

# STUDY ON THE SULFUR MODIFIED PITCH FOR MATRIX OF C/C COMPOSITES

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## 1. Introduction

C/C composites have many outstanding properties, such as low density, high (tensile) strength, high temperature resistance, excellent thermo shock behavior, high thermal and electric conductivity and good wear resistant ability, which qualify them for the application in aircraft brakes manufacture<sup>[1-4]</sup>. Although C/C composites for aircraft brakes application have been industrialized, complicated equipment, long production cycle, and high production expense limit their extensive uses. In the C/C composites process, impregnate is very important. In this paper, the manufacture and properties of modified pitch for C/C matrix and impregnate was studied.

## 2. Experimental

### 2.1 Raw Material

Pitch: High melting point coal tar pitch(AHP) with softening point 106 C and petroleum pitch(DCCP) with softening point 130 C.

Addition: sulfur

### 2.2 Preparation of sulfur modified pitch (AHPS and DCCPS)

Pitch sample is applied in form of fine powder and placed in the melting container and heated to melt. At 130 C, sulfur is added slowly into the pitch and mixed for 10 to 30 min. By changing the amount of sulfur, we obtain modified pitch with different sulfur content.

### 2.3 Test

#### 2.3.1 Elemental analysis

Contents of C, H, and S are determined with CRLOERBA INSTRUMENTATION 1106( Made in Italy)

#### 2.3.2 Softening point

Reference to GB4507-84(Standard Test Method for Softening Point of Petroleum Bitumen in China), the softening point of raw pitch and modified pitch are tested. The method is to place two certain weight steel balls ( $3.5\pm 0.5\text{g}$ ) into the two certain size

metal circles in the sample dish and heat at the rate of  $5\pm 0.5$  C per min.. The temperature at which the sample is soft enough to make the balls fall down 25.4mm is the softening point.

### **2.3.3 Carbon yield**

Pitch sample is placed in a carbonization furnace and heated to 850 C in a nitrogen atmosphere at the rate of 10 C/min. The percent of final weight to original is the carbon yield.

### **2.3.4 Viscosity**

The viscosity of pitch sample is measured at different temperature with Brookfield Synchro-Lectric Viscometer( Made in U.S.A.).

### **2.3.5 Ash content**

Reference to ASTM D482-74, the ash content of pitch sample is tested.

### **2.3.6 Quinoline insoluble**

Reference to ASTM D2318-86, the QI of pitch sample is tested.

## **3. Results and discussion**

Modified pitch is used as binder and impregnate agent for C/C composites and has densification effect. Its physical properties( such as softening point, viscosity, and so on), the chemical reaction outcome during heat treatment and carbon yield have direct effects on modeling technology and performance of the final product. To choose the optimum sulfur content and study the action of sulfur, discussion is made as following.

### **3.1 Effect of sulfur on the softening point and carbon yield of pitch**

From Table 1, we can obviously see that with sulfur content increase, softening point decreases at first and increases again, while carbon yield increases and then decreases. Accordingly, the sulfur content of modified coal tar pitch with the lowest softening point and the highest carbon yield is 20-25%( seen from Tab.1(a)).

Table1 softening point and carbon yield of sulfur modified pitch

(a) Modified coal tar pitch

Sample No.	S,%	SP, □	Carbon Yield, %
AHP	0	106.0	52.4
AHPS-10	10	94.0	58.8
AHPS-15	15	86.0	63.7
AHPS-20	20	82.0	67.4
AHPS-25	25	84.5	68.7
AHPS-30	30	97.0	68.4
AHPS-35	35	98.5	66.9

(b) Modified petroleum pitch

SAmple No.	S,%	SP, □	Carbon Yield, %
DCCP	0	130.0	51.9
DCCPS-10	10	105.0	60.8
DCCPS-20	20	90.0	75.1
DCCPS-25	25	94.0	71.1
DCCPS-30	30	94.0	61.9
DCCPS-40	40	93.0	—

The rising of carbon yield indicates the change of the chemical reaction mechanism of pitch during heat treatment when sulfur is added to it. Generally, when pitch is heated, dehydrogenation, cross-linking, cyclization and condensation polymerization are taken place, giving off H<sub>2</sub>O, CO, CO<sub>2</sub>, CH<sub>4</sub> and heavy hydrocarbon compound, and forming coke. However, as to sulfur modified pitch, dehydrogenation is in form of H<sub>2</sub>S. That is to say, pitch pyrolysis is changed into oxidation-reduction of sulfur and oxygen, which leads to carbon yield increase by 3% (from 52.4% to 68.7%) and softening point decrease by 23%(from 106 C to 82 C) .

This is true of petroleum pitch (seen from Tab.1(b)). Through modification, carbon yield increases form 51.9% to 75.1% and softening point decreases form 130 C to 90 C.

### 3.2 Effect of sulfur on the ash content, QI, and composition of pitch

Table 2 shows that carbon and hydrogen content decrease with the sulfur content increase, but excluding the sulfur content, carbon content and hydrogen content of modified coal tar pitch have a little difference, so do the QI and ash content. For

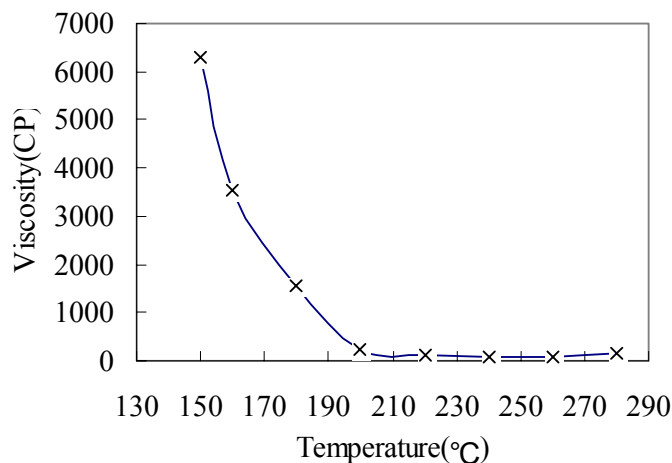
petroleum pitch, QI is 3.88%. After modification, QI is 2.86%.

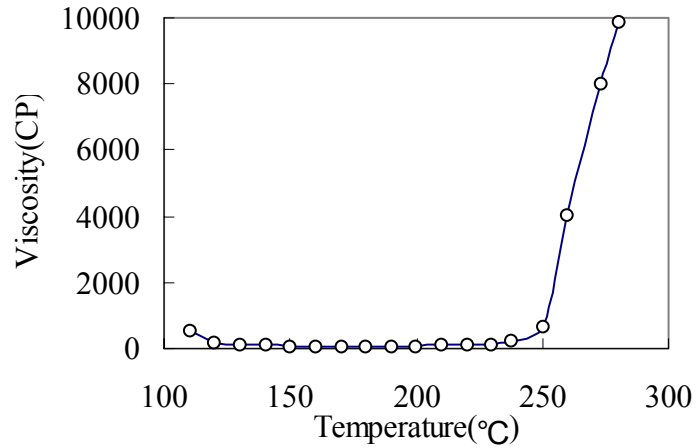
Tab. 2 composition, QI and ash content of sulfur modified pitch

Sample	Element Content, %				QI, %	Ash Content, %
	C	H	S	O		
AHP	92.84	4.55	0.62	1.99	4.2	0.162
AHPS-15	79.80	3.82	14.21	2.17		
AHPS-20	75.01	3.75	19.00	2.24	2.96	0.121
AHPS-25	70.01	3.25	25.07	1.67		0.132
AHPS-30	64.41	3.06	30.61	1.92		

### 3.3 Effect of sulfur on the viscosity of pitch

As shown in Fig. 1(a), at 110□, Anshan coal tar pitch(AHP) becomes soft. Its viscosity is 12200 cp at 140 C . From 150 to 220 C, viscosity decreases from 6300 to 100 cp, which means the viscosity is very sensitive to temperature changes. The reason is that the main composition of pitch is aromatic hydrocarbon molecular. Being the rigid structure, pitch has high viscosity. With the temperature increase, the Vander attraction becomes weak, molecular moving capacity is improved, so viscosity is reduced. At 240□, viscosity change becomes smoothly. Especially, after 260 C, viscosity has little change, only by some cp. Still increasing temperature, viscosity increases and grows a little. Viscosity decrease is the result of interaction decrease between molecular, while viscosity increase is because the condensation between the aromatic ring molecular. Due to slight crosslinkage, sulfur modified pitch(AHPS-20) has larger aromatic molecular . At same temperature, AHPS-20 has higher viscosity. For example, at 240 C, the viscosity of AHP is 80cp, while that of AHPS-20 is 1775cp (seen in Fig.1 (b)).



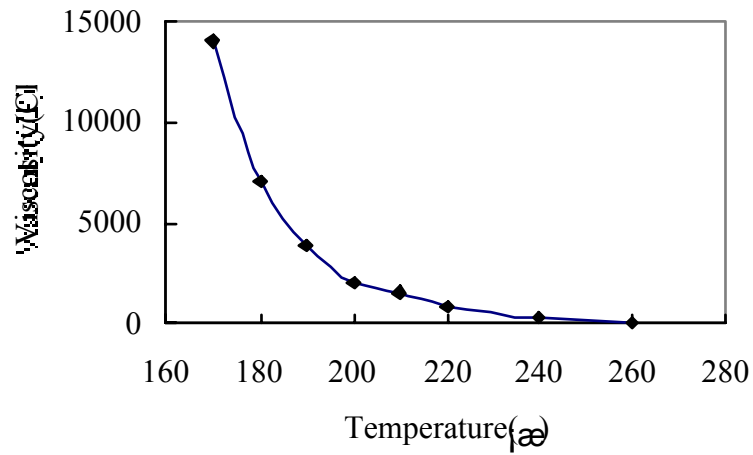


(b) AHPS-20

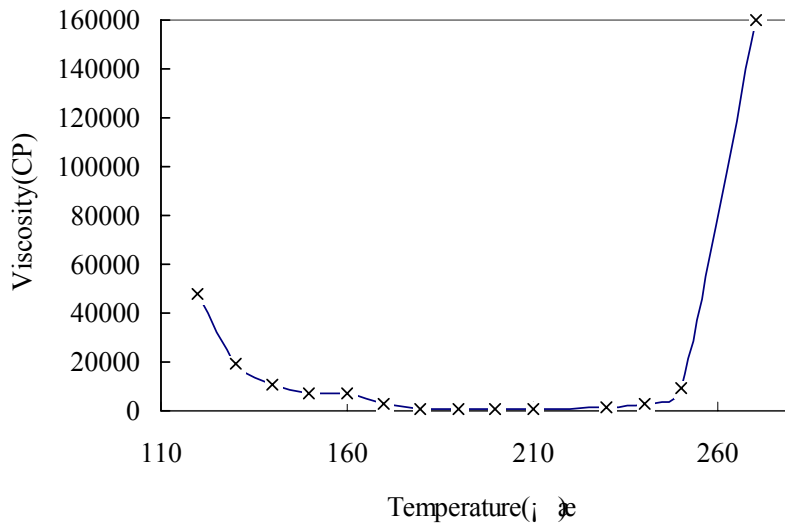
Fig.1 the viscosity-temperature curve of coal tar pitch samples

On the other hand, the viscosity increase temperature of modified pitch is lower than that of AHP. From the viscosity and temperature curve, work temperature at which the modified pitch has low viscosity and good flow property can be determined.

In the same way, the relationship of viscosity of petroleum pitch samples and temperature is also studied. The results seen in Fig.2(a) show that viscosity of petroleum pitch(DCCP) has decreasing tendency with temperature increase below 290°, while that of modified petroleum pitch(DCCPS-20) decreases, then changes a little, finally rise drastically(seen in Fig.2(b)). According to the viscosity and temperature curve of sulfur modified petroleum pitch, we can know that between 180°and 210°, the viscosity of modified pitch arrives at the lowest value and has little change.



(a) DCCP



(b) DCCPS-20

Fig. 2 the viscosity-temperature curve of petroleum pitch samples

Through the study on the relationship of viscosity and temperature, we can choose the temperature at which modified pitch for binder and impregnate agent has good flow capacity and easy processing. For AHPS-20, the temperature is 200-240°C; for DCCPS-20, it is 180-210°C

#### 4. Conclusion

1) Two kinds of sulfur modified pitch with high carbon yield (>60%) and low softening point (<90 C) and good rheological property are prepared, which can be used as suitable binders and impregnate agents in C/C composition.

In detail, for modified coal tar pitch, sulfur content is 20%, carbon yield is 67.4% and softening point is 82.0 C; for modified petroleum pitch, sulfur content is 20%, carbon yield is 75.1% and softening point is 90□.

2) Temperature has obvious effect on the viscosity of the modified pitch. From the research on their relationship, optimum technology parameters can be obtained. For modified coal tar pitch, the processing temperature is 200-240 C; for modified petroleum pitch, it is 180-210 C.

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- [2] Devi GR and Rao KR, Carbon-Carbon Composites –An Overview, Defence Science Journal, 1993; 49(4): 369-393.
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