 1600cm$^{-1}$ are assigned the methyl and methylene bending peak. The absorption band at 860cm$^{-1}$ 4) 815cm$^{-1}$ assigned to the
Fig. 4 Infrared spectra of the A-series fractions and a pure aromatic compound.
isolated aromatic hydrogen is especially strong in the f-spectrum, pure aromatic compound having three ring, but the a-, b-, c-, d-, and e-fraction spectra are moderate.

As it is shown in fig. 4, the aliphatic content is very low in the d-, and e-fraction. It is indicated that the samples were composed of highly condensed aromatic ring structures.

The reflected polarized-light micrographs of G7 precursor pitch and its THF-free fraction are shown in fig. 5. The mesophase texture of G7 precursor pitch formed at 418°C was of the flow type. The mesophase texture was changed from the flow type to the bulk type during heat-treatment to 458°C. The THF-free fraction of G7 precursor pitch formed large bulk mesophase at 480°C. These phenomena are suggested that the G7 precursor pitch can be formed to 100% mesophase pitch without any extraction experiment, and the pitch could be spun into carbon fibers having high modulus and high strength.

Carbonaceous materials from petroleum residue were heat-treated to coke forming temperatures. The pyrolyzed precursor pitches were compared with the microstructure of A240 pitch in fig. 6. In coke yield, carbonaceous materials containing high molecular weights will be high values because the starting materials have fewer alkyls and more aromatic. The coke yield and
mesophase forming tendencies of these materials is apparently controlled by the alkyl groups on the asphaltenes.

Therefore, the pyrolysis behavior of the precursor pitch reflects the range of molecular species present in the initial material.
As it is shown in fig. 6, the microstructures of the G4 and G7 precursor pitch are similar to that of A240 pitch. Therefore, from the results of the mesophase formation experiment in fig. 5 and the coke experiment in fig. 6 the G7 precursor pitch shows to contain higher condensed aromatic molecules capable of forming excellent mesophase pitch than other precursor pitches.

4. Conclusions

It is reduced to the following conclusion from the results of the basic analysis, molecular weight distributions and the chromatograms, coking yields and the photographs, and formation process and orientation of optically anisotropic mesophase spheres of the precursor pitches derived from petroleum residue in this study. It was prepared, that is, a precursor pitch having similar properties to A240 precursor pitch by us.

References

4) Hoover, Davis, Perrotta, Spackmann, "Extended Abstracts of 14th Biennial American Conference on Carbon", (1979)