PREPARATION AND PROPERTIES OF NONGRAPHITIZING PITCHES

by

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I. INTRODUCTION

The carbonization of pitches derived from petroleum, coal tar, or aromatic hydrocarbons is known to involve an intermediate mesophase stage which controls the structure and orientation of the derived carbon. A deformable "fluid" state prior to the development of infusible coke is believed to be a requirement for the formation of mesophase and ultimately graphitizable carbon. It is also known that pitches can vary in their degree of graphitizability. Pitches which transform to a low-viscosity mesophase and produce large anisotropic domains prior to coking, yield highly graphitizable carbon. Pitches which exhibit a highly viscous mesophase and a small anisotropic domain size are less graphitizable. Non-graphitizing carbons are produced from thermoset resins and polymers which convert to coke without any intermediate plastic state. In fact, carbonization in the absence of a mobile phase is believed to be a requirement for formation of non-graphitizable carbons.

This study describes the preparation of pitches which are completely non-graphitizing. These pitches were produced from conventional precursors using chemical procedures. They exhibit the general characteristics of conventional pitches and were used as binders for fabrication of graphite. The preparation procedures, characterization data, and effects on graphite properties are described in the following sections.

II. EXPERIMENTAL

Pitches were prepared by reacting coal tar and petroleum distillates and decant oils with either sulfur, oxygen or nitric acid. The sulfur reactions were carried out by heating the precursor with S at 200-300°C. The oxygen reactions involved bubbling air through the starting material at 300-350°C. The nitric acid reactions were performed by stirring at room temperature a mixture of tar with concentrated (70%) HNO_3.

The solid pitch reaction products were heat treated in an inert atmosphere for extended times at 400°C and at 500°C. Polarized light microscopy was used to quantify the mesophase domain size for the pitches heated at 400°C. The absence of any mesophase or any anisotropy in the 500°C coke was used as a criterion on non-graphitizability. Some of the materials were also heat treated to 3000°C for x-ray diffraction measurement to confirm the absence of graphitization.

Other properties measured for the chemically produced pitches included: Mettler softening point, glass transition temperature (Tg) by DSC, Modified Conradson Carbon Content (MCC), and viscosity versus temperature. Some of the non-graphitizing pitches were used as binders in the fabrication of small graphite electrodes and as impregnants for small carbon/carbon composites.

III. RESULTS AND DISCUSSION

The chemical agents used in this study: S,O_2 and HNO_3 polymerize the aromatic components of the low-molecular weight oil and tar precursors. These reactions produce non-planar oligomers and introduce heteroatoms (S,O,N) into the constituents. Although the reaction products exhibit the properties of pitch, the presence of disordered structures and highly reactive substituent groups result in rapid conversion to infusible coke without development of observable anisotropy when subjected to heat treatment. The ultimate degree of disorder and final graphitizabilities can be controlled by the extent of reaction in transforming the precursor to pitch. Results obtained using each of the cited reactant systems follow.

A. Oxidation of Coal Tar Distillate

A coal tar distillate was sparged with air while being heat treated at 350°C for different times. Following the oxidative treatment, the tar products were distilled in the absence of air to produce high softening point pitches. Some properties of the pitches, including the mesophase domain size after heat treatment at 400°C, are shown in Table I. Molecular weight analyses showed that the oxidative treatment had effected extensive polymerization.

Table I
Pitch Properties for Air-Blown Coal Tar Distillate

Heat Treat Time (hrs.)	5	9	15
S.P.°C	277	280	279
Tg°C	165	128	101
MCC%	73	69	61
Meso (μ)	35	5	0

It is evident that the structural disorder increases with increasing oxidation with the most oxidized material forming no mesophase prior to coking. Even though the three pitches in Table I have nearly identical softening points, pitch properties change drastically with the remaining degree of oxidation. The most oxidized pitch has the lowest Tg and the lowest carbon yield. In fact, the Tg/S.P. ratio of 0.68 is the lowest we have measured on any pitch. The most severely oxidized pitch is non-graphitizing and exhibits a very different viscosity vs. temperature behavior from the graphitizing pitches as shown in Figure 1.

B. Reaction of Coal Distillate with Sulfur

The reaction of a coal tar distillate with sulfur (15%) at 300°C was used to produce a non-graphitizing pitch with the properties shown in Table II.

Table II
Pitch from Coal Tar Distillate +S

S. P. = 209°C
Tg = 81°C
MCC = 55%
% S = 4.0
Meso = None

The carbonized pitch was heat treated to 3000°C for characterization by x-ray diffraction. The x-ray parameters: Co = 0.343 nm, Lc = 5nm, and absence of (100) and (102) peaks, showed the pitch to be non-graphitizable. This pitch was employed as a matrix for C/C composites and after heat treatment to graphitizing temperatures, exhibited no anisotropy. In contrast, a glassy carbon-forming phenolic resin, used as a matrix for the same type of composite, exhibited anisotropic order at the fiber/matrix interface.

C. Reaction of Decant Oil with HNO_3

Treatment of a petroleum decant oil with concentrated HNO_3 at 25°C produced a pitch product with the following properties: S.P. = 90°C, MCC = 65%, N = 5.3%. Infrared analysis showed the nitrogen to be present in the form of NO_2 groups with about two groups substituted on every average aromatic molecule.

The nitrated pitches are unique in that they exhibit the typical characteristics of pitch; yet they behave like thermosetting resins undergoing highly exothermic polymerization well below standard coking temperature. A DSC scan for the pitch derived from nitration of decant oil is shown in Figure 2. The large reaction exotherm peaking at about 310°C with a heat of reaction of 950 J/gm results in a thermoset product. This product exhibited no anisotropy when coked at 500°C and after heat treatment to 3000°C produced a non-graphitizable carbon.

The nitrated pitch was mixed with a standard coal tar pitch and the blend used as a binder to produce small graphite electrodes. These electrodes gave higher strengths, higher densities, and surprisingly a lower coefficient of thermal expansion (CTE) than electrodes produced using a conventional coal tar pitch binder. The reduction in CTE is attributed to stress cracking of the coke filler particles induced by the carbonizing isotropic binder.

CONCLUSION

Pitches which are non-graphitizing have been produced by reacting conventional pitch precursors with polymerizing reagents such as O_2,S and HNO_3. These reactants polymerize the aromatic components of the precursors and introduce O, S and N substituents into the aromatic ring systems. These high-molecular weight pitches, with non-planar components, exhibit rather flat viscosity versus temperature curves and carbonize without developing any anisotropy. They could be of use for applications requiring a highly reactive, non-graphitizing binder or impregnant.

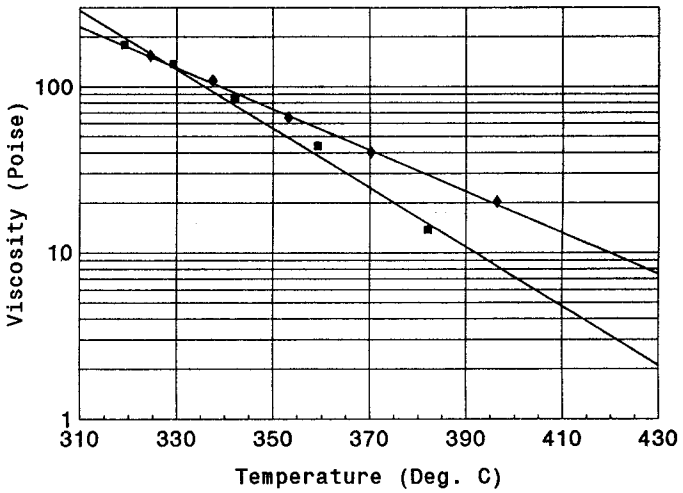

Figure 1 Viscosity vs. Temperature for Nongraphitizing Pitch (♦) and Graphitizing Pitch (■).

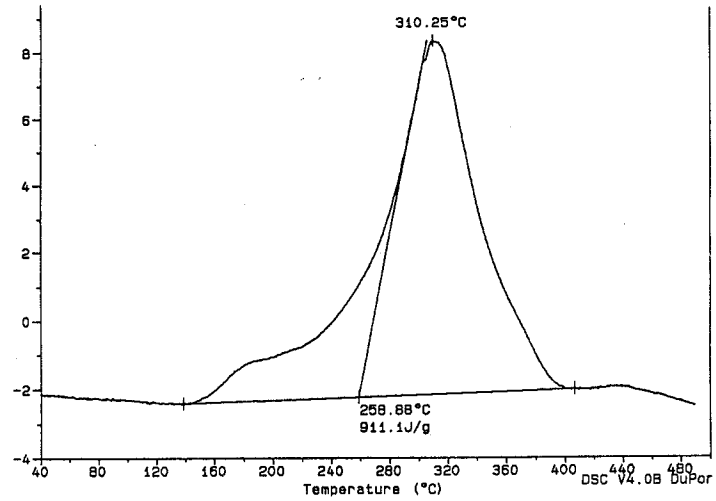

Figure 2 Differential Scanning Calorimetry of Pitch from Nitrated Decant Oil.