Flow Properties and Glass Transition of Coal Tar Pitches

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Introduction

The processing of carbon electrodes for the aluminium industry requires pitches having good binding properties. Some binder pitches easily wet the coke particles and rapidly flow into the interparticle voids. In a recent paper, Ehrburger and Lahaye showed that the flow behavior of some pitches is mostly determined by thermodynamic factors, wetting angle and surface energy and a rheological one, viscosity (1). For other pitch samples however, the flow behavior is more complex and the objective of the present paper is to investigate further the flow properties of molten pitch and to correlate them with the glass transition characteristics of these materials.

Experimental

Twenty coal tar pitches with softening point Kraemer-Sarnow ranging from 85 to 95°C have been selected. Their quinoline insoluble (QI) content varies from 3 to 15% by weight. The penetration of a droplet of molten pitch into a granular coke bed (petroleum coke, particle size 100-150 µm) has been followed by recording the decrease of height of the pitch droplet by means of an optical device (2). A small sample of pitch (200 mg) is set on the coke bed and heated until it melts. Thereafter the temperature is linearly increased from 100 to 200°C at a rate of 20°C h^{-1} and the height of the pitch droplet is recorded as a function of the temperature until complete penetration. The size of the interparticle voids of the coke bed has been measured by mercury intrusion and ranges from 25 to 45 µm in radius. In the following, a mean pore radius of 30 µm will be considered. The glass transition temperature (Tg) has been determined in a DSC Mettler equipment (TA 3000). Prior to the Tg measurements the pitch sample is annealed in the DSC cell at 140°C, quenched to -120°C and the DSC signal is then recorded between -120°C to 140°C at a linear heating rate of 10°C min^{-1}.

Capillary Flow

The volume fraction of liquid pitch V/V_o remaining on the top of the granular coke bed at temperature T can be expressed (1) :

$$\frac{V}{V_o} = 1 - \frac{0.15}{V_o} \left(\frac{r}{\alpha}\right)^{1/2} \left| \cdot \int_{T_o}^{T} a^2 \frac{\gamma \cos\theta}{\eta} \, dT \right|^{1/2} \qquad (1)$$

where r = radius of interparticle voids, a= geometric area of the droplet-solid interface, γ = surface tension, θ = contact angle, V_o = initial volume of the droplet, V = volume of the droplet at temperature T, α = rate of temperature increase and T_o = starting temperature of capillary flow.

Equation (1) indicates that the liquid penetration will depend on several parameters : 1. the radius of the pores ; 2. the size of the droplet (V_o, a); and 3. the physicochemical properties of the liquid (γ,θ,η). Working with a constant droplet size and with a given granular coke, it is possible to relate the flow behavior of a pitch to its surface tension, its contact angle and its viscosity. The integration of Equation (1) requires a knowledge of T_o and of the variation of a,γ,θ and η with temperature. Experiments carried out with 200 mg pitch samples show that during the penetration, the shape of the pitch droplet changes. However, the area of the droplet-solid interface a, remains almost constant after wetting and may be estimated to be 113 mm^2. The surface energy of the pitch does not significantly change in the temperature range where penetration occurs. The physicochemical properties of two samples A and B have been measured for solving Equation (1). The changes in viscosity and in wetting angle with temperature for the two samples were determined experimentally allowing thus to integrate numerically Equation (1). The calculated curves V/V_o versus T are shown for the two pitches A and B in figures 1 and 2 respectively. The experimental curves h/h_o versus T corresponding to the relative decrease of droplet height during the penetration are also shown on the same graphs.

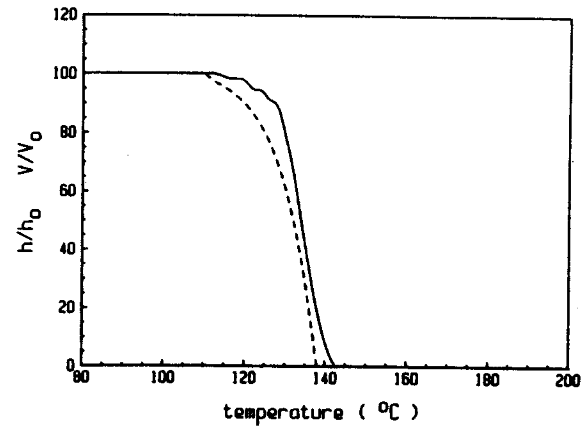

Figure 1. Variation of h/h_o (–) and V/V_o (---) for pitch A with temperature.

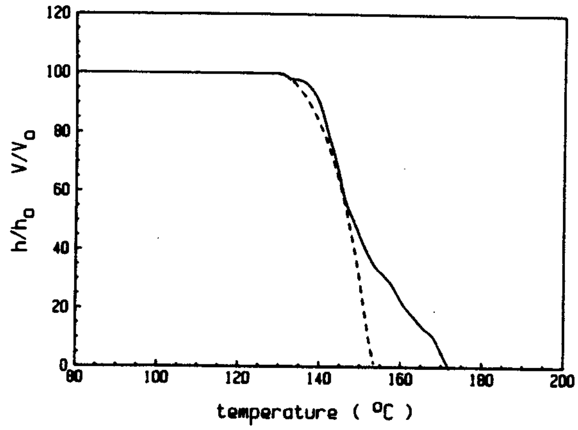

Figure 2. Variation of h/h_o (–) and V/V_o (---) for pitch B with temperature.

For sample A the experimental and calculated curves are in good agreements. In particular, the observed final temperature of penetration Tf is very close to the calculated one. In the case of pitch B, the calculated and the experimental curves are in reasonable agreement only for the first half of penetration. Thereafter a "tail" appears in the experimental curve. Interestingly the extrapolated temperature of penetration Te is close to the calculated temperature of penetration (Figure 2). The importance of the tail may be estimated by the difference Tf-Te. In the present case this difference is equal to 17°C and consequently the flow of pitch B cannot entirely be described by the macroscopic change in wetting angle and in viscosity with temperature.

Origin of abnormal Flow

It has been reported that a high content of α-resins may alter the flow properties of a pitch (3). In particular, the presence of mesophase particles with a diameter close to or slightly larger than the aperture of the interparticle voids ($r = 30\ \mu m$) would lead to a caking effect. In the present work, no correlation could be found between the importance of the tail (Tf-Te) and the mesophase content of the samples (0-13 %). Moreover no clear trend could be evidence between the size of the mesophase particles and the occurence of a tail in the penetration curve. In particular, some pitches with very fine mesophase particles ($r<2\ \mu m$) showed a tail in the penetration curve. Therefore the caking effect cannot satisfactorily explain the abnormal flow for the studied pitches. Consequently the occurence of a tail in the flow curve may result rather from a change in the physicochemical properties of the pitch droplet during its penetration. In order to substantiate this hypothesis, the pitch droplet was quenched at different stage of penetration and its Tg was measured. The results are shown in table 1.

Table 1. Tg of pitch droplet at different stage of penetration.

Remaining volume of pitch (%)	Tg (°C)	
	Pitch A	Pitch B
100	38.2	40.7
75	39.1	41.1
40	39.5	-
30	-	44.4
10	44.2	56

It is seen that in both cases there is an increase in Tg during the penetration. However, the increase in Tg is significantly higher for pitches having an abnormal flow. In addition for pitch B, there is also an increase of Tg in the droplet itself, the higher value of Tg being obtained near the external surface of the droplet. These results clearly indicates a gradient of composition from the outside to the inside of the pitch droplet during penetration. The change in composition during penetration is attributed to a distillation phenomenon of light molecular weight compounds. The departure of these molecules will necessarily affect the viscosity as well as the wetting angle of the remaining pitch. Hence the abnormal flow behavior of some pitches is due to the change in physicochemical properties of the droplet during its penetration.

Conclusion

This study indicates that some pitches behave homogeneously during their flow into a granular coke bed whereas other pitches show a tendency to distillate during the penetration process. In the latter case, the pitch exhibits an abnormal flow behavior.

References

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