INTERACTIONS OF PETROLEUM PITCH, COAL-TAR PITCH AND THEIR BLENDS WITH CALCINED PETROLEUM COKE MONITORED BY MICROSTRENGTH TESTS

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Introduction

Pitch-based carbon materials are widely used in different applications, e.g. anodes, brushes, etc., where the ability to withstand mechanical damage and to resist thermal stresses during use is required. These materials are usually prepared by carbonizing a mixture of filler particles, such as petroleum coke and a binder, for example pitches. The strength of carbon materials depends upon their porosity, optical texture and filler/binder interactions.

In this paper the strength of carbons prepared by blending petroleum coke (filler) with several pitches (binders) is assessed by microstrength tests. This strength is related with the origin of the binder, the percentage of binder in the blend and the conditions used for the preparation of the materials (molding pressure).

Experimental

The materials were obtained from a calcined petroleum coke, < 100 μm, and four pitches of different characteristics. The pitches include a commercial binder coal-tar pitch (A), a pilot-plant scale petroleum pitch (B) and two blends [1] of A and B (30 wt %of B, AB30 and 45 wt % of B, AB45). The main characteristics of these pitches are shown in Table 1.

Table 1. Pitch characteristics.

Pitch	C/H[1]	SP[2]	TI[3]	QI[4]	CY[5]	I_{Ar}[6]
A	1.86	116	29	9	60	0.68
B	1.29	111	13	0	50	0.42
AB30	1.72	116	25	6	58	0.53
AB45	1.62	119	23	5	57	0.47

[1] C/H atomic ratio
[2] Softening point (Mettler, °C)
[3] Toluene insolubles (wt %)
[4] Quinoline insolubles (wt %)
[5] Carbon yield (Alcan, wt %)
[6] Aromaticity index (FTIR)

Calcined petroleum coke was blended with the pitches in the proportions 20/80, 25/75 and 30/70 wt %. Blending was carried out in a steel vessel at 150 °C, 100 rpm and 0.1 MPa of nitrogen pressure. The resultant pastes were then carbonized following a five-day carbonization process (Figure 1). In order to study the effect of the pressure, the pastes were also molded into cylindrical pellets (25 mm in diameter and 5 mm in height), by applying a mechanical pressure of 100 MPa, and then carbonized following the same carbonization program. The density and porosity of carbonized pellets were determined on carbon blocks by geometrical measurements and helium pycnometry.

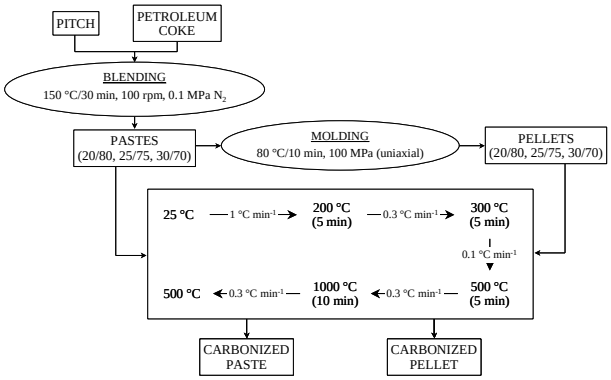

Figure 1. Steps followed in the preparation of the carbons.

Filler/binder interactions were evaluated from the microstrength of the carbonized pastes, carbonized pellets and single pitch-based cokes, using a ball-mill test [2]. Two grams, ground and sieved to a particle size of 0.6-1.18 mm, were placed in a steel cylinder (305 mm long, 28 mm internal diameter) with twelve steel-ball bearings (8 mm diameter). The cylinders were then placed on an electrically driven holding frame which rotated the cylinders around their short axes. After completion of 200, 400 and 600 rotations at 25 rpm, the broken carbon was swept from the cylinders and sieved into three fractions: r1 (> 0.6 mm), r2 (0.6-0.1 mm) and r3 (< 0.1 mm). Carbons before and after testing were studied by polarized-light microscopy.

Results and Discussion

At low rotations, the microstrength of the material is mainly governed by porosity. However, as the rotations increase, porosity is eliminated and other factors, such as optical texture, microcracks and filler/binder adhesion gain importance and finally determine the mechanical behavior of the material. The r1 fraction (particles > 0.6 mm) can be considered as one of the most representative for determining the microstrength behavior of the carbons, because a decrease in this fraction is directly related with the resistance of the material to be broken. In this study, therefore, microstrength is assessed as the variation of r1 with rotation.

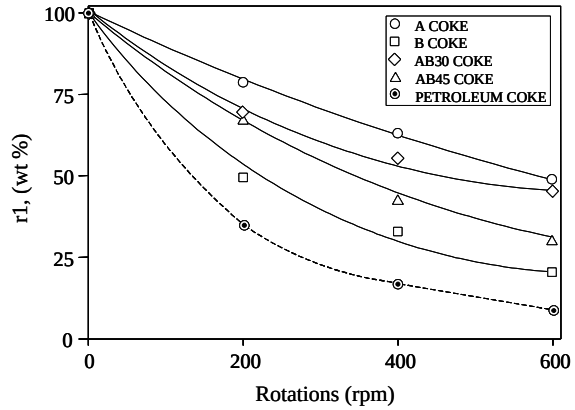

Figure 2. Variation of pitch-coke microstrength with rotation.

Pitch-coke microstrength

Figure 2 shows the variation of r1 with rotation for cokes obtained from single pitches by a five-day carbonization process and from calcined petroleum coke. In all cases microstrength decreases exponentially with rotation. For the pitch cokes, A-coke is the strongest while B-coke shows the lowest values of microstrength. The cokes obtained from the blends (AB30 and AB45) exhibit an intermediate behavior. The microstrength of these materials is closely related with the porosity and microstructure of their cokes, i.e. the smaller the porosity and crystallite structures, the higher the microstrength of the cokes. In fact, A-pitch produces a dense and homogeneous coke with an optical texture of mosaics. A similar optical texture and porosity is observed in the coke obtained from B-pitch. Such similarities are due to a variety of factors. Thus, in A-coke the mosaics are mainly due to the presence of QI particles (Table 1). These particles are totally absent in the case of B-pitch. The small crystallite structures in B-coke must be attributed, therefore, to the intrinsic reactivity of petroleum pitch components. Cokes obtained from AB30 and AB45 show an optical texture similar to that of A-coke. From these results it is clear that QI particles have a positive effect on the microstrength of the cokes.

Microstrength of carbonized pellets

To study the effect that just binder and filler/binder interaction have on the microstrength of the carbons, petroleum coke grains with a particle size < 0.1 mm were used.

The porosity of the carbonized pellets, determined by helium pycnometry, ranged from 33.5 to 37.0 vol %. Variations in microstrength should not be attributed to differences in porosity. The microstrength of the carbonized pellets is extensively affected by the percentage of binder. With the increase in pitch content the microstrength of the resultant carbon increases (Figure 3). This is because in this case the resultant carbons contain a higher amount of the strongest component of the material.

In fact, the microstrength of the materials is higher than what should be expected from theoretical calculations. Given that filler particles are < 0.1mm and assuming that the weight loss by the pellets during carbonization is due to the binder, a theoretical microstrength can be determined. From the comparison of experimental and theoretical microstrength data interactions between filler and binder can be inferred (Figure 4). This effect is more pronounced in carbonized pellets prepared with 30 wt % of binder. At 200 rpm, the difference between experimental and theoretical microstrength is 39.05, 30.83 and 25.42 for carbonized pellets prepared with a

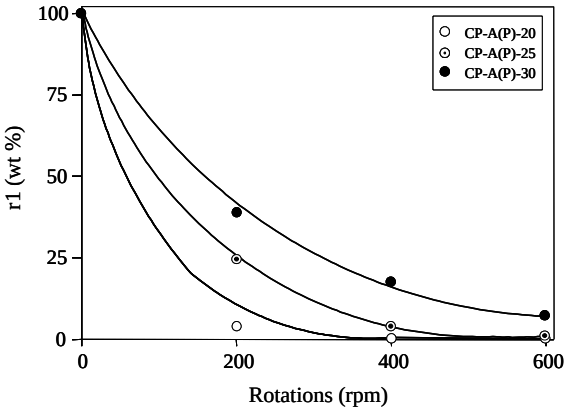

Figure 3. Effect of pitch content on carbon microstrength.

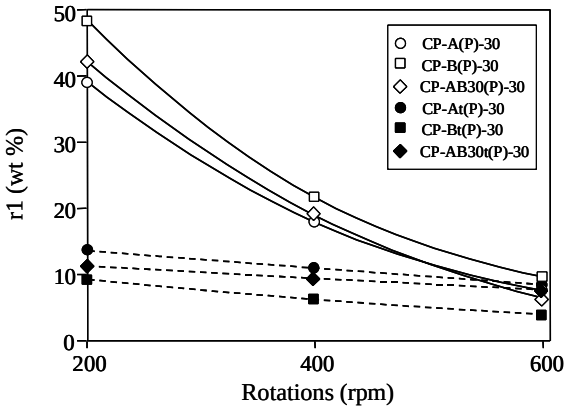

Figure 4. Experimental (empty symbol) and theoretical (filled symbol) microstrength for carbonized pellets.

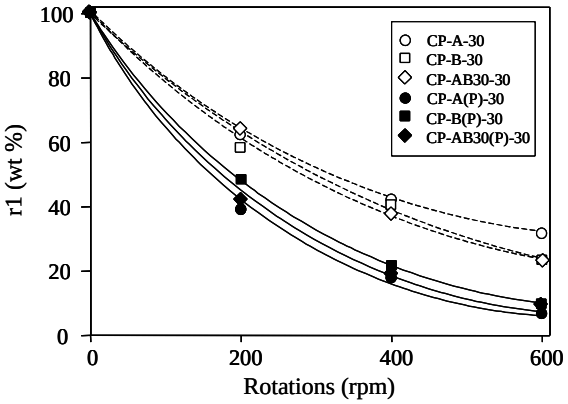

Figure 5. Effect of pressure on the microstrength of carbons.

30 wt % of B, AB30 and A, respectively. These differences become less significant as rotation increases (Figure 4). From these results it would seem that the mechanical properties of the filler and binder improve greatly when blended together.

It is also interesting that the behavior of the carbonized pellets is the reverse of that of the pitch cokes. Thus, microstrength in the pitch cokes follows the trend A-coke > AB30-coke > AB45-coke > B-coke. In the carbonized pellets with a 30 wt % of binder the trend is CP-B(P)-30 > CC-AB45(P)-30 > CP-AB30(P)-30 > CP-A(P)-30. This could be due pitch fluidity. During the molding process, the use of pressure enhances contact between the filler and binder. This enhancement should be more pronounced the higher the fluidity of the pitch. The presence of QI particles in coal-tar pitch (A) reduces the fluidity of the pitch with respect to petroleum pitch (B). Moreover, determinations of porosity, based on helium density measurements in green pellets, powdered pitch and petroleum coke (filler) allow the porosity of the pellets to be estimated. Coal-tar pitch left 2.8 vol % of porosity in the green pellet while porosity in the case of petroleum pitch was virtually zero. These results clearly show that contact between the filler and binder is more effective when petroleum pitch is used.

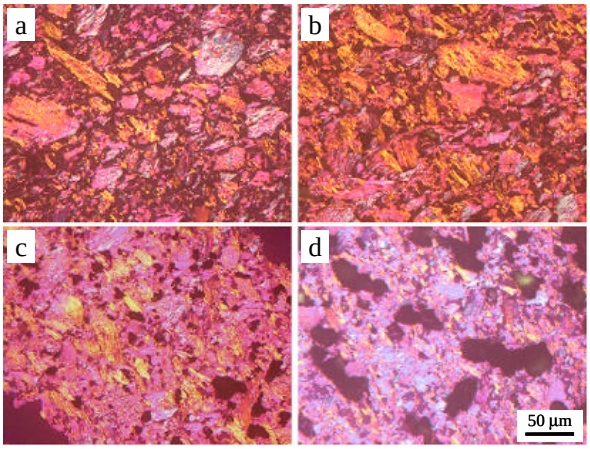

Figure 6. Optical micrographs of (a) CP-A(P)-30, (b) CP-B(P)-30, (c) CP-A-30 and (d) CP-B-30.

Microstrength of carbonized pastes

As with carbonized pellets, the microstrength of carbonized pastes increases as pitch content increases. However, carbonized pastes yield higher values of microstrength than carbonized pellets at any rotation (Figure 5). This shows the importance of the

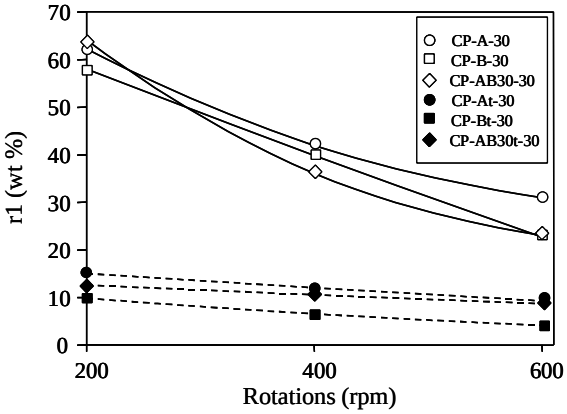

Figure 7. Experimental (empty symbols) and theoretical (filled symbols) microstrength for carbonized pastes.

processing conditions on the microstrength of the materials. It is not easy to explain why the use of pressure at the molding stage leads to materials with lower values of microstrength. One possible explanation could be that in the case of the pellets the gases produced on carbonization need a pathway to be released. Consequently, a substantial amount of pores are generated (Figures 6a and 6b). On the other hand, the gases released by the paste on carbonization can escape freely with the result that fewer pores are produced and these are of a smaller size (Figures 6c and 6d). This would also explain why the filler/binder interaction in the carbonized paste is more acute than in the carbonized pellets (Figure 7). At 200 rpm the differences between experimental and theoretical microstrength are 48.21, 51.54 and 47.28 for carbonized pastes obtained with a 30 wt % of B, AB30 and A, respectively. These values differ from each other to a lesser extent than those determined for carbonized pellets.

Conclusions

The interactions between calcined petroleum coke and pitch lead to a significant improvement in the microstrength of both the filler coke and the pitch coke. This improvement is more pronounced when 30 wt % of binder is used and pressure is not applied at the molding stage.

The use of pressure to prepare the materials enhances contact between the filler and binder (especially in the case of petroleum pitch). However, in subsequent carbonization cracks develop. These cracks have a negative effect on the microstrength of the material.

Acknowledgements

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