

THE EFFECT OF MOLECULAR COMPOSITION ON DEVELOPMENT OF POROSITY IN PITCH-BASED ACTIVATED CARBON FIBERS

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Introduction

Activated carbon fibers (ACFs) are attractive materials for adsorption and desorption applications due to their highly porous structure. Their uniform shape and small diameter allows for more uniform pore size distribution, making them suitable materials for specific applications such as hydrogen and methane storage. Petroleum pitches are among the common precursors used for ACF production. Previous studies have shown that the precursor used to prepare the ACFs has an important effect on both fiber preparation process and the final pore structure of the fibers [1-3]. In order to investigate the effect of molecular composition more systematically, fractions of commercially available petroleum pitch M-50 by Marathon Oil Company with carefully controlled compositions and varying degree of anisotropy were used to prepare ACFs and effects of composition on carbonization and activation behavior of the fibers and the final pore structure were investigated.

Experimental

Isotropic petroleum pitch M-50 (CAS 68187-58-6) was obtained from Marathon Petroleum Company LLC. Fractionation of M-50 was performed in Clemson University, and details are given elsewhere [4,5]. Prepared precursors were analyzed by Bruker Daltonics Autoflex matrix-assisted, laser desorption/ionization, time-of-flight (MALDI-TOF) mass spectrometer equipped with a 337 nm nitrogen laser to obtain absolute molecular weight distributions. Samples were prepared by mixing 10 mg of analyte and 200 mg of the matrix TCNQ for 5 min in a grinding mill (Thermo Electron Corp., model Wig-L-Bug). A thin film of the mixture was then deposited over a target cell using a solvent-free spotting method developed in our laboratories and explained in detail elsewhere [6,7].

Softening points of the prepared precursors were measured by using Mettler FP83HT Dropping Point Cell instrument. The instrument was run under nitrogen flow and at a heating rate of 2 °C/min. The molten samples obtained at the end of the measurements were mounted in epoxy resin and polished in order to be analyzed for microstructure and level of molecular order by reflected polarized-light microscopy.

Prepared precursors were melt-spun into fibers by using Alex&James batch spinning instrument and collected fibers were stabilized by gradually heating up to 264 °C in a Fisher

Scientific air convection oven for 6 days. Most of the stabilized samples were directly activated for 6 hrs using Lindberg tubular furnace at 840°C under a carbon dioxide flow of 0.5lt/min skipping the carbonization step. On the other hand, a small portion of the samples were carbonized under nitrogen flow (1lt/min) in the same tubular furnace in order to calculate % weight loss corresponding to carbonization step.

Surface characterisations of activated samples were carried out with Micromeritics Accelerated Surface and Porosity Analyzer (Model 2020). Nitrogen was used as an adsorbent at a bath temperature of 77°K. Relative pressures as low as 10⁻⁷ were used to collect data. Pore size distribution data was obtained by using the preloaded software on Micromeritics ASAP 2020 instrument based on Density Functional Theory assuming slit shaped pores

Results and Discussion

The mother pitch M-50 has an oligomeric molecular weight distribution (MWD). MWDs of all the precursors used to prepare activated carbon fibers, as well as M-50, are given in **Table 1**. As shown in **Table 1** these extracted pitches differ considerably in oligomeric composition. The polished samples from all the precursors were analyzed under polarized light microscopy prior to spinning process to determine mesophase content. The micrographs of the samples showed that, precursors with higher molecular weight (MW) than 760psig sample have anisotropy at different levels. Approximate mesophase contents, based on % area, of precursors were given in **Table 2**.

Prior to spinning process Mettler softening points (MSP) of all precursors were measured. Based on our previous experience, optimum spinning temperature is found to be approximately 20-25°C above the MSP. Exact spinning temperatures were decided during spinning process based on observation to obtain optimum amount of fibers. **Table 2** summarizes the MSPs and the spinning conditions of all the fractions in increasing MW order.

As-spun fibers were oxidized to prevent them from losing their shape during high temperature heat treatment processes. During stabilization, all the precursors followed a similar trend in terms of weight change and gained around 15-18% weight.

We have observed that carbonization is almost an instantaneous process and direct activation of stabilized fibers in CO₂ environment skipping the carbonization process (direct activation) yields similar results with carbonization of the fibers preceding activation process. Therefore, unlike the conventional methods, stabilized fibers were direct activated. However, in order to see the effect of molecular composition on carbonization behavior and to calculate actual % weight loss corresponding to activation process (% burn-off), some carbonization tests were conducted. The weight loss during carbonization process is slightly higher for lower MW samples up to 760psig sample (isotropic samples) and it is almost the same for heavier fractions (**Fig. 1**). Unlike carbonization process, weight loss corresponding to activation process (%burn-off) is almost constant for samples up to 760psig sample and it dramatically decreases for higher MW samples.

Table 1. MALDI-TOF area percentages

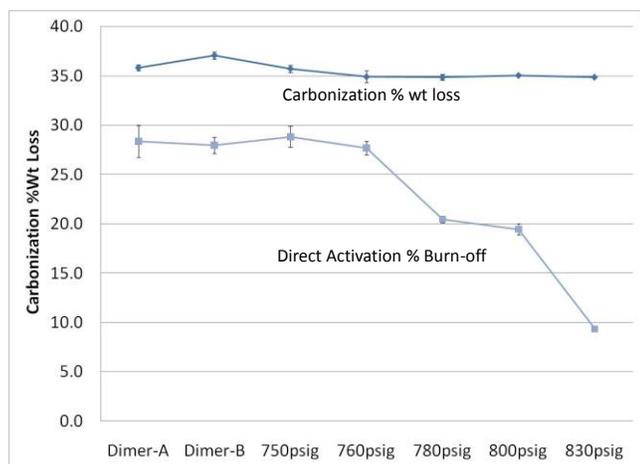
	Monomer	Dimer	Trimer	Tetramer	Pentamer
M-50	33.0	59.9	6.7	0.3	0.0
E-136	0.7	99.0	0.2	0.1	0.0
H-10-11	0.0	99.9	0.0	0.0	0.0
750psig	5.2	78.7	14.0	1.8	0.2
760psig	0.0	52.3	35.2	11.0	1.4
780psig	0.0	44.5	41.3	12.2	2.0
800psig	0.0	41.6	44.6	12.1	1.7
830psig	0.0	11.1	57.9	25.1	5.9

Oligomers were assumed to be in the following molecular weight ranges: Monomer 250-388; Dimer 388-645; Trimer 645-890; Tetramer 890-1120

Table 2. Softening points and spinning conditions of all fractions.

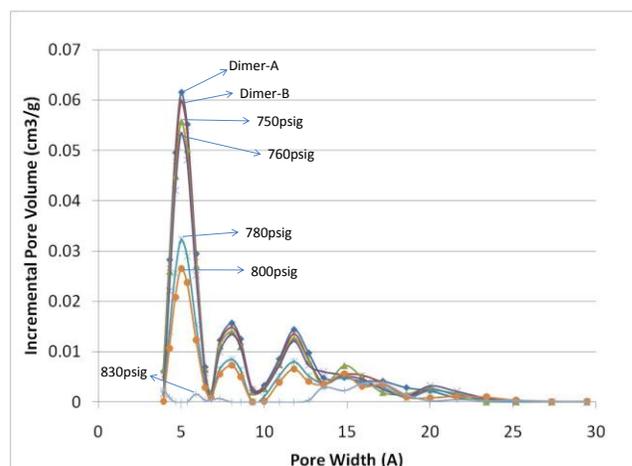
	Mettler Softening Points	Mesophase Content (%)	Spinning Conditions	
	MSP (C)		Temp (C)	Press (psi)
M-50	116	0	-	-
Dimer-A	202	0	222	1050
Dimer-B	212	0	234	600
750psig	210	0	231	700
760psig	257	<1	285	950
780psig	297	4	328	1150
800psig	312	16	341	1400
830psig	339	100	362	900

This also shows that the activation rate is almost the same for all isotropic samples, whereas it dramatically drops with the inclusion of mesophase regions (Fig. 1). Surface characterization of all direct activated fibers were carried out using similar conditions and nitrogen isotherms were used to obtain incremental pore size distributions based on Density Functional Theory assuming slit shaped pores. Fig. 2 shows that volume of narrow micropores (<7Å) significantly differs with composition of the precursor. The decrease in narrow micropore volume with increasing MW among the isotropic

**Fig. 1.** Weight changes during carbonization and activation of oxidized fibers.

fibers (760psig and lower MW) clearly shows the direct effect of molecular composition on final pore structure. With the

addition of effect of the mesophase (molecular order) the change in narrow micropore volume becomes more dramatic.

**Fig. 2.** Incremental pore size distribution of 6hr direct activated carbon fibers.

Conclusions

Activated carbon fibers were prepared from seven different fractions of the same mother pitch, M-50 with different compositions; four of which are isotropic and the three of which have different levels of anisotropy (mesophase content). Presence of high amount of monomer and dimer molecules compared to heavier molecules resulted in higher carbonization weight loss. Also, increase in mesophase content caused a dramatic drop in activation rate. Increase in MW resulted in a drop in micropore volume of the ACFs and this drop became more dramatic with increase in mesophase content.

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