CHANGE IN GLASS TRANSITION TEMPERATURE DURING CARBONIZATION OF THIN FILMS OF PITCH SUPPORTED ON COKES

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Introduction

Numerous studies have been devoted to the investigation of pitch-coke interactions during carbonization. In particular, the enhancement or the inhibition of mesophase growth in presence of different types of carbon (carbon blacks, QI particles and coke particles) has been studied [1-3]. It was shown that the growth of mesophase is hindered by the presence of carbon blacks whereas the addition of needle-coke leads to well-ordered structures [2]. Pitch-coke interactions may occur at the earliest stage of carbonization and the purpose of the present paper is to examine the occurrence of these interactions during pyrolysis of pitch in presence of different types of petroleum cokes.

Previous studies on binder pitches showed that their mean molecular mass is related to their glass-like characteristics and in particular to their glass transition temperature, Tg [4]. Evidencing more closely pitch-coke interactions requires to work with thin films of fluid pitch on carbon surfaces in order to minimize bulk effects of pitch carbonization. Hence, the influence of the surface characteristics of the carbon substrate on pitch properties during carbonization will also be discussed.

Experimental

The coal tar pitch used in this study has a Kraemer-Sarnow softening point equal to 111 °C and a QI content equal to 6.3%. Two commercial samples of petroleum coke, noted A and B were ground to a particle size smaller than 0.038 mm. In all experiments, a know amount of coke was mixed with the same amount of pitch (0.275g) in order to perform reliable DSC measurements on the heat-treated pitch-coke mixture. Pitch weight loss in absence and in presence of coke particles was determined during pyrolysis in argon at a linear heating rate equal to 0.2°C/min. After reaching the desired temperature, the sample was rapidly cooled. Glass transition temperature, Tg, was measured on heat-treated pitch-coke mixture using a Mettler TA 4000 thermoanalyser in a manner described elsewhere [5].

Results and Discussion

The weight loss curve of pitch during heating is not affected by the presence of coke particles (50 wt % in the starting pitch-coke mixture). Hence, for a sufficient small sample size, the presence of coke does not affect the overall weight loss of pitch during its devolatilization. Tg values of pitch after heat treatment at different temperatures in absence and in presence of coke particles (50 wt % in the starting pitch-coke mixture) are shown in Table 1. Unlike to the weight loss behaviour, Tg values of pitch are not the same in absence or in presence of coke particles. Hence, although the overall weight loss of pitch is the same in absence or in presence of a carbon surface, the properties of the pitch compounds vary differently during carbonization. In the following, δTg is defined by the equation :

$$\delta Tg = Tg_c - Tg_a \qquad (1)$$

where Tg_a is the glass transition temperature of the pitch devolatilized in absence of carbon and Tg_c is the Tg of pitch carbonized in presence of carbon. δTg increases with the extent of pitch devolatilization (Table 1).

Table 1. Weight loss and Tg values of heat-treated pitch.

Temperature (°C)	Weight loss (%)	Pitch Tg_a (°C)	Pitch-coke Tg_c (°C)	δTg (°C)
25	-	40	-	-
200	5.0	58	58	0 ± 1
250	17.1	80	88	8 ± 1
300	31.0	116	120	4 ± 2
335	37.8	122	146	24 ± 2

In order to evidence more closely the effect of the carbon surface on the change of Tg, various amounts of coke A and B particles were added to the same amount of pitch (0.275 g). The mixture was then heated up to 335°C and the corresponding weight loss of pitch was in all cases equal to 38%. The resulting values of δTg are shown as a function of the amount of added coke A and B in Table 2. Two main observations can be drawn from these results. At first, there is a definite increase of Tg of the devolatilized pitch due to the presence of coke. This effect is more pronounced when the amount of coke particles in the mixture is higher, *i.e.* when the pitch-carbon interfacial area is more extended. Secondly, the increase of Tg also depends on the type of coke since the values of δTg are higher in the case of coke B as compared to coke A at high loading. Considering the surface area of both types of coke particles (5.3 m^2/g for coke A and 4.8 m^2/g for coke B respectively) one may determine the effect of pitch loading per unit area of carbon on the increase of pitch Tg after devolatilization to 38% weight loss. The change in

δTg as a function of devolatilized pitch loading is compared in Fig. 1 for the two types of cokes. There is a strong dependence of δTg on the type of coke at low loading of pitch, *e.g.* when the mean film thickness of the devolatilized pitch is low enough to allow the detection of interfacial interactions. For pitch loading smaller than 0.3 g/m^2, the mean thickness of the film is estimated to be smaller than 100 nm assuming a density of the devolatilized pitch equal to 1.4 g/cm^3. It is interesting to note that in the case of polymers interacting with a solid surface, an increase in Tg is observed for polymer films of similar thickness [6]. Moreover, an increase of polymer Tg in the vicinity of a surface is attributed to a loss of mobility of the units giving rise to the glass transition phenomenon [7]. Hence, these results suggest that the mobility of the compounds of the devolatilized pitch is significantly restricted in the vicinity of the carbon surface as compared to the one in the bulk.

Table 2. δTg values of pitch-coke devolatalized at 335°C.

Weight fraction of coke	Coke A δTg (°C)	Coke B δTg (°C)
0	-	-
10	0	1
20	2	2
30	4	4
40	7	23
50	10	29

A closer examination of the effect of the nature of the coke on the increase of Tg of the devolatilized pitch may shed some light on the origin of this effect. Petroleum cokes are characterized by a large variety of crystalline texture depending mainly on the chemical nature of their precursor and on the carbonization conditions (heating rate, final temperature...). The crystalline texture of the coke will also be reflected in their surface properties. Its surface is composed of aromatic lamellae of various size which constitute the basal planes. Different types of defects may be present on the surface: vacancies, dislocations, edges of the outer basal planes. They form the so-called 'prismatic planes' or the 'active surface area' (ASA) [8]. An appropriate estimate of the degree of ordering of a carbon surface is given by the ratio of the ASA to the total surface area (SBET). Interestingly, for pitch loadings equal to 0.15 g/m^2 the coke inducing the highest effect on Tg of the devolatilized pitch, coke B (δTg~30°C), has a smaller ASA/SBET ratio (0.06) as compared to coke A (δTg~10°C) which has a value close to 0.09 (Fig. 1). This result indicates that the loss of mobility of pitch compounds is directly linked to the absence of defects in the basal planes. A lowering of the mobility of the pitch compounds may be easily conceived by an alignement of the pitch compounds parallel to the basal planes after removal of the low molecular species during devolatilization. It is also worthwhile to note that a slight

increase in the density of surface defects affects considerably the ordering effect as deduced from the glass transition temperature of devolatilized pitch.
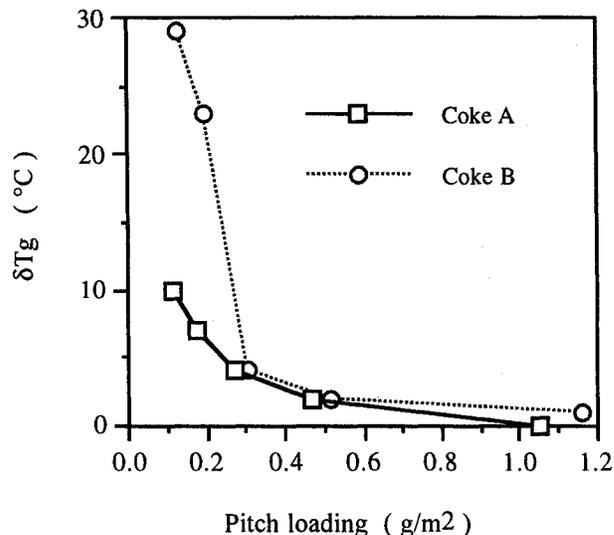

Figure 1. Increase in Tg of pitch devolatilized at 38% weight loss as a function of loading.

Conclusion

The carbonization behaviour of a pitch is different in the vicinity of a carbon surface as compared to the bulk. For a given extent of pitch devolatilization, its glass transition temperature, Tg, increases reflecting a loss of mobility of the pitch compounds in a similar way as observed for polymers. This effect is more pronounced when the density of defects of the basal planes of the coke decreases. The consequences of this surface effect on the pitch carbonization process at the nanometric and macroscopic levels will be discussed.

References

[1] Forrest M, Marsh H. Fuel 1983;62:612.
[2] Fujimoto K, Orita M, Mukai K, Fujimoto KI. In:Extended Abstract of Carbone90, Paris, France, 1990:124.
[3] Taylor GH, Pennock GM, Fitz Gerald GD, Brunckhorst LF. Carbon 1993;31:341.
[4] Ehrburger P, Martin C, Saint-Romain JL. Fuel 1991;70:783.
[5] Ehrburger P, Sanseigne E, Tahon B. Carbon 1996;34:1493.
[6] Kwei TK. J. Polymer Science 1965;3:3229.
[7] Privalko VP, Denchenko SS, Lipatov YS. Macromolecules 1986;19:901.
[8] Laine NR, Vastola FJ, Walker Jr PL. J. Phys. Chem.1963; 67:2030.