CHROM. 5119

THE USE OF GEL PERMEATION CHROMATOGRAPHY IN THE DEVELOPMENT OF HIGH-QUALITY GRAPHITE*

J. M. DICKINSON AND E. M. WEWERKA

Los Alamos Scientific Laboratory, University of California, Los Alamos, N.M. 87544 (U.S.A.)

SUMMARY

Many graphites to be used for nuclear, aerospace or high-temperature applications are now being made with synthetic components rather than with the traditional mixtures of coke filler and pitch binder. This additional control of raw materials results in a higher quality and more reproducible graphite. One class of synthetic polymers finding considerable use as graphite binder materials is furfuryl alcohol resins. The molecular size distributions of furfuryl alcohol resin binders as determined by gel permeation chromatography have been shown to play an important role in determining the physical properties of the resulting graphites. Gel permeation chromatographic data were related to graphite physical properties by two methods. In the first, the amount of material in a given molecular size interval was computed, and the effect of each size interval on the properties of graphite was determined using a graphical method. Secondly, the total molecular size distribution was then related to the physical properties of graphite by a statistical method, which was used to calculate parameters describing the gel permeation chromatographic data. The results of these studies have led to a more thorough understanding of the role played by furfuryl alcohol resins as related to their use in the manufacture of graphites, and to specifications for the synthesis of an improved furfuryl alcohol resin for use as a graphite binder material.

INTRODUCTION

Artificial graphites are usually made by molding or extruding a semi-plastic mass of petroleum coke and coal-tar pitch, and subsequently heating the piece, over a period of several months, to a temperature of 2500 to 3000°. Such graphites, which find wide spread use in the aluminum and steel manufacturing industries, usually have rather low densities, high conductivities and moderate strengths. By careful selection of materials, nuclear grade graphites have been and still are being manufactured from mixtures of coke and coal tar pitch[1]. However, the increasingly stringent demands being made on the purity and uniformity as well as on the properties of

graphites for use in nuclear reactors have made it desirable to examine other raw materials.

Most of the materials that are used as binders in graphite are polymeric in nature and are chemically heterogeneous; i.e., they usually contain many different kinds of chemical compounds. Coal tar pitch binders[2], for example, are composed of a myriad of distinct organic compounds, and often contain an assortment of extraneous impurities. In addition, they can vary considerably, both chemically and physically, from batch to batch. These factors make it difficult to control the reproducibility of graphite made using pitch binders.

Binder materials that are based entirely on synthetic polymers have distinct advantages. A number of such synthetic binder materials have been used; however, this discussion will be limited to the various furfuryl alcohol polymers which are used as binders.

Furfuryl alcohol polymers are also heterogeneous but they possess several desirable characteristics for the manufacture of high-quality graphite. In particular, the amounts of undesirable impurities can be kept to a minimum. They are liquid at room temperature, which greatly simplifies the mixing and fabrication operations; they result in high yields of carbon upon high-temperature pyrolysis; and they are thermosetting, which is desirable if complex shapes are to be fabricated. In addition, by controlling the degree of polymerization of the resins, a variety of viscosities and molecular size distributions can be reproducibly synthesized.

Considering the numerous purposes served by the binder material during the manufacture of graphite it has been suggested[3,4] that the molecular sizes, or more precisely the molecular size distribution, of the binder might be an even more important characteristic of it than its exact chemical composition. Based on this postulate, a study was undertaken to determine the effects of the molecular size distributions of furfuryl alcohol polymers on the properties of graphites made from them.

The molecular size distributions of the various furfuryl alcohol polymers were determined using gel permeation chromatography (GPC). The resulting data were treated using a statistical method which resulted in a numerical description of the molecular size distribution of the polymer. Correlations were made between the molecular size distributions of the binder polymer and the physical properties of the graphites made from them. These studies resulted in a better understanding of the relationships between the binder and the resulting graphite, and in a set of specifications for an improved furfuryl alcohol polymer for use as a binder in the manufacture of high-quality, high-density graphite.

EXPERIMENTAL

The furfuryl alcohol polymers were made by the polymerization of furfuryl alcohol in the presence of maleic anhydride by methods which have been reported elsewhere[5].

GPC was done with a Waters Model 200 gel permeation chromatograph which was equipped with a series arrangement of five 4-ft. polystyrene gel columns having maximum pore sizes of 3000, 500, 250, 250 and 60 Å. Samples for GPC analysis were either 0.5 or 1 % by weight in tetrahydrofuran (THF). These were injected for either 15- or 30-sec periods. A solvent (THF) flow rate of 1 ml/min was used.

Most of the polymer molecular size distributions used in this study were made by blending furfuryl alcohol resins of differing degrees of polymerization with one another or with furfuryl alcohol until the desired viscosity of 1600 cP was reached. This resulted in a number of polymer binders having equal viscosities and rather widely differing molecular size distributions. The resin viscosities were measured with a MacMichael-Fisher viscometer at 25°.

The graphites were manufactured using a mixture of 85 parts of graphite powder, 15 parts of carbon black, and 27 parts of one of the experimental furfuryl alcohol polymers that had been catalyzed with 4 % maleic anhydride. A manufacturing process that has been described earlier[6,7] was used. It involved a complex mixing and multiple extrusion procedure prior to making the final extrusion in the form of a 1/2 in. diameter rod. The rods were thermally set by heating them to 200° over a period of several days. Then the rods were heated slowly to 900° to carbonize the binder material. The carbonized rods were finally given a graphitization treatment at 2800°. This procedure has been demonstrated to be satisfactory for the production of an exceptionally uniform, high-quality graphite[6].

Property measurements were made on the graphitized rods, using standard methods, and these properties were related to the molecular size distributions of the polymers used to make the graphites.

MATERIALS

Furfuryl alcohol (Eastman white label), maleic anhydride (MCB standard quality) and tetrahydrofuran (Dupont commercial grade) were used in this study. The graphite powder was Great Lakes 1008S grade and the carbon black was Thermax, manufactured by the Thermatomic Carbon Company.

RESULTS

Correlations between molecular size regions of the polymer and the physical properties of the graphites

It has previously been shown that the binder viscosity, up to about 1600 cP, has a strong influence on both the manufacturing processes and the properties of the resulting graphite[8]. Consequently, the molecular-size-distribution studies were carried out using a series of furfuryl alcohol polymers all having viscosities of about 1600 cP. This value was chosen since at viscosities near 1600 cP a small change in the viscosity of the resin caused only minor changes in the properties of the graphite, while at lower viscosities a change in viscosity resulted in an appreciable change in properties. In addition, at viscosities much above 1600 cP fabrication difficulties increased appreciably.

The molecular size distributions of the furfuryl alcohol polymers were determined using GPC. The resulting elution curves were divided according to molecular size, and the size regions were numbered 1, 2, 3 and 4 as shown in Fig. 1. These divisions were chosen such that the first region represents the amount of monomer-size molecules in the resin; the second represents the low-molecular-weight species such as the dimer, trimer and tetramer; the third represents the medium-size molecules of molecular weights up to about 1000; and the fourth represents large molecules having molecular weights to about 5000.
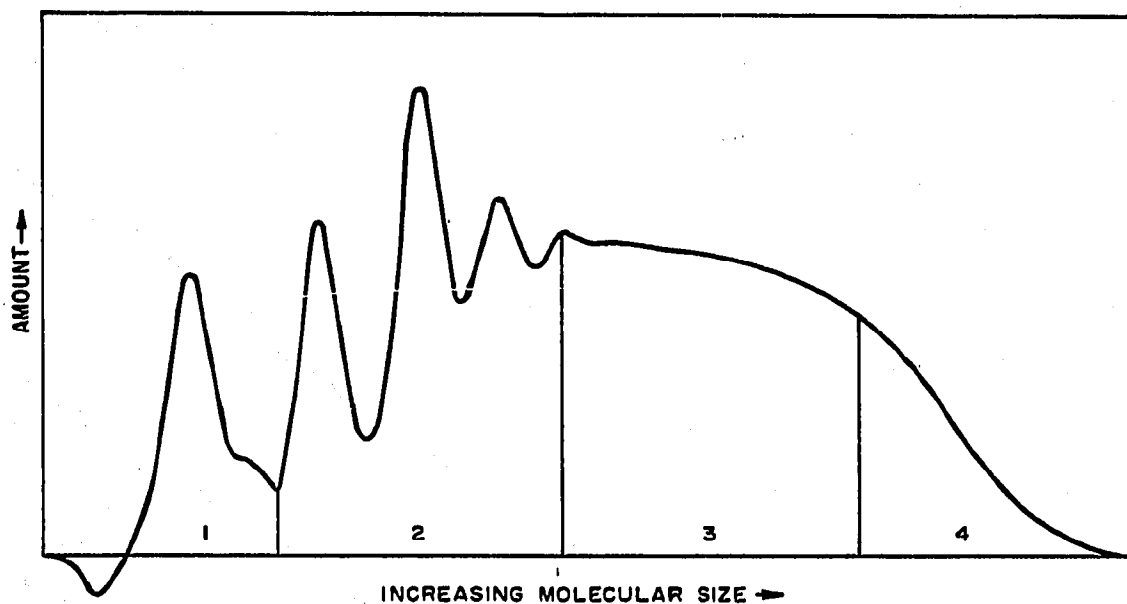
Fig. 1. A GPC trace of a furfuryl alcohol polymer showing the size intervals chosen for the molecular-size-distribution studies.

The amount of material in each of the numbered regions was estimated from the GPC curves using weight integration. These data, expressed as fractions of the total distribution of each resin, are shown in Table I. The relationships between the fraction of polymer in each of these regions and both the extrusion parameters and physical properties of the graphite were examined.

As the proportion of the distribution in region 1, monomer-size molecules, increased the extrusion characteristics changed appreciably, and the properties of the resulting graphite were affected. A distinct drop in the bulk density of the graphite rods occurred as the amount of monomer-size molecules in the resin used to make the graphite increased (Fig. 2). The drop in density appears to be due to a combination of factors, all related to the molecular size distribution and, in particular, to the

TABLE I

MOLECULAR SIZE DISTRIBUTIONS OF SOME FURFURYL ALCOHOL POLYMERS

Resin identification No.	Fraction of polymer in each of the molecular size regions			
	Number 1 (%)	Number 2 (%)	Number 3 (%)	Number 4 (%)
1600	9.5	38.6	40.7	11.2
144	10.0	35.4	41.5	13.1
234 + 236	12.0	35.4	39.3	13.3
240 + FA	12.6	31.2	40.9	15.3
235 + 236	13.7	35.2	37.2	13.9
163 + 215	16.5	40.0	34.5	9.0
239 + FA	21.1	23.7	36.2	19.0
154 + FA	24.5	22.6	34.5	18.4
163 + FA	29.0	30.2	32.4	8.4
241 + FA	31.9	22.6	32.5	13.0

monomer-size molecules. These factors include a lowering of the extrusion pressure, the adhesiveness of the resin, and the carbon residue realized from the polymer upon pyrolysis.
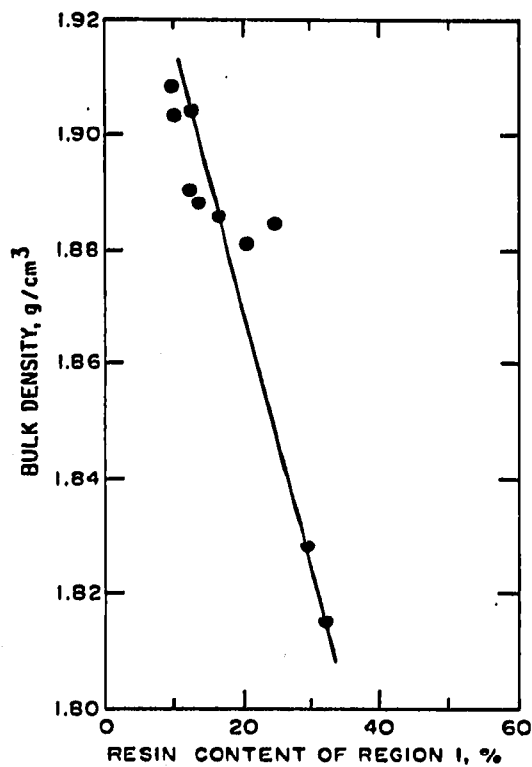

Fig. 2. The change in bulk density due to the amount of monomer-size molecules in the polymers.

Accompanying this large drop in density were corresponding changes in such properties as strength, modulus, and the thermal and electrical conductivities. Measurements of the preferred orientations of the rods using X-ray methods indicated that, in general, only minor changes occurred. These were too small to affect the properties that are sensitive to crystallographic orientation.

The amount of the polymer in the intermediate size regions, 2 and 3, of the distribution did not individually affect the properties of the graphites in a systematic manner. However, it was observed that in order to make a high density graphite it was necessary to have over 70 % of the molecular size distribution contained in these two regions (see Table I).

Increasing the amount of the largest polymer molecules did not appreciably increase the densities of the graphites, perhaps because such an increase necessitated a corresponding increase in the amount of the smaller molecules required to maintain the viscosity at 1600 cP.

Statistical descriptions of the polymer distributions and their relationship to the properties of the graphites

A non-functional statistical treatment[9] of the GPC data was used to obtain a numerical description of the molecular size distributions of the polymers. This

treatment has proven useful for handling porosity distributions[10] as well as particle-size distributions[9] and appears to be equally applicable to GPC data.

The molecular size intervals used for this study were selected as described earlier in this paper and are shown in Fig. 1. If comparisons between the polymers are to be valid, the same interval widths must be used for all of the distributions.

Since the sizes of the polymer molecules in each of the four intervals chosen for this study were not known accurately, the numbers 1, 2, 3 and 4 were used to represent the midpoints of the molecular size intervals. It would, of course, be more desirable to use the actual molecular sizes if they were available; however, useful comparisons can be made from data treated in this way.

The mean, $\bar{M}$, of the sample data for each distribution was calculated using eqn. 1, where W_i/W represents the fraction of the polymer present in the ith molecular size region, whose midpoint is represented by M_i, the number of the interval.

$$\bar{M} = \sum_{1}^{I} \frac{W_i}{W} M_i \tag{1}$$

Similarly, the variance, S^2, of the distribution was determined using eqn. 2.

$$S^2 = \sum_{1}^{I} \frac{W_i}{W} (M_i - \bar{M})^2 \tag{2}$$

A third statistic, the coefficient of variation, CV_d (ref. 9), which can be used to describe the distribution with a single numerical value, was determined using eqn. 3.

$$CV_d = \frac{S}{\bar{M}} \tag{3}$$

The means and variances of the molecular size distribution data are shown plotted against the bulk densities of the graphites in Fig. 3. Increasing the mean molecular size resulted in an increase in bulk density, while decreasing the variance resulted in an increase in density. It can be noticed that for polymers with nearly equal mean molecular sizes, those having the smaller variances result in graphites having higher densities.

This is further suggested by the curve shown in Fig. 4. The bulk density of a graphite increased if the coefficient of variation of the binder used to make the graphite decreased. This statistic, which relates the "average" molecular size of the polymer to the "width" of its molecular size distribution, has been particularly useful in examining relationships between binder materials and the graphites made from them. It points out that a low value of the variance coupled with a high value of the mean is desirable, and implies that a binder containing a single molecular size would be ideal. However, other factors such as the need of a certain amount of monomer to provide lubrication for the extrusion process, coupled with the 1600 cP viscosity requirement, limit the degree of monosizedness that is desirable. Also, from a practical standpoint, the manufacture of a polymer with monosized molecules and a specified viscosity, to say the least, presents substantial problems.

However, by minimizing the coefficient of variation, which can be done by choosing proper experimental conditions and by polymerizing directly to the desired viscosity, a superior furfuryl alcohol polymer binder can be made.
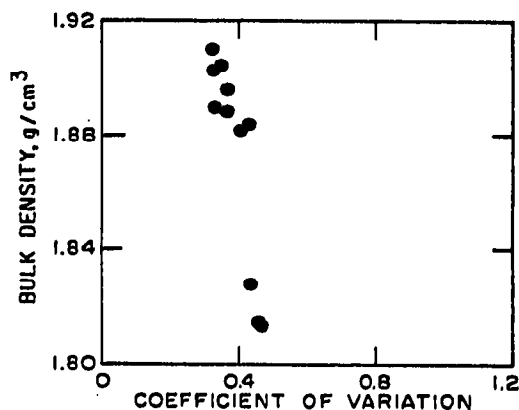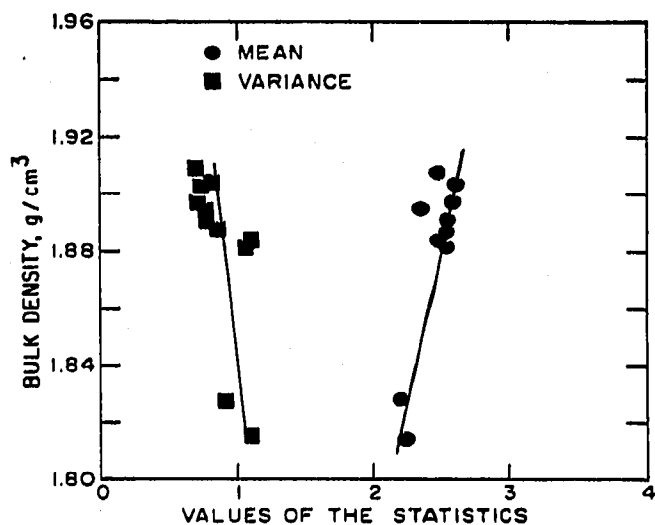
Fig. 3. The change in bulk density with statistical parameters describing the molecular size distribution of the polymers.

Fig. 4. The effect of the coefficient of variation of the polymers upon the bulk density of the graphite.

CONCLUSIONS

GPC has been used to determine the molecular size distributions of furfuryl alcohol polymers which were used as binders in the manufacture of high-density graphites. The GPC data were evaluated in such a way that a direct correlation could be made between the molecular size distributions of binder materials and the properties of graphites made from them. This led to a better understanding of the role played by the binder in graphite, and to the production of improved furfuryl alcohol polymer binders.

REFERENCES

1 R. E. NIGHTINGALE, Nuclear Graphite, Academic Press, New York, 1962.
2 J. R. HOOKER, Pitch Binders for Graphite: A Survey of the Literature, USAEC, Division of Technical Information, GA3985, General Atomics, San Diego, Calif., 1963.
3 E. M. WEWERKA, Carbon, 6 (1968) 93.
4 E. DE RUITER, J. F. M. OTH, V. SANDOR AND H. TSCHAMLER, Characterization of Binders used in the Fabrication of Graphite Bodies, WADD Technical Report 61-72, Vol. XI Supplement, Union Carbide European Research Associates, Brussels, 1964.
5 E. M. WEWERKA, J. Appl. Polym. Sci., 12 (1968) 1671.
6 M. C. SMITH, The Manufacture and Properties of an Extruded, Resin-Bonded Graphite, CMF-13 Lot AAQ1, LA-3981, Los Alamos Scientific Laboratory of the University of California, Los Alamos, N.M. 1968.
7 P. WAGNER AND L. B. DAUELSBERG, Carbon, 7 (1969) 273.
8 J. M. DICKINSON AND E. M. WEWERKA, Carbon, 8 (1970) 249.
9 H. D. LEWIS AND A. GOLDMAN, Theoretical Small Particle Statistics: A Summary of Techniques for Data Analysis with Recent Developments in Data Comparisons, Notations, and Mixture Theory, LA-3656, Los Alamos Scientific Laboratory of the University of California, Los Alamos, N.M., 1968.
10 J. M. DICKINSON AND H. D. LEWIS, Porosity Data Interpretation, LA-3938, Los Alamos Scientific Laboratory of the University of Calif., Los Alamos, N.M., 1968.