CHEMICAL- AND MESOPHASE-FORMING CHARACTERISTICS FOR AN EXTRACT FROM HYDROTREATED COAL

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Introduction

The extraction of hydrotreated coal with N-methylpyrollidone (NMP) solvent has been shown to produce pitch-like products which can be transformed into mesophase and anisotropic coke [1]. We have chemically characterized and studied the mesophase formation for several of these extracts, and found that the anisotropic domain size can be related to the degree of coal hydrotreatment. In this presentation, we describe the mesophase development and chemical properties for the NMP extract of an extensively hydrotreated coal. This extract had also been converted to coke, and we produced a graphite artifact using the coke as a filler and the extract pitch itself as a binder.

Experimental

The coal extract material was obtained from the West Virginia University (WVU) group and was produced by NMP extraction of a bituminous coal that had been hydrotreated at 450°C for 2 hours. We carried out a variety of analytical measurements on the material.

Direct observations of the melting behavior, gas evolution characteristics, and mesophase formation rate were made by heating the extract on a microscope hot stage at 400°C. The domain size for the coalesced mesophase was also determined quantitatively using a published procedure [2].

Results and Discussion

A. Analytical Characterization

The properties measured for the extract material are summarized in Table I.

Table I
Properties of Coal Extract

Soft. Pt., °C	105
MCC, Wt. %	53
% C	88.9
% H	5.85
Atomic C/H Ratio	1.28
% N	2.20
% O	2.74
% S	0.45
% Aromatic H (NMR)	45
Avg. Mol. Wt. (GPC)	367

The softening point of 105°C and MCC of 53% are in the range of values for commercial binder and impregnating pitches. From the elemental analysis data, it is evident that the extract has very high N and O contents.

Multiple bands from 1 to 4 ppm in the proton NMR spectrum for the extract demonstrate the presence of extensively hydrogenated aromatic rings that were generated during the coal hydrotreatment. The GPC molecular weight measurement showed the extract to contain a broad distribution of species with molecular weights ranging from 250 to 630 daltons with a number average molecular weight of 367 daltons.

B. Mesophase Development

The extract began to soften at about 104°C during heat up and developed anisotropic spheres after 25 minutes at 400°C. Pyrolysis gases were continuously evolved during the initial portion of the heat treatment.

In a separate experiment, the extract was heat treated at 400°C to produce a mesophase pitch containing about 50% mesophase. After annealing, the average mesophase domain size was measured by optical image analysis as 272 μ. This extremely large domain size, which is characteristic of very highly graphitizing precursors, is rather surprising for a material with such a high oxygen content.

C. Analysis of Derived Mesophase Pitch

We further characterized the mesophase pitch formed from the extract to determine what chemical changes occurred during the heat treatment process. The elemental analysis data measured for the mesophase pitch were the following: % C = 92.6; % H = 4.37; C/H = 1.78; % N = 1.89; % O = 1.35. A comparison of these results with those for the precursor in Table I, demonstrates that substantial dehydrogenation had occurred during the mesophase heat treatment. Additionally, both the O and N contents had decreased significantly, but still remained high compared to conventional coal tar-based materials.

In an effort to identify the types of functional groups that might be present in the extract materials, we measured FTIR spectra for both the extract and the derived mesophase pitch. The spectrum for the extract is shown in Figure 1 and contains bands at 3260 cm^{-1} and at 1664 cm^{-1} which could be attributed to OH groups and carbonyl groups, respectively. The oxygen functionality could, therefore, be present in the form of aromatic carboxylic acid groups. An alternate interpretation is to postulate the presence of aromatic phenols and quinones, but these functionalities usually do not produce a well-ordered mesophase. It was difficult to obtain a well-resolved FTIR spectrum of the mesophase pitch, however, the absorption intensities for the 1664 cm^{-1} and 3260 cm^{-1} bands appeared to be appreciably decreased.

D. Graphite Fabrication

We produced 19 mm-diameter extruded graphite rods using the original extract pitch as a binder and a calcined coke that had been prepared from the extract by the WVU group as the filler. Properties measured for the graphite artifact were the following: Coefficient of Thermal Expansion (CTE) = 0.26 x 10^{-6}/°C and Electrical Resistance = 9.55 micro ohm-meters.

Conclusions

Our studies show that the NMP extraction of hydrotreated coal can produce a pitch product which forms a very large-domain mesophase and a well-ordered coke. This result is achieved despite a high content of oxygen-containing groups. The very low CTE value for the extract coke is consistent with the large mesophase domain size and indicates that the hydrotreated extract could be a suitable precursor for graphite electrode-type coke.

Acknowledgments

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References

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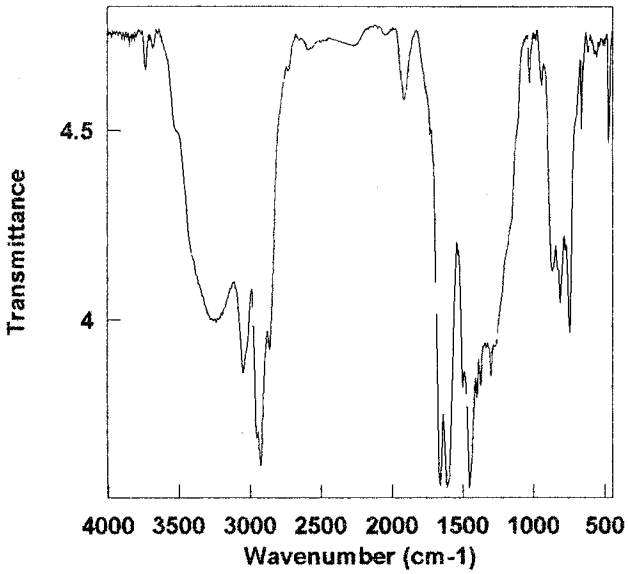

Figure 1. FTIR for extract of hydrotreated coal.