THE DETERMINATION OF THE MOLECULAR DISTRIBUTIONS OF GRAPHITE BINDER MATERIALS BY GEL PERMEATION CHROMATOGRAPHY*

by

Eugene M. Wewerka

Los Alamos Scientific Laboratory
The University of California
Los Alamos, New Mexico

ABSTRACT

One aspect of the study of polymeric graphite binder materials which has had relatively little investigation in the past is the effect of the molecular distributions of the binder materials on the physical and mechanical properties of the resulting graphites. The lack of information in this area is largely due to the complex chemical natures of these polymers. Instances appear in the literature of detailed studies of this type. However, the extent of time, materials, and specialization involved has a priori ruled out such investigations as routine methods of classifying and studying the molecular distributions of large numbers of binders of the many types available. The relatively new technique of gel permeation chromatography, on the other hand, is a fast, general means of obtaining the molecular distributions of polymers, lending itself to many applications in the field of binder chemistry.

Gel Permeation Chromatography: Gel permeation chromatography (GPC) is a type of liquid-solid chromatography which separates molecules according to their size and shape. The separation takes place in a column packed with beads of a crosslinked polystyrene gel of known maximum pore size(1). A dilute solution of polymer is introduced into the solvent stream at the column inlet. The molecules flowing through the column, penetrate the polystyrene gel to the extent permitted by the size and shape of the individual molecule. Therefore, the largest molecules (penetrating the gel network to the least degree) are eluted through the column first. Smaller molecules, diffusing into the gel to greater degrees, are eluted in order of decreasing size. The molecules emerging from the column flow through a differential refractometer balanced by a dummy column for pure solvent. The refractometer response is recorded continuously, giving a record of amount (refractive index change) versus molecular size and shape (time or volume of solvent eluted).

With suitable calibration the size/shape distributions can be converted to true molecular weight distributions. However, for most instances encountered in graphite binder studies, this step is unnecessary. A rough, but useful, calibration curve is provided by the elution positions of model compounds.

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(1) By controlling the manufacturing process, polystyrene gels with maximum permeabilities ranging from 50 Å to more than 1,000,000 Åcan be made. Ideally, gel permeability is chosen so that the largest molecules of the polymer are able to penetrate the gel to a small degree.

Furfuryl Alcohol Resins: The molecular distributions of commercial furfuryl alcohol resins (Reichold Chemical Company) and a series of experimental resins have been investigated by GPC. The experimental resins were made with either a maleic anhydride or a phosphoric acid catalyst, and ranged in viscosity from 100 cps to approximately 1,000,000 cps. The molecular distributions of the furfuryl alcohol resins are broad, ranging in molecular weight from approximately 2000 to 3000 down to monomer. They are well resolved in the low molecular weight region.

Coal Tar Pitch: Of fundamental interest to the graphite industry is the effect of the "free carbon" content on the coking yields and graphitization of coal tar pitches. A series of Allied Chemical Company coal tar pitches with "free carbon" values ranging from 4 to 20 percent has been investigated with GPC. Of main interest is the molecular distributions of the soluble part of the coal tar pitches covering a wide range of "free carbon" contents. These distributions (broad and nonspecific) are easily compared using the GPC technique.

Synthetic Thermoplastic Resins: Recent investigations show that thermoplastic materials giving relatively low coking values when isolated may, on combination with another resin or filler system, give respectable coking values. Two thermoplastic resin types with low coking values were investigated by GPC leading to further studies of this effect (Coumarone-Indene resins manufactured by the Neville Chemical Company, and Gilsonite resins manufactured by the Crowley Chemical Company). The Coumarone-Indene resins (ranging from hard to soft) displayed varied molecular distributions, with good resolution of low molecular weight compounds. The series of Gilsonite resins varied little in the shapes and positions of the molecular distributions.