CHARACTERIZATION OF PITCHES USING GEL PERMEATION CHROMATOGRAPHY

Helen K. Mayer
UCAR Carbon Company Inc.
12900 Snow Road, Parma, OH 44130

Pitch is a complex material comprised of thousands of components, mainly polyaromatic hydrocarbons and their heterocyclic analogs. Even though pitch has a complex molecular composition, it behaves homogeneously; that is, its properties tend to change with increasing molecular weight (1). The molecular weight distribution of a pitch is important in the production of graphite because low molecular weight molecules act as plasticizers while high molecular weight species control the coking value. Due to the complexity of pitch, very few analytical techniques provide much information about composition. However, gel permeation chromatography (GPC) provides a "fingerprint" of pitch with respect to its molecular composition.

GPC separates molecules based on size, which typically correlates to molecular weight. For pitches, interpretation of GPC curves is not easy. Some of the difficulties are: the entire pitch cannot be characterized because of incomplete solubility in common solvents; GPC detection options that may result in more molecular weight information are limited due to the low average molecular weight; pitch components exhibit some nonideal elution behavior resulting in molecules not being eluted in order of molecular weight; and the constituents of pitch have varying refractive indices which result in different detector responses for the same number of molecules. Due to varying refractive indices and nonideal elution behavior, absolute ratios of "small" vs. "large" molecules cannot be obtained. This limits direct GPC comparisons to pitches in similar classes (e.g., coal tar, petroleum, etc.). Despite its limitations, GPC provides discrete information on composition which can be related to processes and properties, unlike most analytical determinations of molecular weight that give only an average value.

EXPERIMENTAL

Pitches were analyzed by GPC at elevated temperature (90°C) using a DuPont 850 chromatograph connected to a Knauer high-temperature differential refractometer. 1,2,4-Trichlorobenzene (TCB) was pumped at 1 mL/min through a Polymer Laboratories precolumn and two 5-μm 100 Å columns. A polystyrene standard ($M_n > 200{,}000$) was used as a flow rate marker. In addition to over one hundred commercially-available coal-tar pitches, a number of bench-scale pitches with various precursors were analyzed using GPC.

RESULTS AND DISCUSSION

Comparison of Pitch Types. GPC can differentiate pitches made from various precursors, such as coal tar, petroleum, and hydrocarbons. Caution needs to be exercised in directly comparing pitches made from different precursors due to variations in molecular composition. When analyzed by GPC, coal-tar pitches have the characteristic shape shown in Figure 1a, with two poorly resolved peaks eluting at the same retention volume. The molecular weight distributions of coal-tar pitches vary in the relative heights of the two poorly resolved peaks, as well as in the shape and width of the shoulder at the high molecular weight end. In comparison, petroleum pitch distributions are usually broader and are shifted to the higher molecular weight region of the chromatogram (see Figure 1b). If a pitch is made from a coal-tar/petroleum blend, the resulting distribution (see Figure 1c) reflects characteristics of both precursors, especially in the middle molecular weight range.

Comparison of Coal-Tar Pitches Made From Various Tar Sources. Four base tars with various QI and aromaticity levels (see Table 1) were used to make pitches to study the effect of thermal treatment on carbon anode properties (2). When comparing the molecular weight distributions of the control pitches (no thermal treatment), Pitches A and P have similar GPC curves while Pitches C and Q have narrower distributions (see Figure 2). Although Pitches A and P have different QI levels, their GPC curves are similar, showing that the amount of material potentially soluble in TCB has no effect on the resulting curve. Both Pitches A and P have lower aromaticities and higher degrees of substitution of aromatic rings than do C and Q. Less aromatic and more substituted molecules tend to elute in the high molecular weight region, contributing to the broader distributions.

Comparison of Coal-Tar Pitches Made Using Various Processing Conditions. For the experiment described above, pitches were made from the four base tars by thermal treatment to achieve various β-resin levels. With increasing thermal treatment, the molecular weight distributions all changed dramatically: the width of the distribution *decreased*, the height of the high molecular weight shoulder peak increased, and the relative height of the first of the two partially resolved peaks increased (see Figure 3). Although it appears that the high molecular weight character decreases with thermal treatment, several factors may be contributing to this unexpected behavior. The methyl/methylene ratio of the pitch increases with increasing thermal treatment, but the number of aliphatic carbons per side chain remains constant. If the methyl/methylene ratio increases, the apparent size of the molecule will be decreased (even though the molecular weight is increased), resulting in a narrower distribution. In some cases, polymerization can decrease the linear molecular size. Also, as smaller molecules are polymerized, they are no longer acting as cosolvents for the larger molecules, making them less soluble in TCB.

CONCLUSIONS

For the characterization of pitches, GPC distributions, when interpreted with caution, contain much useful information. GPC can differentiate pitches with various precursors. As shown in previous work with commercial pitches (3), within a class of pitches, the major advantage of GPC is its ability to differentiate pitches based on their processing background. In limited cases, it is useful in assessing the effects of changing the starting material. In combination with other tests, GPC is a useful tool for the comparison of pitches.

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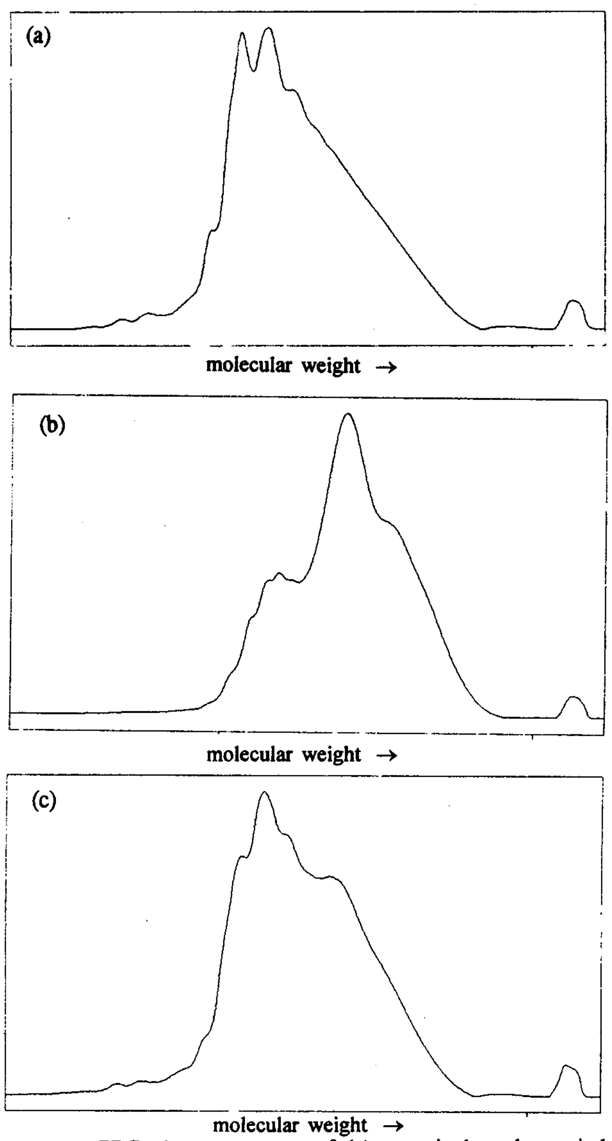

Figure 1: GPC chromatograms of (a) a typical coal-tar pitch, (b) a typical petroleum pitch, and (c) a pitch made from both coal-tar and petroleum precursors.

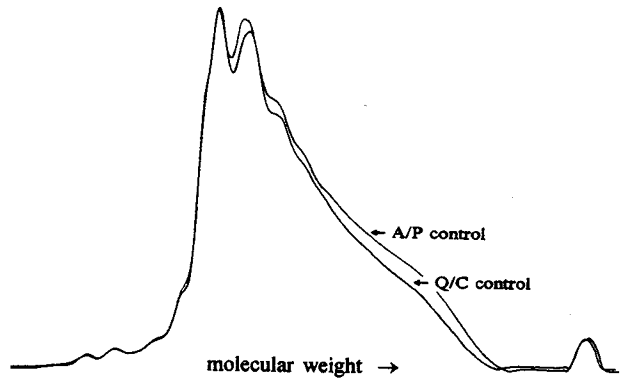

Figure 2: Comparison of GPC curves from pitches made with different coal-tar precursors.

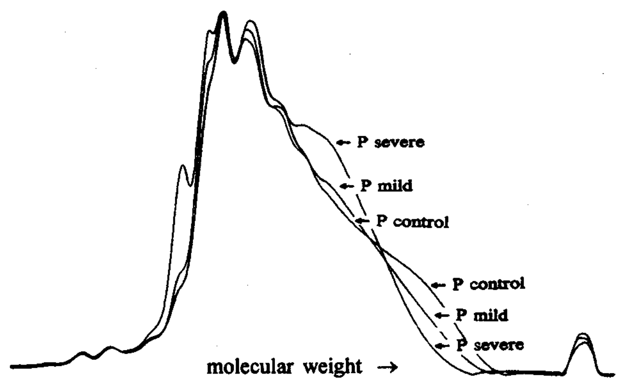

Figure 3: Comparison of GPC curves from pitches made from a single coal-tar source with different levels of thermal treatment.

Table 1: Pitch Properties

Pitch	Thermal Treatment	SP, °C	QI, %	β-Resin, %	NMR, Ha/Hn	NMR, α-Methyl/ Methylene
A	Control	109.2	4.0	14.1	4.6	2.7
A	Mild	108.0	3.8	17.6	4.3	3.2
A	Severe	108.2	4.3	21.6	4.5	3.3
C	Control	107.5	4.8	14.5	8.9	1.2
C	Mild	111.8	5.4	19.6	8.4	1.7
C	Severe	108.1	5.7	20.1	8.3	2.4
P	Control	111.7	11.7	12.3	6.0	2.3
P	Mild	109.7	11.4	17.3	5.8	2.6
P	Severe	107.7	11.4	19.4	6.1	3.6
Q	Control	109.7	12.2	13.1	8.1	1.0
Q	Mild	111.0	12.5	17.8	8.0	1.1
Q	Severe	108.8	13.5	20.1	8.1	2.7