

# CARBON FOAM PRODUCTION FROM A THERMO-CHEMICALLY MODIFIED COMMERCIAL COAL TAR PITCH

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## Introduction

The unique properties of carbon foam mainly depend on the precursor features and synthesis conditions. For the highly thermal and electrical conductive carbon foam, an anisotropic pitch precursor is required [1, 2]. A lot of factors influence the foaming process, but temperature and pressure are the most critical aspects [3]. The aim of the present investigations is to adjust by appropriate modification the composition and properties of commercial coal tar pitch for carbon foam formation. The subject of this study is developing of carbon foam samples from modified coal tar pitches using simple process without stabilization step.

## Experimental

The initial coal tar pitch was treated with H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> (drops of acid were added to the pitch at starting temperature 120°C until reaching appropriate softening point of the pitch). An exhaustive extraction is carried out consecutively by Soxhlet apparatus with petroleum ether to extract maltenes and with toluene to extract asphaltenes. After distilling off the solvent the extracts were dried in vacuum and separated. Softening points of pitches are determined by the Ring and Ball method using stainless steel balls of diameter 20 mm. For each measurement an average of three readings is taken. The variation is found to be within ±4°C. The elemental analysis was performed on Carlo Erba 1106-type equipment. Oxygen was determined by the difference. Foaming process was carried out in a ceramic crucible by heating the pitch up to 550°C (heating rate 5°C/min) in a N<sub>2</sub> atmosphere at atmospheric pressure. The final temperature of treatment was selected on the base of DTA data high enough (550°C at the end of the exothermal effect), which ensures that the polymerization and condensation reactions was completed. The resultant “green” foams were calcined at 1000°C in N<sub>2</sub> atmosphere to increase the strength and further evolving of volatiles. The resultant foams were cut to form monolithic cuboids that were used for the further study. The foam samples were heat treated at 2000°C (heating rate 3°C/min, soak time 1h) in argon atmosphere. The surface and cavities formed during pyrolysis have been examined by SEM (JEOL JSM-6390). X-ray diffraction analyses were performed with a Bruker D8 Advance diffractometer using CuK $\alpha$  radiation. The average crystallite size was calculated according to the Scherrer formula by using the Topas V3 programme.

## Results and Discussion

Commercially available pitches are not suitable for obtaining carbon foam directly. The key problem is that usually the viscosity is too low to hold the foam cell shape. Therefore, the pitch properties of these materials were tailored to meet the foaming requirements using thermo-oxidative modification with H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>.

**Table 1. Selected Properties of Studied Pitches**

Sam- ple	C wt.%	H wt.%	N wt.%	S wt.%	O (diff.)	C/H
P	90.60	5.25	0.90	0.50	2.75	1.44
P <sub>H<sub>2</sub>SO<sub>4</sub></sub>	91.20	3.83	0.80	2.12	2.05	2.01
P <sub>HNO<sub>3</sub></sub>	91.45	4.24	2.01	0.40	1.89	1.81

P-initial pitch; P<sub>H<sub>2</sub>SO<sub>4</sub></sub>-coal-tar pitch, modified by oxidation treatment with H<sub>2</sub>SO<sub>4</sub>; P<sub>HNO<sub>3</sub></sub> - coal-tar pitch, modified by oxidation treatment

The increase of the oxygen content in modified pitches, according to data in Table 1, indicates the formation of oxygen containing structures due to thermo-oxidation treatment. The increase the C/H value of the heated samples indicates that this treatment induces polymerization and condensation processes through de-hydrogenation of polyaromatic molecules, which results in the formation of larger condensed and more planar molecules. This is more expressive for P<sub>H<sub>2</sub>SO<sub>4</sub></sub> due to its catalytic effect of sulfuric acid on the condensation reactions.

Table 2 lists the properties of initial and modified pitch samples. Data show that enhancing the degree of polymerization and condensation reaction during thermo-oxidation treatment results in increase of the softening temperature and the content of quinoline insoluble of the modified pitches. In addition, modification treatment increases thermal stability of the pitch, and thus decreases the weight loss in the foaming stage. This is relevant to the formation of bubbles, because the amount of bubble agents is related to the weight loss, caused by the evolving volatiles in the foaming stage.

**Table 2. Solubility Class Separation of the Pitches Determined by Sequential Soxhlet Extraction**

Sam- ple	PES %	PEI-TS %	TI %	QI %	Softening point, °C
P	37.00	34.39	27.31	1.30	72
P <sub>H<sub>2</sub>SO<sub>4</sub></sub>	11.19	31.40	40.30	17.11	340
P <sub>HNO<sub>3</sub></sub>	13.40	33.02	38.52	15.06	320

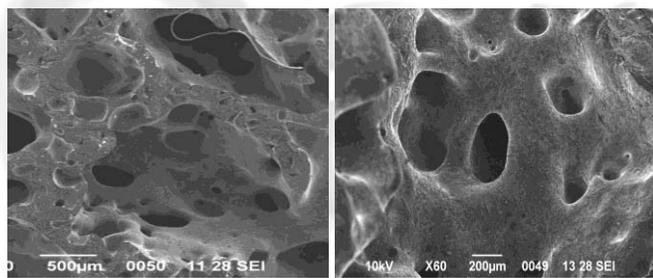
The properties and composition of modified coal tar pitches can be controlled by the temperature of thermo-oxidation treatment and amount of added acid. This allows adjusting the properties of modified pitches to meet the requirements of the foaming process by right choice of treatment condition. Table 3 summarizes the compressive strength of the materials studied - 8.9 MPa for CFPS and 7.8 MPa for CFPN. Data show that the compressive strength depends on the apparent density of the foam.

**Table 3. General Properties of the Carbon Foam Derived from Modified with H<sub>2</sub>SO<sub>4</sub> (CFPS) and HNO<sub>3</sub> (CFPN) Pitches**

Foam	Apparent density (g/cm <sup>3</sup> )	Porosity %	Open-cell %	Compressive strength MPa
CFPS	0.52	70.4	91.1	8.9
CFPN	0.49	69.0	90.3	7.8

The cell structure (thickness of cell ligament, *t*, and the length of the cell ligament, *L*) also affects the foam strength. For a regular foam, *t* and *L* have the relation with relative density  $D_a/D_t$ , where  $D_a$  is the apparent density and  $D_t$  is the true density, respectively. Usually measuring *t* and *L* of the foam is difficult, but relative density can be determined easily. Although obtained carbon foams do not have a perfect and regular cell structure, for a first approximation, the relative density is still used to describe the foam cell structure.

The results in Table 3 show that the compressive strength increases with the apparent density. The increase of apparent density implies an increase of the thickness of the cell ligaments or decrease of the length of the cell ligaments. Thicker cell ligaments and shorter cell ligaments promote higher compressive strength.

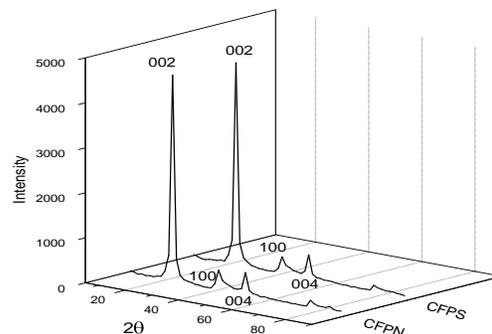


(a)

(b)

**Figure 1.** SEM images of carbon foam derived from pitch modified with H<sub>2</sub>SO<sub>4</sub> (a) and HNO<sub>3</sub> (b)

Figure 1 shows the SEM images of the derived carbon foams. Figure 1a shows the carbon foam derived from HNO<sub>3</sub> treated pitch. The foam cell size is relatively uniform with size around 200-250 μm. Figure 1b shows the H<sub>2</sub>SO<sub>4</sub> treated pitch based carbon foam. The foam cell is mainly open with size around 300-350 μm. SEM images clearly show that there are cracks in the samples, characteristic for well-developed carbon foam [3]. These cracks mainly occur between the layers aligned parallel to the cell surface, especially in the junction area of the foam cells. However, there are no major cracks found on the cell membranes of obtained foams. CFPS has smaller anisotropic domain than CFPN.



**Figure 2.** XRD of carbon foam derived from pitch modified with H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>.

Figure 2 shows the X-ray diffraction spectra for a carbon foams produced from pitches modified with HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> and heated to 2000°C (CFPN and CFPS). The 002 peaks (which are characteristic of interlayer spacing) of foams heated to 2000°C are narrow and asymmetric, indicative of relatively high ordered structure. The interlayer spacing calculated with the Bragg equation are 0.3423 nm for CFPS and 0.3424 nm for CFPN. X-ray data indicate that heat treatment to 2000°C of CFPN and CFPS lead to considerable arrangement of the foam structure.

### Conclusions

It was shown that thermo-oxidation modification of commercial coal tar pitch with HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> is appropriate treatment to adjust its plastic properties before foaming process. The properties and composition of modified coal tar pitches can be controlled by the temperature of thermo-oxidation treatment and amount of added acid. The regulation the composition and amount of volatiles of modified pitches allow to synthesize from them carbon foam without using the pressure during foaming process. It was found that pitch precursor characteristics affect foam structure and properties such as compressive strength and apparent density. The X-ray data show that the interlayer spacing found in the CFPS is higher and crystallite size in c-direction (*L<sub>c</sub>*) is smaller than that found in CFPN. Heat treatment to 2000°C of CFPN and CFPS lead to appreciable arrangement of the foam structure.

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### References

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