

SELF-SINTERING CARBON MATERIALS FROM PETROLEUM RESIDUE: A COMPARISON OF MATERIALS PREPARED USING DIFFERENT METHODS

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Introduction

Self-sintering materials can be used to prepare high strength fine grain graphite as an alternative preparation route to using mixtures of coke and binder. Self-sinterizable carbon powders have been reported to be obtained by different techniques, i.e. uncompleted carbonisation, carbonisation and stabilisation of carbon precursors, solvent extraction of mesophase spheres (MCMB), etc [1-5]. The sintering ability of the powders is a function of preparation conditions, as they determine the amount of volatile matter and binder phase [4-5].

The use of semicoke produced by controlled pyrolysis of petroleum residues is difficult, as the operation window is small. The self-sintering abilities of the powders can be improved by different techniques [1-6]. In this work a comparison of different treatments to adjust the sintering ability of the powders is carried out: second heat-treatment, oxidation and solvent extraction. The objective of this work is, therefore, to analyse the effect of the treatment on the composition of the self-sintering powders and to relate it to the sintering ability of the powders and the properties of the subsequent carbon artefacts prepared.

Experimental

a) Preparation of self-sintering carbon powders

Pyrolysis of the petroleum residue

The semicoke used to obtain the self-sintering powders was prepared by pyrolysis of an aromatic petroleum residue in a laboratory-sized pilot plant. Pyrolysis was performed at 460 °C, 3h soak time and a pressure of 1 MPa supplied by nitrogen. This semicoke was ground using a ball-mill for 1 hour, and sieved to a particle size < 60 µm.

Heat-treatment of the semicoke

The sieved semicoke was heat-treated in a horizontal furnace, under N₂ atmosphere (60 ml/min) and a heating rate of 2 °C/min at 400°C during 1.5 h.

Oxidation of the semicoke

The sieved semicoke was heat-treated in a horizontal furnace, under a dry air atmosphere (60 ml/min) and a heating rate of 2 °C/min at 200°C during 3 h.

Solvent extraction of the semicoke

The original semicoke, particle size < 500µm, was extracted with toluene at 100°C for two hours. The extraction product was dried in a vacuum drier at 80°C for 12 hours.

b) Preparation and characterization of compacts

Analysis of the powders

All the carbon solids (semicoke and self-sintering-powders) were analysed by solubility measurements (toluene, 1-methyl-2-pyrrolidone (NMP)), elemental analysis, FTIR, TG, DSC. Also the sintering ability of the powders was evaluated by TMA. Conformation and heat-treatment of raw semicokes and heat-treated powders

The semicoke and all the self-sintering powders were ground using a ball-mill for 1 hour, and sieved to a particle size < 60 µm before conformation. Three gram samples of the powders were uniaxially pressed (50 to 240 MPa) at room temperature to prepare compacts of 50x10x5 mm. The compacts were heat treated under nitrogen flow of 60 ml/min to 1000°C using a heating rate of 1 °C/min.

Mechanical Properties

Three point bending strength of the heat-treated compacts as measured. The typical sample dimensions of the heat-treated compacts used for the test were approximately 4.5x8.5x45 mm. The span length was 32 mm, and the crosshead speed 0.5 mm/min.

Results and Discussion

Three different self-sintering powders have been prepared by solvent extraction, mild oxidation and heat-treatment under inert atmosphere of a semicoke produced by pyrolysis of an aromatic petroleum. Table 1 shows the analysis of the starting semicoke and the three self-sintering powders prepared.

Table 1. Analysis of the raw semicoke and the self-sintering powders.

	Original semicoke	Extracted toluene	Heat- treated	Air- oxidised
<i>Weight change treatment (wt%)</i>	--	-16	-8	+2
<i>TI (wt%)</i>	81	97	96	90
<i>NMPl(wt%)</i>	67	92	88	83
<i>β-resin (wt%)</i>	14	5	8	7
<i>Mesophase (%)</i>	88	93	91	89
<i>Volatile Matter (%)</i>	15	11	9	14
<i>FTIR (C-Har/C-Hal)</i>	3.0	3.1	5.6	4.1
<i>C/H_{at}</i>	2.00	2.08	2.17	2.13

In all cases the treatment produced an increase of the insolubility in toluene and NMP, aromaticity, C/H_{at} ratio, and a decrease in β-resin and volatile matter. The amount of mesophase is only slightly varied by the solvent extraction) and the heat-treatment methods, as a result of a preferential extraction of isotropic phase and the high temperature-treatment, respectively. When comparing the self-sintering powders, it is observed that the solvent extraction method produces a larger reduction of the amount of β-resin, but a lower increase of the aromaticity. The heat-treatment method produces the larger increase in aromaticity, the larger reduction of volatile matter and the lower reduction of β-resin content. The oxidised sample has the lower reduction of volatile matter as a result of the mild heat-treatment and the possible formation of oxygenated groups.

Figure 1 shows the dTG vs temperature curves for the original semicoke and the self-sintering powders. The solvent extraction technique provides the highest decrease of volatile matter in the temperature range of 200-550°C. However, there is an increase of volatile matter produced at very low temperature, assigned to the evolution of rests of solvents used in extraction. The heat-treatment under inert atmosphere reduces mainly the amount of volatile matter produced at temperatures lower than 350-400°C, but the amount of volatile matter evolved above this

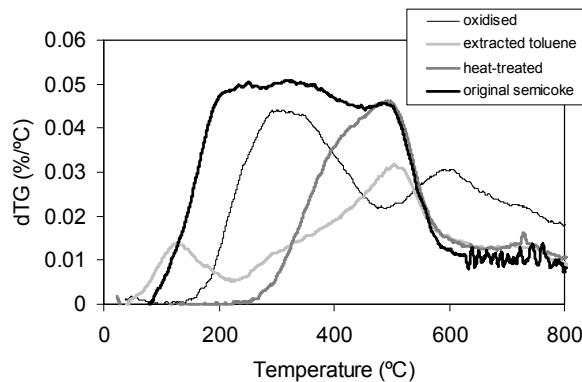


Figure 1. DTG of the semicoke and the self-sintering powders

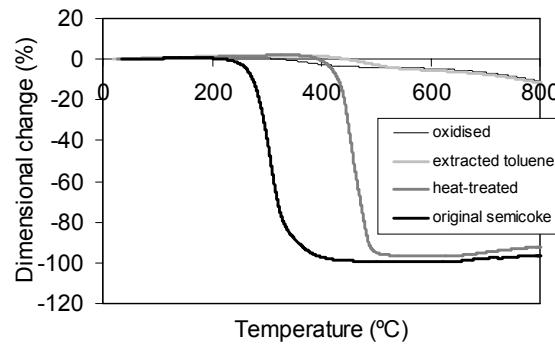


Figure 2. TMA of the semicoke and the self-sintering powders

temperature range is similar to that of the initial semicoke. The mild oxidation treatment only, due to the low temperature used, only reduces volatile matter evolved below 200-250°C and even increases the amount of volatile matter produced above 450°C, due to release of oxygenated carbon groups.

The evaluation of the sintering ability of the powders has been carried out using TMA in the penetration mode (Figure 2). The heat-treated powder presents a large thermoplasticity that begins at approximately 400°C. Extracted powders and oxidised powder present a much lower thermoplasticity than the heat-treated powders, due to the removal of binder by extraction and the creation of cross-linking between carbon layers in the case of oxidation. The temperature of initiation of the dimension change is the highest for the extracted powders. It is expected that the heat-treated powders present the best sintering between the grains but the thermoplasticity is so high that it may cause swelling of the sample upon heat-treatment.

Table 2 presents the results of the heat-treated compacts (1000°C) obtained with the self-sintering powders. Forming pressure has been optimised in each case to provide the highest density and mechanical properties. In the case of the original semicoke, the compacts swelled in all the pressure range studied. The heat-treated powders have to be conformed at pressure lower than 100 MPa to avoid swelling. In the case of the extracted and oxidised powders, compacts did not swell and present the best results at a forming pressure of 200 MPa. These samples are more rigid and present lower deformability than the original semicoke and the heat-treated powders. Weight loss of the compacts which did not swelled followed the same trend observed in the powders, the heat-treated powder being the sample that presents the lowest amount of volatile matter and the oxidised sample the highest. Density of the compacts increases with increasing forming pressure, in spite of the inferior fusibility of the oxidised and extracted powders. Bending strength for all the samples is over 80 MPa. The heat-treated sample present the best mechanical properties

even considering the lower density of the samples. The observation of the fracture surface of the compacts by SEM indicates that the heat-treated sample present the best sintering between grains. The low density can be attributed to the existence of porosity caused by the retention of volatile matter during thermal treatment of the sample.

Table 2. Results of heat-treated compacts (1000°C) using the semicoke and the self-sintering powders.

	Original semicoke	Extracted toluene	Heat- treated	Air-oxidised
<i>Forming pressure (MPa)</i>	50-200	200	100	200
<i>Weight loss (wt%)</i>	20.0	10.5	9.5	14.5
<i>Shrinkage (%vol)</i>		33	31	35
<i>Density (gcm⁻³)</i>	SWELL	1.71	1.60	1.69
<i>Open porosity (%)</i>	IN ALL CASES	5	8	4
<i>Bend Strength (MPa)</i>		80	105	100
<i>Young Mod. (GPa)</i>		15.0	16.0	17.0

Conclusions

Self-sintering carbon powders have been prepared by three different techniques: heat-treatment, oxidation and toluene extraction of a semicoke. The powders exhibit different composition and sintering abilities, that can be controlled with the preparation treatment. All the compacts, once the preparations conditions are optimised, exhibited high density and excellent mechanical properties, comparable or superior to those obtained using commercial mesocarbon microbeads.

References

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