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Estimation of Optimum Binder Concentration
for Molded Carbons

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by

R. J. Imprescia

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ESTIMATION OF OPTIMUM BINDER CONCENTRATION FOR MOLDED CARBONS

by

R. J. Imprescia

ABSTRACT

The optimum binder concentration of a given filler-binder system is usually determined by measuring properties of fabricated carbons as a function of binder content. This technique is necessarily lengthy and expensive. In this paper two other methods are described for estimating the binder optimum, both of which are based on the determination of the void volume within the network of the compacted filler. The first of these makes use of a simple relation for calculating an apparent void volume from measurements on a hot-molded, pitch-bonded carbon. In the second method, a highly volatile lubricant is substituted for the binder in the mix and, by the weight loss on evaporation of the lubricant, an equivalent volume is calculated. The optima estimated by these two techniques agree well with those determined by the direct measurement of properties.

1. INTRODUCTION

The dependence of the properties of carbon materials on the amount of binder in a green mixture is well established.^(1, 2, 3) Strength, Young's modulus, and electrical conductivity all increase with increasing binder up to a value corresponding to an optimum concentration, and beyond this steadily decrease. The bulk density may either decrease or become constant at contents above the optimum, depending on whether or not the excess binder is squeezed out of the mixture during forming. Optima determined by measurement of each of these different properties seem to agree well,^(2, 3) indicating that measurement of any one of them as a function of binder content may be sufficient for determining binder requirements. Furthermore, it appears that this optimum content corresponds to the volume of binder necessary to fill all accessible space within

the void network of a compacted filler.⁽²⁾

The determination of optimum binder content by the measurement of properties, although a direct and positive method, can be time-consuming and expensive. There are other means by which optimum binder content has been estimated, the most common of which is the subjective observation by an operator of some characteristic of the green mix. The appearance of a particular degree of wetness of the mix and the difficulty involved in extruding it are both commonly used as a means of getting a "feel" for the binder requirement. One investigator reports that an apparent sudden decrease in viscosity as binder is gradually added during mixing is an indication of an optimum binder content.⁽⁴⁾ These methods, although useful as rapid operational controls, may be subject to large errors because of their subjective and indirect natures.

A more direct approach is that reported by Wiggs⁽⁵⁾ in which a combination of mercury porosimetry and an oil-absorption test is used to estimate the void volume available to pitch in a compacted filler. Here the filler is first sieved into closely graded size fractions, and then mercury porosimetry is used to determine a weighted average internal pore volume from the fractions. The total pore volume is then determined by the oil-absorption test. This test consists of slowly adding linseed oil to a filler with continual rubbing until the mass has a putty-like appearance with no excess of oil. Assuming that the internal pore volume is inaccessible to binder, the difference between the total pore volume and the internal pore volume then gives an estimate of the volume of accessible pores in a compacted filler. In spite of the subjective nature of the oil-absorption test, the one case reported in Wiggs' paper was in excellent agreement with the optimum determined from strength measurements. One shortcoming of this method, however, is that it is not applicable to fine fillers that cannot be conveniently separated into closely sized fractions. Also, because of the large number of porosimetry measurements, it can be a long and expensive process and without much advantage over the equally long, but more positive, properties method.

This report describes two other techniques developed in this Laboratory for estimating the binder requirements of carbon fillers. Optima determined from both techniques are based on the void volume accessible to binder within the network of a compacted filler. The first technique makes use of a simple relation that calculates the accessible void volume from easily determined density parameters. In the second method, a highly volatile lubricant is substituted for the binder in the mix and, by the weight loss on evaporation of the lubricant, an equivalent void volume is calculated. Optima determined from both techniques seem to correlate well with those determined by the direct measurement of properties. Although both techniques are used routinely in this Laboratory, the lubricant evaporation method has proved to be, by far, the more rapid and less expensive of the two.

In the development of these methods, the initial assumption was made that the optimum binder concentration

is that which is sufficient to fill all accessible pores within the filler network of a compacted green body.

2. CALCULATED VOID VOLUME METHOD

The calculation of void volume depends on the measurement of two density parameters. The first of these is the particle density of the filler, D_F , which in this work was determined on a Beckman Model 930 gas pycnometer with helium as the fluid medium. The second is the bulk density of the filler constituent, D_C , in a compacted specimen, and is calculated by dividing the initial weight of filler in the mix by the geometrical volume of the specimen. The density, D_C , must represent reasonably the minimum bulk volume of the filler on compaction. This can be true only if any excess binder in the mix (that amount greater than necessary for filling of the void network) is allowed to be squeezed out of the die during forming. Alternatively, if less binder than optimum is used, it is necessary only that there be sufficient binder to provide adequate lubrication on forming; in the absence of interparticle and die-wall lubrication afforded by the binder, the filler will not compact to a density as high as that achieved when the binder is present.⁽⁵⁾

Knowing the two density parameters, and fulfilling the condition on D_C , the estimated optimum binder concentration, C , in percent of filler weight, can be calculated from

$$C = 100 \left(\frac{1}{D_C} - \frac{1}{D_F} \right) D_B \quad (1)$$

where the term $(1/D_C - 1/D_F)$ is the volume of voids per unit weight of filler within the compacted filler network, and D_B is the density of the binder. This expression is similar to one presented by Okada and Takeuchi⁽²⁾ in their paper on the properties of bonded carbons as a function of binder concentration, but appears never to have been used for the application described here.

Equation (1) assumes that the binder has essentially the same accessibility to pores in the filler particles as does the pycnometer fluid used in the determination of D_F . The pycnometer fluid, however, will usually penetrate the filler more deeply than does the binder. The net

result of this kind of error is an estimate of binder concentration, C , greater than optimum, and if the fluid happens to be gas the error may be appreciable. Another source of error in using this equation lies in the possible loss of filler by die squeeze-out during compaction. Any loss of filler during processing will be reflected in a calculated filler density, D_C , greater than the actual filler density, and therefore a binder concentration less than the optimum. In spite of these shortcomings, this method has been used by the author for estimating binder requirements and, as will be shown later, can be quite successful.

For the development of this method, a hot-molding technique was used by which green mixes were molded and baked simultaneously in cylindrical double-acting graphite dies. The dies were machined with ample die-plunger clearances to allow squeeze-out of excess binder in the mixes.

3. LUBRICANT EVAPORATION METHOD

The lubricant evaporation method differs from the calculated void volume method in that the accessible void volume is determined by the weight loss on heating of a volatile binder substitute, rather than by a calculation based on density parameters. The binder substitute acts much as does the pycnometer fluid of the void volume method but has the advantage of penetrating less of the very fine porosity available to pycnometer fluids, thus behaving more nearly as would an actual binder.

In this method, the filler to be used is mixed with an excess of some lubricant having a melting point above room temperature and a low residue after evaporation. (Various waxes and stearates have this property. Stearic acid was used almost exclusively in the development of the method.) The mixture is placed in a cylindrical die between the bottom plunger, which fits very closely and the top plunger, which fits more loosely. The die is then heated under pressure, equal to the actual processing pressure for pitch-bonded specimens, to a temperature above the melting point of the lubricant. As compaction occurs, excess lubricant squeezes out of the die around the

loosely fitting plunger. Initially it carries with it a small amount of filler material, but this soon ceases and the extruded lubricant becomes clear. When plunger movement has stopped, as indicated by a dial gauge, the die is cooled under pressure to a temperature at which the lubricant is again solid, and pressure is relieved.

The specimen is removed from the die, weighed, and heated in flowing helium to evaporate the lubricant. It is then reweighed, giving the final weight of the filler. The loss of weight on heating represents the weight of lubricant present in the compacted specimen, from which an equivalent volume may be calculated. The weight of binder necessary to fill the void network of the compacted filler can then be calculated from

$$K = 100 \left(\frac{W_C - W_F}{W_F} \right) \frac{D_B}{D_L} \quad (2)$$

where K is optimum binder concentration in percent of filler weight, W_C and W_F are the weights of the compacted specimen and of the filler after evaporation, respectively, and D_B and D_L are the densities of the binder and of the lubricant, respectively.

It is not evident that the lubricating properties of a real binder, and its squeeze-out behavior, will be the same as those of the lubricant used, and so it is not obvious that the value determined actually represents the optimum binder concentration. Results cited below, however, indicate that it is very close to the optimum.

4. EXPERIMENTAL

General

Four different filler materials, with widely differing particle-size characteristics, have been examined for optimum binder concentration by three of the techniques described above: (1) direct measurement of properties on a series of specimens with varying binder concentration, (2) calculation of the optimum by Eq. (1), and (3) determination of the optimum by the lubricant evaporation technique. Because carbon blacks are commonly used as filler additives, two of the fillers used for these experiments included 15 percent by weight regular Thermax

TABLE I
RAW MATERIALS USED FOR BINDER OPTIMIZATION STUDIES

Raw Material	Mfr	Screen Size Analysis, % by Wt. in Fraction (U.S. Std. Sieve Series)					Density g/cc	Melting or Softening Pt. °C
		> 45	45/80	80/170	170/325	<325		
Petroleum Needle Coke (NC)	CPD	trace	1.8	26.5	32.8	38.8	2.12	---
Graphite 1008	GLC	0	0.5	24.4	35.4	39.6	2.20	---
Petroleum Coke 3020	GLC	0	trace	1.1	13.4	85.5	2.05	---
Graphite GP-48	CPD	0	0	trace	10.3	89.7	2.21	---
Thermax	TC	(mean dia. = 0.328 μ , std. dev. = 0.118)					1.88	---
Coal Tar Pitch 30 MH	PD	7.0	1.0	20.3	33.0	38.7	1.33	105
Stearic Acid P-402	E	(nominally < 45 mesh)					0.84	69

CPD --- Carbon Products Div. of Union Carbide Corp.
GLC --- Great Lakes Carbon Corp.
TC --- Thermatomic Carbon Co.
PD --- Plastics Div. of Allied Chemical Co.
E --- Eastman Organic Chemicals Div. of Eastman Kodak Co.

carbon black. Table I identifies and summarizes the screen-size analyses and properties of the raw materials used in the work described here. The densities of the filler material components were determined by helium pycnometry and of the coal tar pitch (D_B) and stearic acid (D_L) by measuring the molten volume of a given weight of material in a graduated cylinder. The filler compositions used are identified in Table II, which also includes the average helium pycnometer density, D_F , of the filler particles.

Measurement of Properties

To determine optimum binder concentration by direct measurement of properties, a series of specimens was prepared from a blend of each filler with varying amounts of pitch by a hot-molding procedure in which the green mixtures were simultaneously molded and baked in graphite dies. The components of the mixtures were blended

TABLE II
FILLER COMPOSITIONS USED FOR BINDER
OPTIMIZATION STUDIES

Filler No.	Composition, Parts by Wt.	Average Particle Density, D_F , g/cc
10	85 Coke NC plus 15 Thermax	2.08
26C	Graphite GP-48	2.21
26D	85 Graphite 1008 plus 15 Thermax	2.15
26E	Coke 3020	2.05

dry in a twin-shell blender just prior to molding. In the case of filler No. 10, maximum molding pressure was 2000 psi and heating was linear at a rate of 170°C/hr to a maximum temperature of 700°C. For the other three fillers, the heating rate was the same but maximum pressure and temperature were 850 psi and 900°C. Subsequent graphitization was at 2750°C in flowing helium. Normally,

only one specimen was made from each filler mix. Densities, electrical resistivities, and Young's moduli for these specimens are plotted versus binder concentration in Figs. 1, 2, 3, and 4. The behavior shown by these data is typical of that observed by others⁽³⁾ for hot-molded graphites. For all fillers, the plot of each property versus binder concentration shows an optimum, represented by either a maximum or a minimum, which correlates well with the other properties.

Binder Optimum from Calculated Void Volume

From the molding data collected on each specimen used for property determinations, it was possible to calculate an optimum binder value using Eq. 1. For prediction of this optimum, the compacted filler bulk density, D_C , was determined from specimen measurements after molding. Using this value of D_C , the appropriate value of D_F from Table II, and $D_B = 1.33 \text{ g/cc}$ (see Table I) the optimum, C , of Eq. 1 was calculated.

Table III summarizes the calculated optima and the

Fig. 1. Graphite properties as a function of pitch concentration. Filler No. 10.

Fig. 2. Graphite properties as a function of pitch concentration. Filler No. 26C.

corresponding values of D_C . In spite of the fact that the early members of each filler series were deficient in binder, agreement within each series was good, indicating that for this method the calculated optimum is independent of binder content, provided, of course, that there is some minimum amount of binder present to afford sufficient lubrication.

Optimum Binder by Lubricant Evaporation

The lubricant evaporation technique described above was also used to predict the optimum binder concentration for the four fillers. Throughout these experiments, stearic acid with a melting point of 69°C and a molten density

Fig. 3. Graphite properties as a function of pitch concentration. Filler No. 26D.

of 0.84 g/cc was used as the lubricant. The filler and the stearic acid were blended in a household-type food mixer (Waring blender). To avoid overheating during blending, which softens the stearic acid and produces a lumpy mix, it was necessary to blend in a series of cycles, each cycle consisting of 15 seconds of mechanical agitation in the blender at low speed, followed by about 1/2 minute of hand stirring while the mix cooled. For the work reported here, 15 blending cycles were used.

The blended mixture was molded in a 1.5-in. diam steel die whose bottom plunger had a diametral clearance of 0.0005 in. and whose top plunger had one of 0.0030 in. To minimize squeeze-out through the bottom of the die, the bottom plunger was fitted with a rubber O-ring. Molding pressures were the same as those used in the preparation of the hot-molded specimens described above;

Fig. 4. Graphite properties as a function of pitch concentration. Filler No. 26E.

i.e., 2000 psi for filler No. 10, and 850 psi for the others. The die was pressurized, heated with an electric tape to 80°C, and then held under load until all plunger movement stopped and no further lubricant extrusion was apparent at the top of the die. After removal from the cooled die, the specimen was weighed, placed in a tared evaporating dish, and heated in flowing helium to 410°C at a rate of 25°C/hr. The specimen, which was then a dry powder, was reweighed and the optimum binder concentration, K , was determined from Eq. 2.

The optima predicted by the lubricant evaporation technique are summarized in Table IV and are compared with those predicted by the measurement of properties and by the void volume calculation of Eq. 1. Agreement among the three techniques is good except for filler No. 26D, for which the optimum predicted by Eq. 1 is too low. This may be attributed to excessive loss of filler entrained in pitch squeezed out during hot-molding.

TABLE III
BINDER OPTIMA CALCULATED FROM EQUATION 1

Filler No.	Initial Binder Conc., % of Filler	Filler Compacted Density D _C , g/cc	Calculated Optimum C, % of Filler
10	10	1.545	22.5
	13	1.555	21.9
	15	1.565	21.4
	18	1.564	21.4
	20	1.570	21.2
	22	1.603	19.4
	24	1.593	20.0
	26	1.593	20.0
	28	1.592	20.0
	Average:	1.575	20.9
	Standard Deviation:	0.020	1.0
26C	13	1.436	32.5
	19	1.409	34.3
	25	1.443	32.6
	28	1.442	32.1
	31	1.455	31.3
	34	1.435	32.6
	37	1.433	32.7
	40	1.435	32.6
	Average:	1.436	32.6
	Standard Deviation:	0.013	0.8
26D	13	1.530	25.1
	21	1.544	24.3
	24	1.540	24.5
	27	1.543	24.3
	31	1.540	24.5
	35	1.543	24.3
	Average:	1.540	24.5
	Standard Deviation:	0.005	0.3
26E	24	1.251	41.4
	30	1.262	40.4
	37	1.266	40.2
	43	1.257	41.0
	46	1.255	41.8
	51	1.252	41.4
	Average:	1.257	41.0
	Standard Deviation:	0.006	0.6

TABLE IV
OPTIMUM BINDER CONCENTRATIONS DETERMINED
BY THREE DIFFERENT TECHNIQUES
FOR FOUR DIFFERENT FILLERS

Filler No.	Optimum Pitch Conc., % of Filler, Determined by:		
	Properties	Equation 1	Lub. Evap.
10	22-24	20.9	21.8
26C	30-33	32.6	34.8
26D	28-30	24.5	28.5
26E	37-40	41.0	37.0

Consideration of Variables

During the course of the development of the lubricant evaporation technique, a number of variables was examined, some of which were found to have significant effects on the determination of an optimum.

In initial experiments, difficulties were experienced in blending the lubricant with the filler. A series of blending experiments was therefore run, summarized in Table V. Filler No. 10 was used with three different blending

TABLE V
EFFECT OF BLENDING PROCEDURE ON BINDER
REQUIREMENT ESTIMATED BY THE LUBRICANT
EVAPORATION METHOD (FILLER NO. 10)

Blending Procedure	Binder Requirement % of Filler
Twin-Shell, 2 min	28.1
Twin-Shell, 20 min	26.9
Twin-Shell, 120 min	21.8
Waring, 3 cycles	22.6
Waring, 15 cycles	21.9
Waring, 30 cycles	21.8
Kneading, 2 passes	22.3
Kneading, 10 passes	22.1
Kneading, 30 passes	22.5

techniques: (1) twin-shell blending in a 2-quart unit with an intensifier bar (2) kneading and extruding in a commercial food chopper, such as is used to grind meat and (3) Waring blending. As indicated by the apparent binder requirements listed in the table, equivalent results can be obtained from all three of the above blending techniques, provided that blending time is sufficient.

Although the lubricant evaporation method depends on the squeeze-out of excess lubricant during molding, it was found that the amount of excess can affect the determination of apparent optima. Therefore, a series of specimens was prepared from mixtures of filler No. 10 with varying amounts of stearic acid. The data summarized in Fig. 5 show a sharp increase in the apparent optimum with increasing proportion of stearic acid up to a maximum above which the apparent optimum becomes constant. Too much lubricant in the mix obviously may have the disadvantage of carrying away with it an appreciable quantity of fines from the filler during the squeeze-out phase of the procedure. This may account for the increase in apparent optimum with increasing lubricant observed in Fig. 5. Because of this behavior, the procedure for determining the optimum values reported in this report consisted of first determining an apparent optimum from a filler mixture containing a large excess of stearic acid, and then making the final determination on a mixture containing just slightly more stearic acid than that determined as the apparent optimum. The consideration of this variable, however, may not be important; the spread in apparent optimum values observed in Fig. 5 is still less than 5%.

Fig. 5. Apparent binder optimum as a function of amount of lubricant used in the lubricant evaporation test.

Because of the possibility of losing filler fines during the squeeze-out period of the molding operation, it was thought that the diametral clearance of the top plunger in the die might be an important variable. To examine this possibility, several specimens were made using three different top plungers with diametral clearances of 0.0030, 0.0020, and 0.0010 in. It was found that plunger clearance was not significant, the maximum difference in determined optima being less than 5%.

Besides stearic acid, two other stearates (zinc stearate and sodium stearate) and a paraffin wax were tried as lubricants for this method. Because of high viscosity, the two stearates proved unsuitable, and the paraffin wax, although yielding results in good agreement with those derived from stearic acid, was much too soft for easy and satisfactory mixing with the filler.

Molding pressure during compaction of the lubricant-filler mixture was found to be an important variable. Moldings of filler 26C were made at three different pressures and, as expected, it was found that the optimum binder concentration decreased with increasing pressure. In Table VI are listed the optima determined from these moldings together with comparative data calculated from Eq. 1 for hot-molded materials. Over the range of pressures examined, the agreement between the two techniques is good.

TABLE VI

EFFECT OF MOLDING PRESSURE
ON ESTIMATED BINDER OPTIMUM (FILLER NO. 26C)

Molding Pressure, psi	Optimum Pitch Concentration, % of Filler	
	Determined by:	
	Lub. Evap.	Equation 1
380	46.7	45.2
850	34.8	32.6
1890	28.5	25.0

5. CONCLUSIONS

Optimum binder concentration can be estimated by the lubricant evaporation technique described in this report. Agreement between this method and the properties method of determining binder optima is good.

Binder requirements can also be estimated by calculating the void volume within the filler network of pitch-bonded carbons, and although agreement with the properties optima is not as good as that shown by the lubricant evaporation technique, the calculation can be useful.

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