Suitable pitch materials for MP carbon fiber

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In the previous papers,[1,2] it has been reported that carbon fibers were prepared from polyvinylchloride (PVC) pitch, petroleum asphalt, coal tar pitch and other pitch-like materials. We refer to the fiber so produced as MP carbon fiber. The suitable pitch materials for MP carbon fiber requires at least two characteristics, that is, an excellent spinnability and an ability to be easily converted into an infusible form by oxidation at the low temperature range. Above raw materials themselves other than PVC pitch leave much to be desired. Some special treatments, therefore, have been required to achieve the desirable characteristics. The present investigation was undertaken in order to determine the chemical structure of the each suitable pitch material prepared from petroleum asphalt and coal tar pitch and to define the significance of the special treatments.

The starting raw materials and the special treatments used in the present experiment were as follows:
(1) Petroleum asphalt -- The asphalt was dry distilled at 380 C for one hour by bubbling nitrogen gas and then heat-treated under vacuum at 300 C for 2 hours. (2) Coal tar pitch -- Five % of tetra-methyl-thiurum-disulfide (TMTD) was added to the soluble fraction in chloroform (yield 86 %) of the raw material and the mixture was heated at 150 - 200 C for 6 hours and then heated under vacuum at 300 C for 2 hours. (3) PVC pitch -- The sample was the pyrolyzed residue itself prepared at 400 C under nitrogen from PVC powder and it was used without any further treatment.

The pitch materials at each stage of the above special treatments were fractionated by extraction in turn with n-hexane, carbon disulfide and chlorofoem. In order to investigate the nature of each fraction obtained, use was made of N.M.R., I.R. and U.V. spectra as well as elemental analysis and measurement of mean molecular weight with VPO method.

PVC pitch The major portion (94.1 %) of this pitch is the n-hexane-insoluble and carbondisulfide-soluble fraction which we refer to as "CS" fraction. This fraction exhibits 970 of mean molecular weight. On the basis of N.M.R. spectra, the atomic ratio of aromatic hydrogen vs. aliphatic hydrogen (Haro/Hali) is about 40/60. Other results obtained in the present experiment were essentially identical to that previously reported. These results lend some support with minor correction to the formula suggested before.[1]

Petroleum asphalt The variation observed through out the above treatment process were as follows: (a) The yield was 50 % at the stage of distillation and 60 % at the final stage. The mean molecular weight of the raw asphalt, the distillation residue and the residue finally obtained are 840, 850 and 1530 respectively. (b) The "CS" content, 31 % in the original, increases up to 73 % and the n-hexane-

soluble fraction "Hx" content, 69 % in the original, decreases to 27 %. (c) Haro/Hali atomic ratio of "CS", 9/91 in the original, increases to 15/85 and the mean molecular weight, 3050 in the original, decreases to 2350. Haro/Hali ratio and the mean molecular weight of "Hx" are about 4/96 and 650 respectively through out the whole process, and the content of methyl hydrogen against the total aliphatic hydrogen of "HX", 22 % in the original, decreases to 11 % at the stage of distillation. (d) The H/C atomic ratio, 1.36 in the original, decreases to 1.09. (e) U.V. spectra exhibit the presence of aromatic plane structures with three or four rings members.

In view of the above results, it has beđn found that the dominant roles of the treatment are to increase the mean molecular weight and aromaticily of the molecules. And it seems reasonalbe to consider that the suitable pitch finally obtained are characterized by consisting of many different hydroaromatic structural units, which contain the polynuclear aromatic part with three of four rings members, and great amounts of aliphatic carbon chains.

Coal tar pitch The raw pitch, which exhibits the H/C atomic ratio of 0.62 and the mean molecular weight of 340, is separated by extraction into "Hx" (15 %), "CS" (60 %), the carbondisulfide-insoluble and chloroform-soluble fraction "CH" (11 %) and the insoluble fraction (14 %). The mean molecular weight of each fraction is 215 ("Hx"), 350 ("CS") and 500 ("CH") respectively.

The above treatments gave the following variations. (a) The yield was 90 % at the stage of the treatment with TMTD and 35 % at the final stage. (b) By the first treatment, "CS" content decreases by 9 % and "CH" content increases by 10 %. By the final treatment, "Hx" content decreases by about 14 % and the insoluble fraction content increases by 8 %. The pitch finally obtained consists of 1.4 % of "Hx", 52 % of "CS", 26 % of "CH" and 21 % of the insoluble fraction. (c) The mean molecular weight of each fraction increases gradually. (d) The H/C atomic ratio, 0.62 in the original, decreases to 0.54. Haro/Hali atomic ratio are about 80/20 through out the whole process. (e) U.V. spectra exhibit the presence of aromatic compounds with rings members from two to seven, mainly four or five.

On the basis of the above and other results, it seems that the treatments promote the increase of the mean molecular weight together with the removal of the low molecular weight components. And one might conclude that the pitch finally obtained consists of many different molecules which contain some polynuclear aromatic compounds of such condensed type as perylene or coronene substituted by only a few methyl groups in a molecule.

Reference

1) S. Ohtani, Carbon , 3, 31 (1965)
2) S. Ohtani, K. Yamada, T. Koitabashi and A. Yokoyama, Carbon, 4, 425 (1966)