EFFECT OF ELEMENTAL SULFUR ON PROPERTIES OF PITCH AND ITS DERIVED COKE

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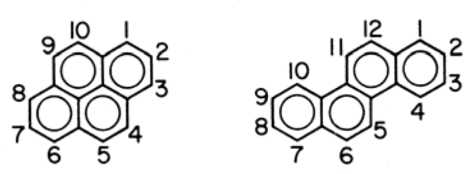
Introduction

Pitch is an important raw material widely used as a binder for carbon/graphite electrode and carbon/carbon composite, etc. The viscosity and coking value of pitch as well as the microstructure of its derived coke have significant effect on the material processing and the property of the final product. The lower viscosity is often desired to have a more uniform distribution of binder pitch in the matrix. The higher coking value of binder pitch is beneficial to make the higher density carbon material. The coking value of pitch is mainly determined by chemical composition of pitch. Normally, the pitch containing larger polynuclear aromatics has a higher coking value, but its viscosity is also higher. The addition of certain additives to the pitch increases its coking value and viscosity. Metal chlorides (Shao et al., 2004; Mochida et al., 1975) and sulfur (Lewis et al., 1982; Fernandez et al., 1998) have been reported as coking additives to increase the coking value. The mechanism for each additive is different, but in general, the additives cause the polymerization of polynuclear aromatics in pitch, which increases the pitch's coking value.

Sulfur has been known to cause polymerization of polynuclear aromatics. GrafTech has extensively studied the reaction between sulfur and the model compounds of pitch. The results indicate that the polymerization was effected through the dehydrogenative action of sulfur and leads to thermally stable heterocyclic ring systems. Part of the sulfur was incorporated into the ring system, but the majority of sulfur was eliminated at carbonization temperature above 1000°C. Based on the applications, sulfur can be used to increase the coking value of pitch or produce isotropic carbon (Lewis et al., 1995), etc. In this paper, the reaction between sulfur and pitch's model compounds, the thermal stability of resulting coke and the effect of sulfur on the viscosity, coking value of pitch and microstructure of its derived coke will be summarized and discussed.

Experimental

Pitch model compounds, pyrene (a) and chrysene (b), as shown below, were treated respectively with sulfur (20% in the reactant) at 350°C for five hours. After the reaction, pitch like products were collected, and then carbonized at a temperature range from 500 to 1900°C. The pitch like products were characterized by Field Desorption Mass Spectrometry (FDMS), Nuclear Magnetic Resonance (NMR), and Gel Permeation Chromatography (GPC) etc. The sulfur content of coke carbonized at different temperatures was also measured (Lewis et al., 1982).



(a) (b)

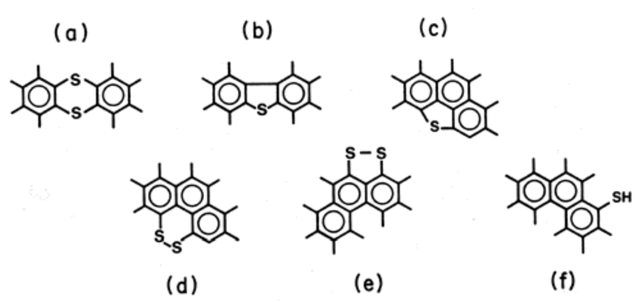
Coal tar pitch with the softening points (S.P.) of 130°C and 170°C were selected to investigate the effect of sulfur on pitch's viscosity, coking value and microstructure of the derived coke. Pitch and sulfur powder were blended at room temperature. The viscosity and coking value of this blend were measured by a viscometer and a Thermal Gravimetric Analyzer (TGA). The coke derived from pitch-S was mounted in epoxy resin and polished, then observed under an optical microscope.

Results and Discussion

Model compound study (summary)

Pitch is a complex mixture of polynuclear aromatics. In order to have a better understanding of pitch-S reaction, model compounds, pyrene and chrysene, were selected. Pyrolysis of pyrene and chrysene at atmospheric pressure does not form any coke. However, with sulfur addition, they are converted to pitch like material, which have a coking value of 68% and 42% at 500°C, respectively. Large amount of sulfur is incorporated into coke, and the sulfur content in the 500°C coke is 10.7% and 9.6%, respectively.

The analysis of the reaction products (pitch like material) by GPC and FDMS suggested that the sulfur reaction resulted in a stepwise polymerization to produce polymers consisting of molecular units of the starting compounds substituted by varying the amount of sulfur. Sulfur initially forms C-S bonds and bridges the condensed ring systems. This reaction is effected by the de-hydrogenative action of sulfur and with liberation of H_2S. The molecular weights of these products range from approximately 200 to 1300. Sulfur acts as a polymerization agent for polynuclear aromatic hydrocarbons and incorporated into coke. Based on the structural characterization, several different types of aromatic sulfur structures (a)-(f) were proposed for the pyrene and chrysene products (Lewis et al., 1982):



Structures (a)-(c) contain sulfur in the form of stable five- and six-membered heterocyclic ring systems. Among them, structure (a) appears to be a dominant result of the polymerization process. Structures (d)-(f) are not involved in bridging condensed ring system, and are probably the least stable sulfur group which decomposed at lower carbonization temperature.

During the carbonization process, the sulfur-containing species polymerized into even larger aromatic ring system, which then desulfurized only at high temperatures. A plot of sulfur loss as a function of heat treatment temperature is shown in Figure 1. Between 500 and 700°C, almost no sulfur is evolved from

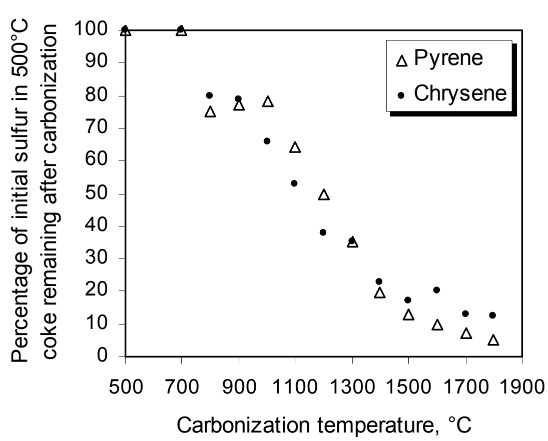


Figure 1. Sulfur loss from pyrene-sulfur coke and chrysene-sulfur coke as a function of carbonization temperature

coke, but there is a rapid sulfur loss at higher temperatures, especially above 1000°C. Approximately 90% of sulfur in 500°C coke is lost at a temperature of 1700°C for both pyrene-S and chrysene-S coke. Sulfur was mainly eliminated in the form of H_2S and CS_2 at temperatures below ~800°C, and in the form of elemental sulfur and carbon monosulfide (CS) at temperatures above 1000°C (Lewis et al., 1982).

Pitch-S system study

Whether sulfur could be a moderate plasticizer or a polymerization agent depends on the temperature pitch and sulfur were mixed. Pitch-S reaction starts at approximately 130~150°C. Below this temperature, sulfur acts as a moderate plasticizer. It does not increase but decreases the softening point of pitch. For example, blending 20% sulfur with pitches of 106°C and 130°C softening point and then measuring the softening point(drop method), the softening points were found decreased to 82 and 90°C, respectively (Chi et al., 2004). Above this temperature (130~150°C), pitch-S reaction starts and results in the increase of softening point and viscosity of pitch, as well as coking yield.

Figure 2 shows the increase of viscosity of pitch as a result of pitch-S reaction. A 130°C softening point pitch was blended with 15% S and the change of viscosity with reaction time was measured at 200°C and 250°C, respectively. The results show that the viscosity increases with reaction time at both temperature levels, but the increase of viscosity is much faster at higher temperatures. As shown in Figure 2, at 200°C, it takes 340 minutes to reach the viscosity of 1000 poise, but it only takes 24 minutes to reach the same viscosity at 250°C. The result indicates that the rate of reaction increases with reaction temperature.

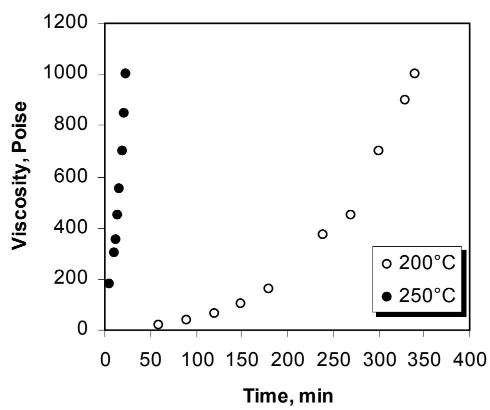


Figure 2. Change of viscosity of pitch with reaction time at 200°C and 250°C. Sulfur amount, 15wt%.

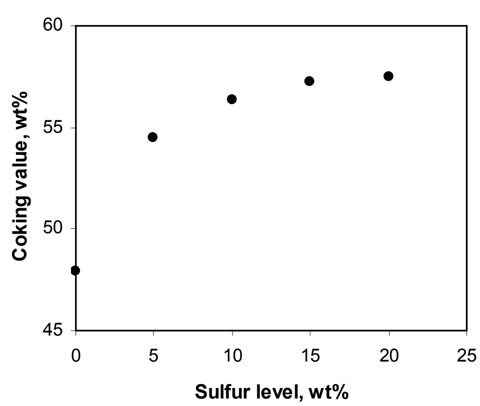


Figure 3. Change of coking value with different level of sulfur addition. Measured by TGA, 5°C/min, in Ar. RT to 800°C

In addition to increases in viscosity, sulfur also increases the coking value of the pitch. Figure 3 shows the increase of coking value of 170°C S.P. pitch-S blends at different levels of sulfur addition measured by TGA. The coking value is significantly increased by sulfur addition from 0 to 15%, but only a slight increase was observed above this level. The result suggests that the excess sulfur does not further increase the coking value. There is approximately a 20% increase in coking value with 15% sulfur addition. The experiment also found that large excess of sulfur generated more H_2S and changed the microstructure and the graphitizability of coke.

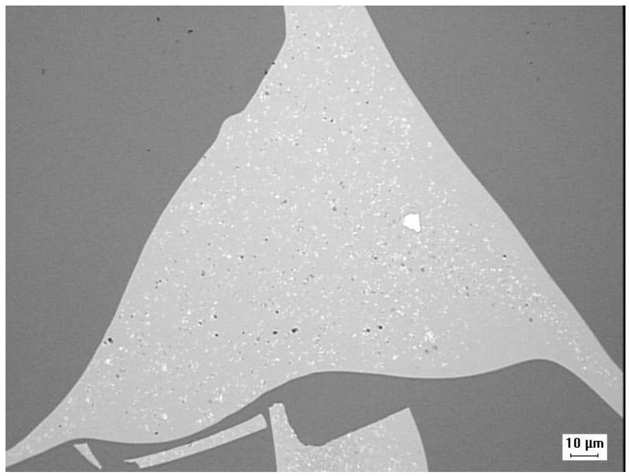


Figure 4. Optical micrograph (bright field) of coke derived from coal tar pitch with 15% sulfur addition

Observation by optical microscopy indicated that sulfur treated pitch tends to generate small anisotropic domain or fine mosaics, and eventually turns to isotropic carbon at high sulfur levels. Figure 4 is the optical micrograph of the coke derived from 170°C S.P. pitch with 15% sulfur addition. It shows the isotropic texture of pitch-sulfur derived coke. This type of coke is not graphitizable, has higher electrical resistance, and higher coefficient of thermal expansion (CTE), but is stronger.

Conclusion

Sulfur causes a polymerization of polynuclear aromatics through the dehydrogenative action of sulfur. Approximately 90% of incorporated sulfur is eliminated at carbonization temperature of 1700°C. Sulfur also increases the coking value and viscosity of pitch. A 20% coking value increase was observed for a 170°C softening point coal pitch with 15% sulfur addition. The rate of pitch-sulfur reaction was found to increase with temperature. The addition of large excess of sulfur does not further increase the coking value of pitch but tends to generate isotropic texture of its derived coke.

Acknowledgement

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