

Fabrication of Poly(*p*-phenylene) by Powder-Forming Techniques

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Synopsis

Application of powder-metallurgical forming techniques to poly(*p*-phenylene), PB, resulted in solid objects with tensile strengths as high as 35 MPa (5000 psi). Powders were characterized by BET surface area, x-ray crystallinity, scanning electron microscopy (SEM), and impurity levels in an effort to relate intrinsic powder properties with strengths attainable on fabrication. High surface area (>35 m²/g) and low Cl impurity levels were generally associated with highest strengths. Forming variables were studied in some detail. Tough objects were obtained in a narrow sintering range of about 580°–615°C. Perchloropoly(*p*-phenylene) was also successfully fabricated.

INTRODUCTION

Poly(*p*-phenylene), PB, conveniently prepared by direct polymerization of benzene,¹ has been of much interest because of its simple structure and excellent stability.^{1,2} Efforts to fabricate^{1,2} the red-brown "brick dust" polymer powder have been largely unsuccessful, although tensile strengths as high as 14 MPa (2000 psi) have been reported.³ We report here a systematic study of PB fabrication applying the techniques of modern powder metallurgy. In the following paper properties of fabricated PB will be reported and compared with some commercially available polyimide and graphite parts.

EXPERIMENTAL

Preliminary Experiments

Unless stated otherwise, poly(*p*-phenylene), PB, powder was prepared by the method described in reference 1(a). Batches were assumed equivalent and possessed the following typical properties: surface area: 50 m²/g; appearance: brown, free-flowing powder; x-ray crystallinity: low to moderate, half-width of strongest crystalline reflection usually greater than 2° 2θ; DTA: 5% wt loss in N₂ at 620°C and in air at 540°C, 50% wt loss in air at 1040°C; Compositional analysis: carbon 90–92%, hydrogen 4.5–5%, oxygen 0.5–1%, chlorine 1.8–3.1%, copper 0.1–0.2%, aluminum 0.3–0.6%, silica trace to 0.3%. As will become clear, powder properties are important in controlling the ultimate strength of the finished article.

Our basic approach was to compact PB powder into standard ASTM E8 tensile bars and study the effect of forming conditions on strength and elongation. Usually compaction was at room temperature, followed by free sintering with N₂ at high temperature. Preliminary experiments indicated that compaction

at 520 MPa (37 Tsi) at room temperature, followed by sintering at 590° for 1 hr, gave improved strength. Therefore, we studied the effect of powder treatments (Table I) with the idea of achieving optimum fabricated strengths through powder purification. While none of the treatments grossly altered the powder's chemical structure, subtle changes did occur, and in the case of runs D (sintering before compaction) and E (slight oxidation), the special physical form of the powder needed for successful fabrication was essentially destroyed. The result from run E is particularly significant because we will conclude later that, all things being equal, high surface area and low Cl content are *beneficial* to high strength on fabrication. Ball milling (runs F, H, K, and L) tends to destroy powder structure and thus low ultimate strength. Treatment with NH₄OH (run M) was frequently employed in subsequent studies.

Once a powder had been subjected to the "sintering conditions" it would not even compact (run D), let alone sinter to a high-strength object. This result favors a metal-like sintering mechanism.

High-Pressure Studies

We studied the effect of heat and pressure on the ability of PB to fuse with itself once it had been compacted into pellets to better understand the sintering process. In all cases PB was compacted at 141 MPa (20,000 psi) in five successive moldings into a gold cylinder. The sealed cylinder containing the five pellets was then pressed at the ends or in a tetrahedral anvil at pressures ranging from 6 to 65 kbar (80,000–1,000,000 psi) and held at room temperature or heated at various temperatures up to 650°C for 1 hr. The resultant gold cylinder was opened so as not to disturb the PB sample and examined. Whether or not fusion

TABLE I
Pretreatments of Powder Before Compaction

Treatment	Effect on final product
(A) None	Sintered bars blistered, high strength, high crystallinity
(B) One-wk Soxhlet extraction with <i>o</i> -dichlorobenzene	Sintered bars smooth to slightly blistered, high strength, high crystallinity
(C) One-to-two-wk Soxhlet with extraction with constant boiling HCl	Sintered bars blistered, high strength, high crystallinity
(D) Heating under N ₂ at 590° for 1 hr	Will not form compact, high crystallinity, surface area 25 m ² /g, chlorine content reduced
(E) Heating in air at 300°–500°C for 3 hr	Will not form compact, surface area 114 m ² /g, oxygen increased (2.5%) and chlorine decreased
(F) Ball milling	Sintered bars smooth, some loss in strength, high crystallinity
(G) 100 psi H ₂ /Pd(OAc) ₂ /HOAc 100°/16 hr	No evidence for hydrogenation, good green strength, sintering not investigated
(H) Ball milled, extracted with HCl and <i>o</i> -dichlorobenzene	Very smooth bars on sintering, some loss in strength, high crystallinity
(I) Screened to remove very large aggregates	Same as for no treatment at all (see A above)
(J) Ultrasound + concd. HCl	Slight reduction of powder surface area
(K) Ball milled, extracted with HCl	Sintered bars smooth, some loss in strength, high crystallinity
(L) Ball milled, extracted with <i>o</i> -dichlorobenzene	Sintered bars smooth, some loss in strength, high crystallinity
(M) NH ₄ OH/150°C/8 hr	Some Cl → NH ₂ , high strength, sintered bars smooth

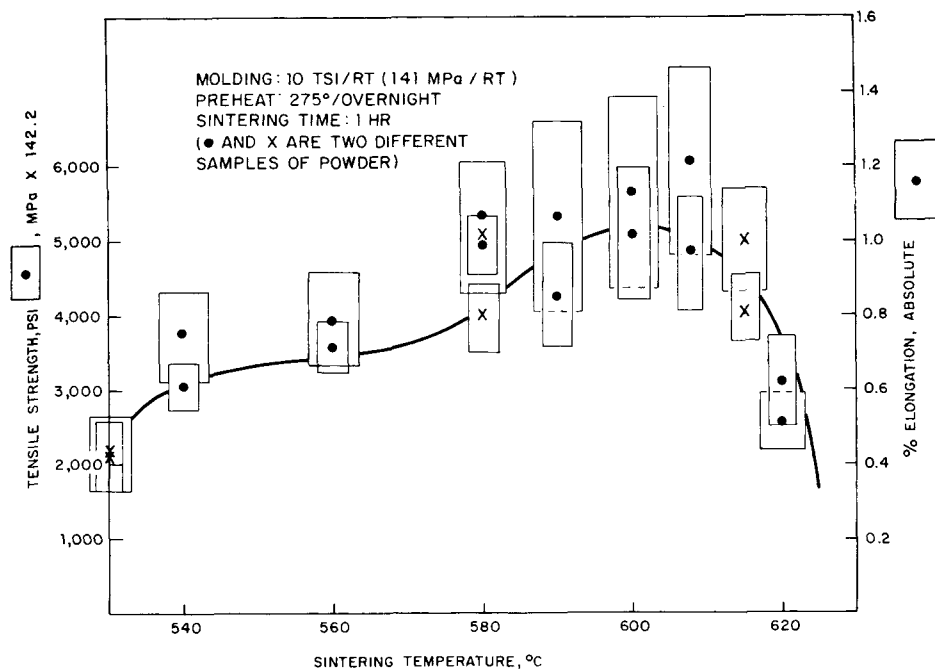


Fig. 1. Effect of sintering temperature of tensile properties of PB (NH_4OH treated).

had taken place could easily be determined by noting how the cylinder behaved on fracture. Usually the five individual pellets retained their integrity so that cleavage occurred perpendicularly to the axis of the cylinder. The ends of the pellets were examined for retention or loss of microscopic striations imparted during molding so that the degree of interpellet interaction could be judged. In cases where interpellet interaction was strong (i.e., the same order of magnitude versus intrapellet forces), fracture did not occur at the pellet-pellet interface but occurred randomly (oblique angle) at the weakest point along the cylinder.

Little or no permanent interpellet interaction occurred below 500°C in the

TABLE II
Effect of Sintering Conditions of PB Tensile Properties^a

Sintering conditions		Tensile properties—E8 bars		
Time	Temperature, °C	T_B , psi ^b	E_{abs}	M_i , Mpsi ^c
10 min	580	3963 ± 361	0.94 ± 0.16	646 ± 61
10 min	605	4588 ± 656	1.17 ± 0.29	565 ± 56
10 min	620	4034 ± 968	0.83 ± 0.22	548 ± 13
1 hr	530	2101 ± 477	0.43 ± 0.09	549 ± 91
1 hr	580	3951 ± 509	1.06 ± 0.19	529 ± 57
1 hr	615	4069 ± 487	1.00 ± 0.14	556 ± 45
24 hr	490	1292 ± 200	0.58 ± 0.11	274 ± 20
24 hr	540	4159 ± 325	1.02 ± 0.15	567 ± 55
24 hr	590	1508 ± 603	0.45 ± 0.24	375 ± 84

^a All bars were molded at 141 MPa (10 Tsi) at room temperature from an NH_4OH -treated PB powder and preheated at 275°C overnight before sintering.

^b MPa \times 142.2.

^c MPa \times 0.1422.

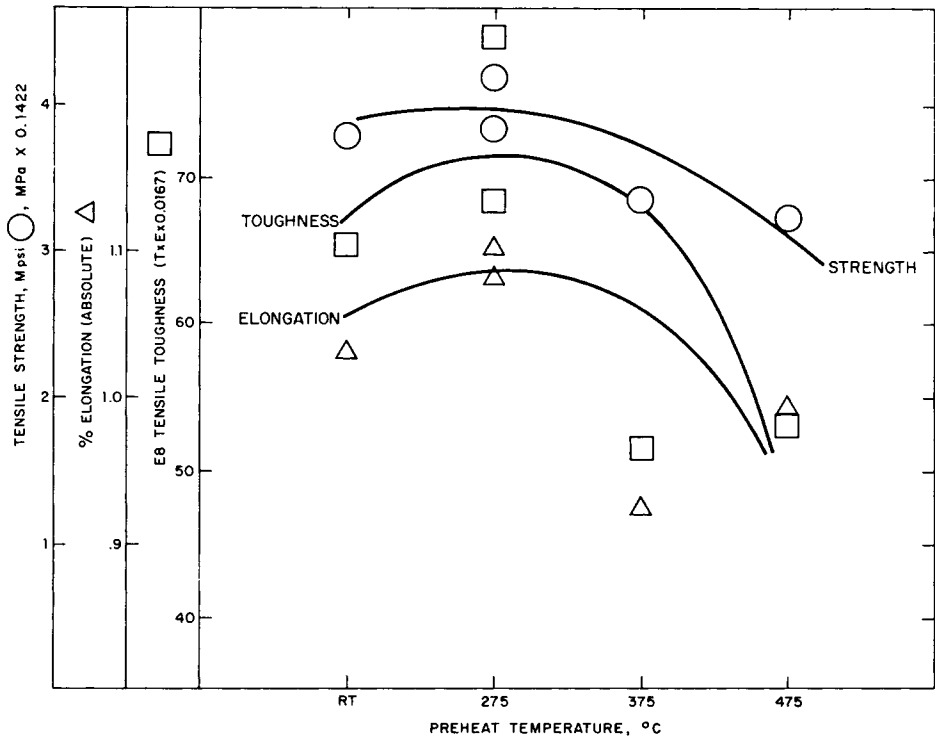


Fig. 2. Variation of tensile properties with preheat temperature (overnight).

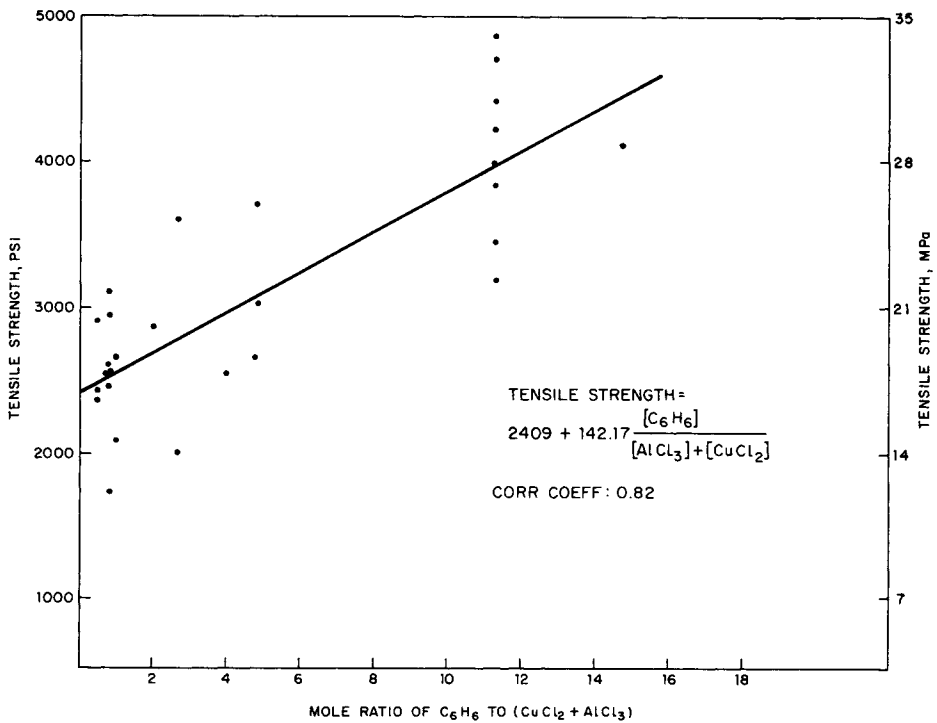


Fig. 3. Effect of C₆H₆ concentration on tensile strength of untreated PB direct-formed bars.

pressure range of 6–65 kbar. It is important to distinguish between *interpellet fusion* and *intrapellet coalescence*. Coalescence occurs long before fusion. For example, a sample of PB tetrahedrally pressed at 65 kb and heated to 400°C for 1 hr showed, on careful scanning electron microscope (SEM) examination, a high degree of coalescence while the interpellet fusion was nil (mold imparted striations completely intact). Above 525°C, interpellet fusion occurs to varying extents, higher pressures tending to give greater fusion. At 650°C, decomposition occurs, fusion is slight, and crystals (PB oligomers?) are formed on the interpellet surfaces.

Two mechanisms would seem to explain interpellet fusion. One deals with an extension of metallurgical-like sintering, that is, fusion due to further reduction of surface area or crystallization or even plastic flow. Another mechanism involves a chemical process unique to PB. Because interpellet fusion and intrapellet coalescence occur at different temperatures, we might infer they have different activation energies and follow separate mechanisms, so that the second (chemical process) bears careful consideration.

PB prepared by the $\text{CuCl}_2\text{-AlCl}_3$ technique¹ contains a few percent Cl as an impurity. When heated above 500°C, Cl is lost as HCl.⁴ It is reasonable to expect that H and phenylene-bound Cl are not always lost from the same benzene ring (to form a benzyne) so that intermolecular crosslinking should also occur.⁴ We were able to show that PB powder contains both corrosive and noncorrosive forms of Cl as judged by a brass corrosiveness test. These forms are probably AlCl_3 and aromatic Cl, respectively. Both are lost on sintering.

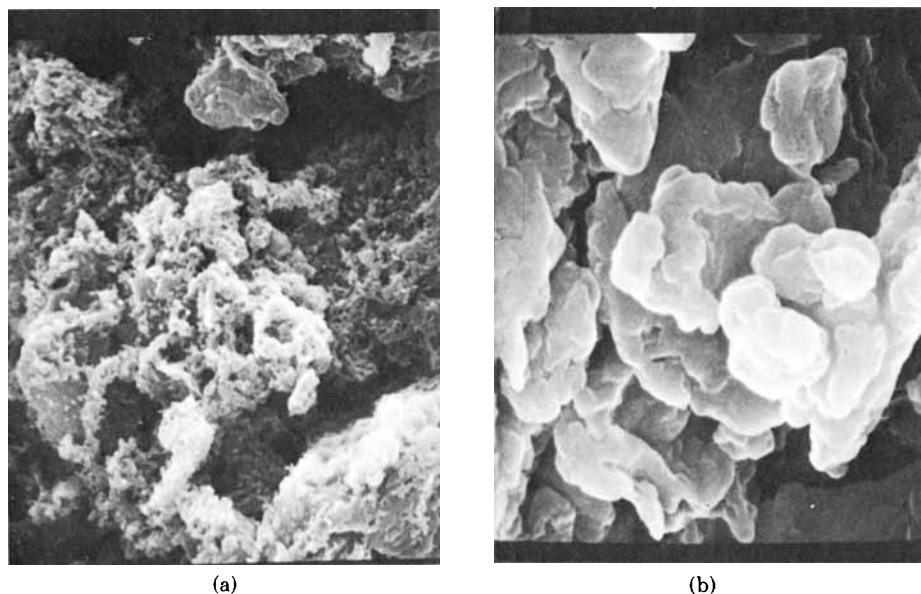


Fig. 4. Scanning electron micrographs of PB powders (10,000 \times). (a) Excellent powder structure. Prepared by low-speed stirring by $\text{AlCl}_3/\text{CuCl}_2$ method at high dilution. After NH_4OH treatment. (b) Poor powder structure. Prepared by standard macromolecular syntheses preparation ($\text{AlCl}_3/\text{CuCl}_2$).

TABLE III
Effect of Various Treatments of PB Properties

Treatment	S.A., m ² /g	% Cl	Cu, ppm	Cryst. ^a	Toughness, T × E × 10 ⁻² (D1708) ^b
(a) 10% Aqueous NaOH					
Start	59.1	1.58	50-250	2.5	—
200°/8 hr	45.1	0.72	100-500	1.6	43-65
300°/8 hr	45.1	0.32	100-500	1.9	20-51
400°/8 hr	40.8	0.00	200-1000	1.8	25-51
550°/0.5 hr	30.0	0.00	<10	1.4	very low
200°/24 hr	46.2	0.89	50-250	3.0	10-49
(b) NH ₄ OH					
Start	63.3	1.16	50-250	2.3	—
200°/8 hr	65.2	0.64	100-500	1.6	26.69
300°/8 hr	57.5	0.47	100-500	1.7	36-80
400°/8 hr	42.8	0.20	50-250	1.6	35-51
550°/0.5 hr	31.2	0.00	50-250	1.1	30-41
(c) H ₂ , 100 atm					
Start	63.3	1.16	50-250	2.3	—
200°/8 hr	54.0	0.96	200-100	4.0	40-62
300°/8 hr	38.8	0.77	200-1000	2.0	24-60
400-8 hr	28.9	0.73	200-1000	3.0	63-83
550°/0.5 hr	16.8	0.24	—	1.1	18-35
(d) Ultraviolet Light (2537 + 3500 Å)					
Start	63.3	1.16	50-25	2.3	—
hν/1 week	58.8	0.86	200-1000	4.0	6-45
(e) H ₂ O (After Extraction With <i>o</i> -Dichlorobenzene)					
Start	51.8	2.64	200-1000	2.0	43-54
400°/8 hr	—	1.73	50-250	2.2	32-40
550°/8 hr	33.1	0.00	>10	1.4	very low
(f) NH ₃ Gas (After Extraction With <i>o</i> -Dichlorobenzene)					
Start	51.8	2.64	200-1000	2.0	43-54
300°/8 hr	50.6	1.61	100-500	1.8	32-77
400°/8 hr	27.5	0.99	—	2.0	20-32
550°/8 hr	22.9	trace	100-500	amorph.	very low

^a Half-width of strongest cryst. reflection in degrees 2θ .

^b Microtensile toughness (high and low values of four bars) of bars molded at 520 MPa (74,000 psi) at room temperature and sintered at 590°/1 hr

Perhaps the most significant conclusion drawn from the tetrahedral press experiments is not that interpellet fusion is due to crosslinking, but that intrapellet coalescence is *not* due to it. SEM pictures of the 400°C/65 kbar experiment (little HCl lost) show the same coalescence as found for "direct-formed PB," that is, PB compacted and then free-sintered (sintered at 590°) which loses HCl.

X-Ray Crystallinity Studies

Another distinction between interpellet fusion and intrapellet coalescence may be reflected in x-ray crystallinity measurements.^{1c} Whereas direct-formed PB always increases crystallinity on sintering as expected by powder metallur-

gical mechanisms, PB pressed and heated so that interpellet fusion occurs is usually amorphous. Under conditions of *free* sintering, usually employed for practical work, it seems reasonable that physical interactions, tending toward greater crystalline order, give improved strength, while chemical changes, tending toward disruption of order and crosslinking, lessen strength. This is why oversintering lessens strength (see discussion below and Fig. 1). This view is in contrast to the increase in strength obtained in the crosslinking of more flexible polymer systems. In the present case the rate of strain employed for an ordinary tensile strength is sufficiently high, because of exceptionally high-strain sensitivity in the inflexible PB, to have the effect of a toughness determination (tensile impact test).

Optimization of Sintering

Optimization of sintering conditions are shown for NH₄OH-treated PB (Table II, Fig. 1). Ranges for tensile properties are standard deviations. We see a clear time-temperature relationship expected for true metallurgical-like sintering (Table II). At the convenient time of 1 hr (Fig. 1), little or no strength improvement occurs below 530°C and properties optimize at 580°–615° and fall off sharply above that range because of decomposition. For the above optimization we employ a preheat of 275°; this preheat drives off the last traces of sol-

TABLE IV
Effect of Stirring of CuCl₂-AlCl₃ Preparation

Type of stirring	Yield	S.A., m ² /g	D1708 strength	% Cl
High speed	OK	48.8	Good ^a	1.05
Moderate	OK	58.9	Fair ^b	3.92
Low speed	OK	52.9	Good	2.87
Ultrasonic	OK	50	Good	2.09
Vibro stirring	OK	58	Good	2.16
High speed (short stopped)	Poor	52	Good	0.62

^a About 28 MPa (400 psi).

^b About 21 PMa (3000 psi).

TABLE V
Effect of Solvent Dilution on CuCl₂-AlCl₃ PB Preparation

Modification	Yield	S.A., m ² /g	D1708 strength	% Cl
Replace 1/2 C ₆ H ₆ with C ₆ H ₁₂	OK	68	Good	—
As above, but added C ₆ H ₆ dropwise	OK	67	Good	—
Replace 3/4 C ₆ H ₆ with C ₆ H ₁₂ and add C ₆ H ₆ dropwise	Low	130	Good	2.11
Replace 1/2 C ₆ H ₆ with CS ₂ and add C ₆ H ₆ dropwise	OK	56	Good	2.28
Replace 1/2 C ₆ H ₆ with pentane and added C ₆ H ₆ dropwise	Fair	75	Fair	1.12
Replace 2/3 C ₆ H ₆ with C ₆ H ₁₂ and added C ₆ H ₆ dropwise	Fair	94	Good	1.61

TABLE VI
 PB Powder Synthesis with Various Metal Oxidants

Modification	Yield	S.A., m ² /g	D1708 strength	% Cl
Substitute FeCl ₃ for CuCl ₂ in std. CuCl ₂ -AlCl ₃ prepn.	Trace	83.8	—	—
Literature ⁷ FeCl ₃ ·H ₂ O prepn. (70°/0.5 min)	Low	54	Very low	6.71
FeCl ₃ ·H ₂ O at 60°/4 hr	Low	57.2	Very low	10.25
Literature FeCl ₃ ·H ₂ O prepn. with ½C ₆ H ₁₂ for C ₆ H ₆	Trace	53	—	—
FeCl ₃ ·H ₂ O/AlCl ₃	Low	59.4	Good	1.68
FeCl ₃ ·H ₂ O/AlCl ₃ but H ₂ O added before AlCl ₃	Fair	66.5	Good	2.61
Replaced ½CuCl ₂ with FeCl ₃ in CuCl ₂ -AlCl ₃ prepn.	Fair	56.3	Good	0.74
FeCl ₃ ·H ₂ O/AlCl ₃ ½C ₆ H ₁₂ for C ₆ H ₆ (added dropwise)	Low	25.5	Very low	—
As above except only ¼C ₆ H ₆ replaced by C ₆ H ₁₂	Low	59.7	Very low	5.55
Literature ⁸ MoCl ₅ ·H ₂ O	Fair	30.7	Low	6.37

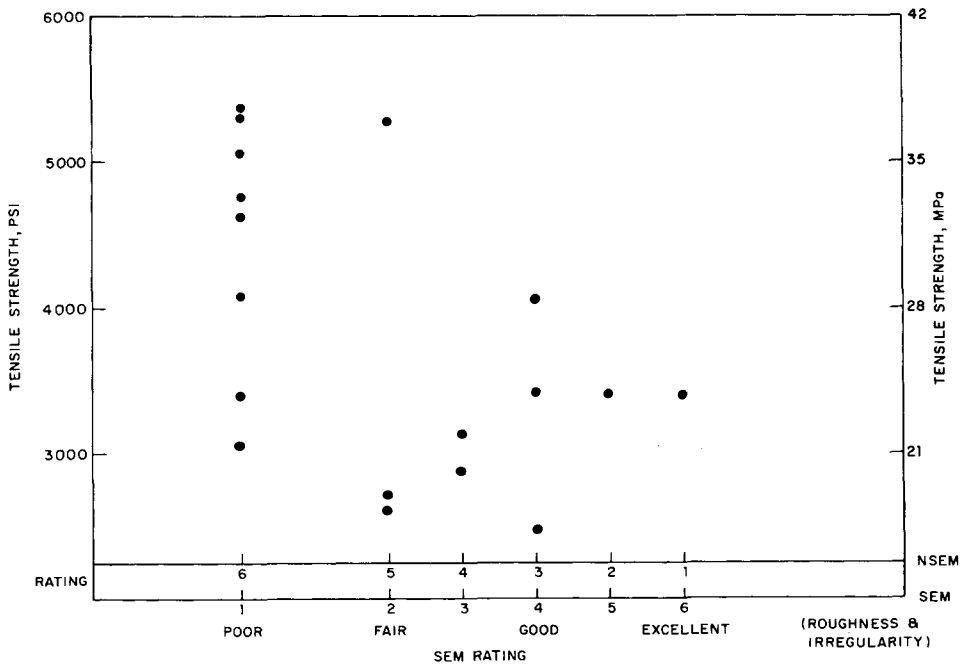


Fig. 5. Direct formed PB vs SEM powder rating.

vent and other volatiles. It is important (Fig. 2) that the preheat not be carried out at too high a temperature, because if even partial sintering is induced while PB is still in powder form the ultimate properties will suffer after compaction-free sintering (direct forming).

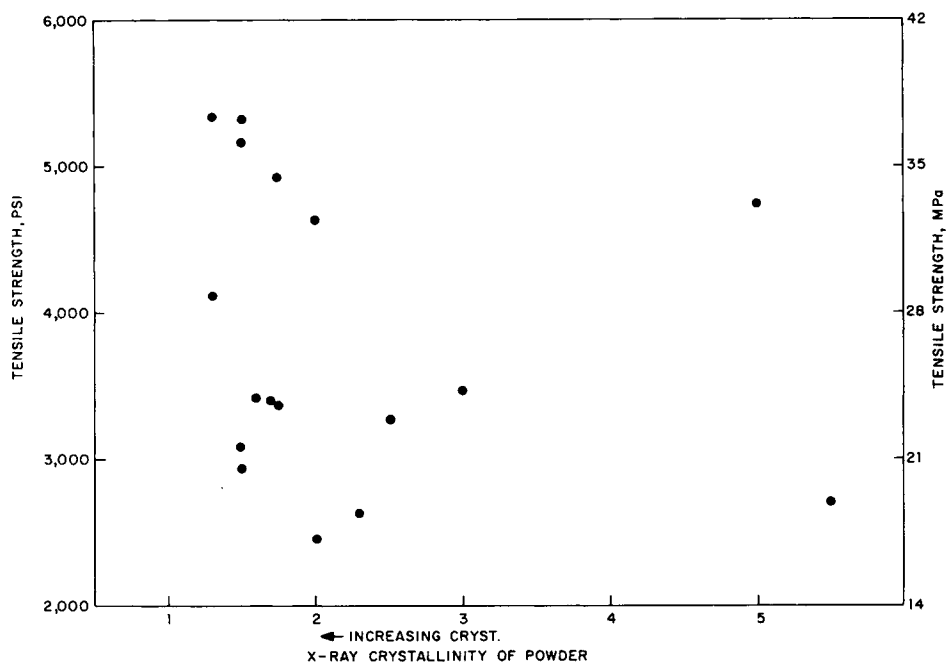


Fig. 6. PB strength vs x-ray crystallinity.

MODIFICATION OF POWDERS

Powder Treatments

Once satisfied that the forming of PB closely paralleled metallurgical forming, we set out to modify the fundamental powder properties of PB since powder characteristics should hold the key to ultimate properties after forming. We have already mentioned posttreatment of PB powder prepared by the $\text{CuCl}_2\text{-AlCl}_3$ technique. Details (Table III) of powder properties and tensile toughness of direct-formed bars prepared from these posttreated powders (the ASTM D1708 test was nonstandard) suggest that most treatments reduce undesirable Cl, but the high temperature required also destroys the powder characteristics needed for effective sintering.

Synthesis with High Dilution

A better approach seemed to be to alter powder properties during synthesis. High dilution was explored in some detail, since one would predict higher surface areas and hopefully better powders.

Rate of Stirring. Since the standard $\text{CuCl}_2\text{-AlCl}_3$ preparation is heterogeneous, one method of varying "concentration" was to change stirring speed and/or method. Indeed, we observed that powder properties varied from run to run and suspected that our "standard" run was not always the same. Changing the rate of stirring (Table IV) caused changes in the rate of HCl evolution and the all important Cl content, but surprisingly had little effect on surface area.

Solvent Changes. Reports in the literature^{2,5} suggest that polymerizations

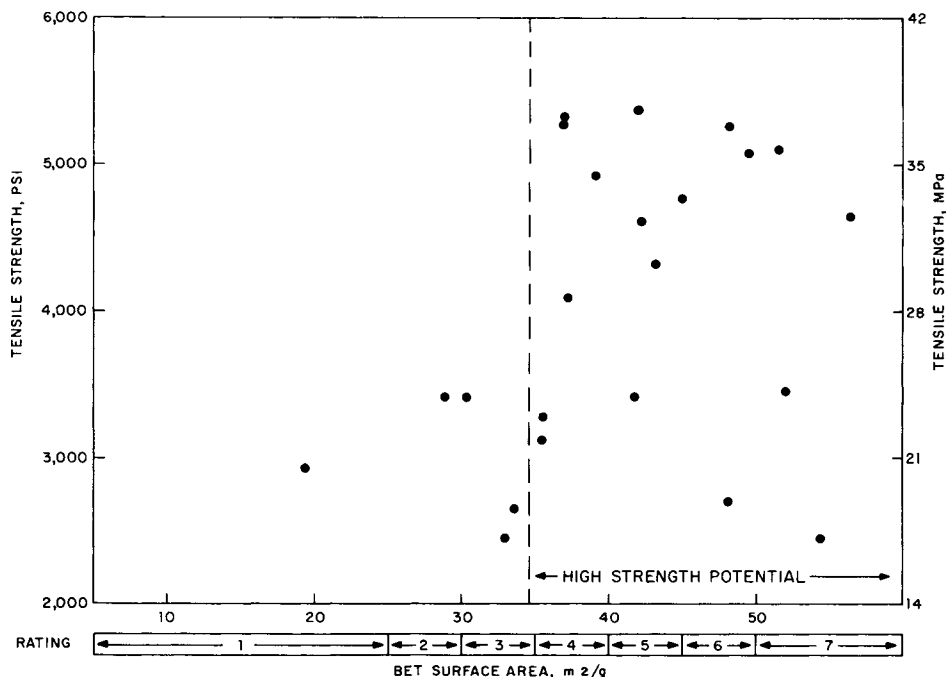


Fig. 7. PB strength vs BET surface area.

of benzene in inert polar solvents only lead to lower molecular weight, less desirable products. We therefore concentrated on inert nonpolar solvents to affect the desired dilution (Table V). BET surface area was increased on dilution but at a yield sacrifice.

Miscellaneous Synthetic Changes. Attempts to prepare a good PB molding powder by changing the reactant metal led to some PB powders with very high Cl contents (Table VI). A sample of Marvel's PB⁶ (prepared by anionic polymerization of cyclohexadiene followed by aromatization) had a BET surface area of only 2.42 m²/g and gave bars of poor strength (bent out of shape on sintering at 590°/1 hr).

RESULTS AND DISCUSSION

Using the methods discussed above, we prepared a large number of PB powder samples and thus sought to correlate the ultimate tensile strength with powder synthesis conditions. For this study all tensile values were measured on *untreated* powders, to avoid treatment effects. The only trend noted was an improvement in strength on dilution (Fig. 3) with benzene. A 28-point plot of mean E8 tensile strengths (the best value regardless of molding pressure required) had a correlation coefficient of 0.82 for the equation

$$\text{tensile strength} = 2409 + 142.17 \frac{[\text{C}_6\text{H}_6]}{[\text{AlCl}_3] + [\text{CuCl}_2]} \quad (1)$$

It should be noted that while the constants of eq. (1) are not likely to have a predictive value, the general form is probably valid. Since for practical reasons we were not able to vary the AlCl₃:CuCl₂ ratio greatly, either reagent alone might appear in the denominator of an equally "valid" equation.

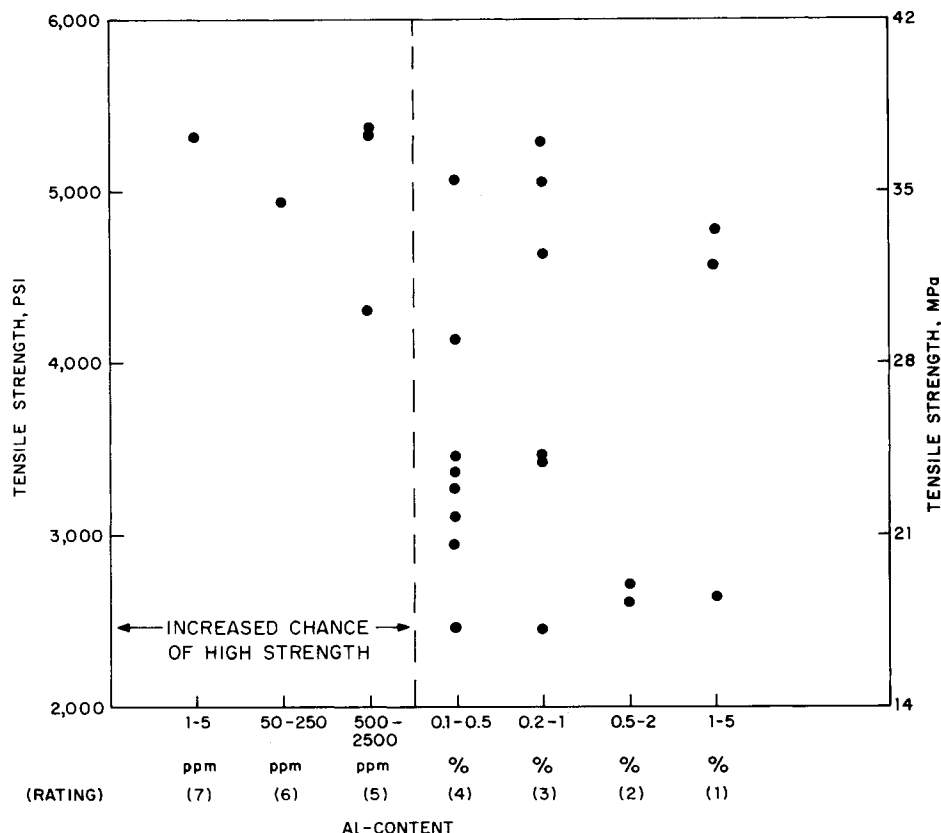


Fig. 8. PB strength vs Al content of powder.

What is most clearly indicated by this result is that powders derived from dilute solution polymerization are in a better physical form than those derived from concentrated solution. We did not find correlation with other process variables such as stirring rate or temperature.

We next sought correlations between tensile strength and powder properties. It would be unusual if correlations existed between strength and a single powder property because of the complex sintering process, but it is useful to isolate each property. Scanning electron microscopy (SEM) was used to characterize each powder as to its irregularity or smoothness. It seems reasonable that rough, spongy, irregular powder particles would compact better than smooth, dense particles. Using these criteria we set up a semiquantitative rating system to rate powders according to how they look (Fig. 4). Unfortunately, tensile strength (Fig. 5) did not correlate with SEM rating; if anything, the reverse, NSEM (smoothness assumed best), showed some vague relationships with the better strengths.

X-Ray crystallinity (Fig. 6) of the powder as judged by the half-width of the strongest reflection in degrees 2θ showed little or no correlation with fabricated strength. The BET surface area of the powder also showed little tendency to correlate with final object strength (Fig. 7) except that surface areas above 35 m^2/g seemed to be required for higher strengths. No correlation was noted for strength versus aluminum content (Fig. 8), except that none of the powders with

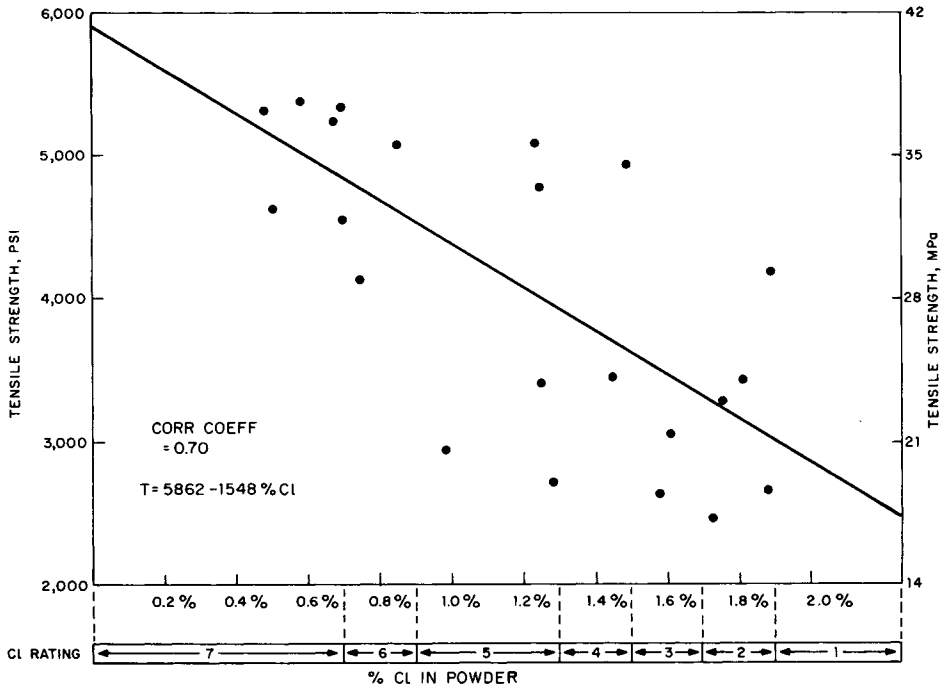


Fig. 9. Direct formed PB vs Cl content of powder.

the lowest Al contents had the lowest strengths. The correlation of Cl content of the powder and ultimate fabricated strength was better (Fig. 9), although the least-squares line had a correlation coefficient of only 0.70. It was only when several powder properties are considered together, for example, when the products of powder ratings defined above for Cl content and surface area are plotted (Fig. 10) versus strength did clearer relationships appear. A plot of a three-property powder rating (the product of ratings defined in Figures 7, 8, and 9) versus individual powder ratings (Fig. 11 gives an even better correlation). For comparison, the "straight line" correlation coefficient was computed as 0.78; the actual fitted curve line must have a value higher.

CONCLUSIONS

All in all, we have established that good powder characteristics are essential to achieving high strength but that the interrelationship of these characteristics is complex. Better correlations might result by giving unequal emphasis to the individual ratings, changing the rating systems, considering other powder properties, taking into account the effect of one property on another, etc. Having noticed a vague inverse relationship between strength and Cl content, it was interesting to note that the Cl content of the powders tended to increase on dilution (Fig. 12). Since surface areas also increase with dilution, we find a major conflict in obtaining higher fabricated strengths: attempts to increase surface area by going to higher dilutions are foiled because higher Cl contents also are obtained.

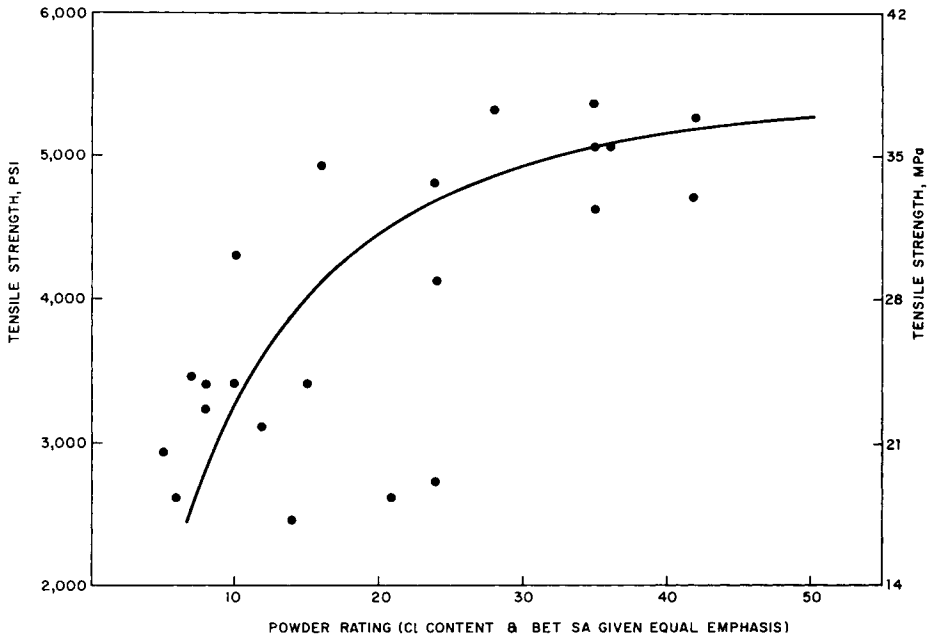


Fig. 10. PB strength vs powder rating (Cl content and BET surface area).

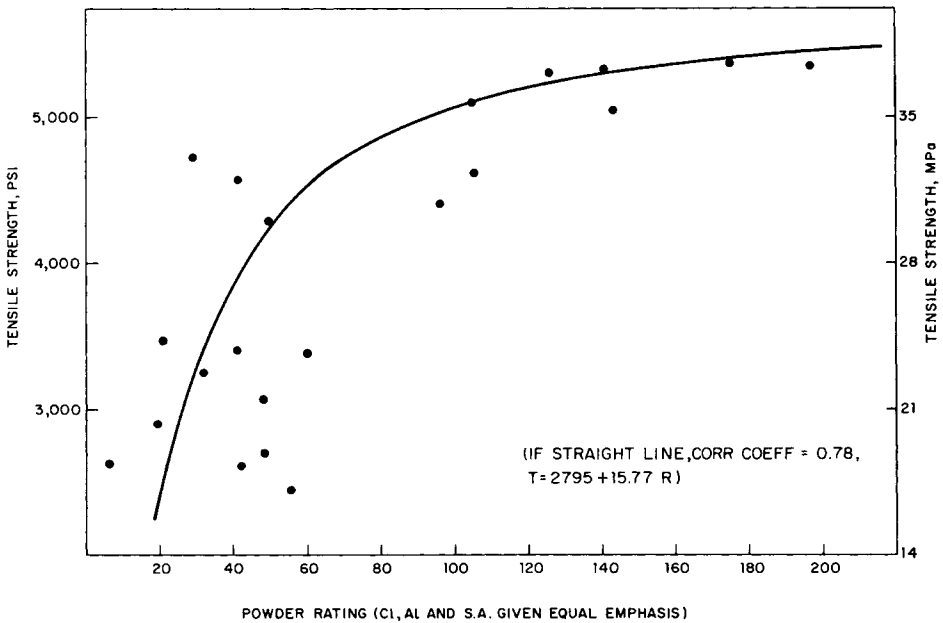


Fig. 11. Direct-formed PB strength vs powder rating considering three properties.

FABRICATION OF PCPB

Fabrication of perchloropoly(*p*-phenylene), PCPB, obtained by direct chlorination of PB according to a literature⁷ procedure, was also studied using powder-forming techniques, although in less detail. Sintering at 512°C for 1 hr under N₂ after compaction at 520 MPa (74,000 psi) and room temperature

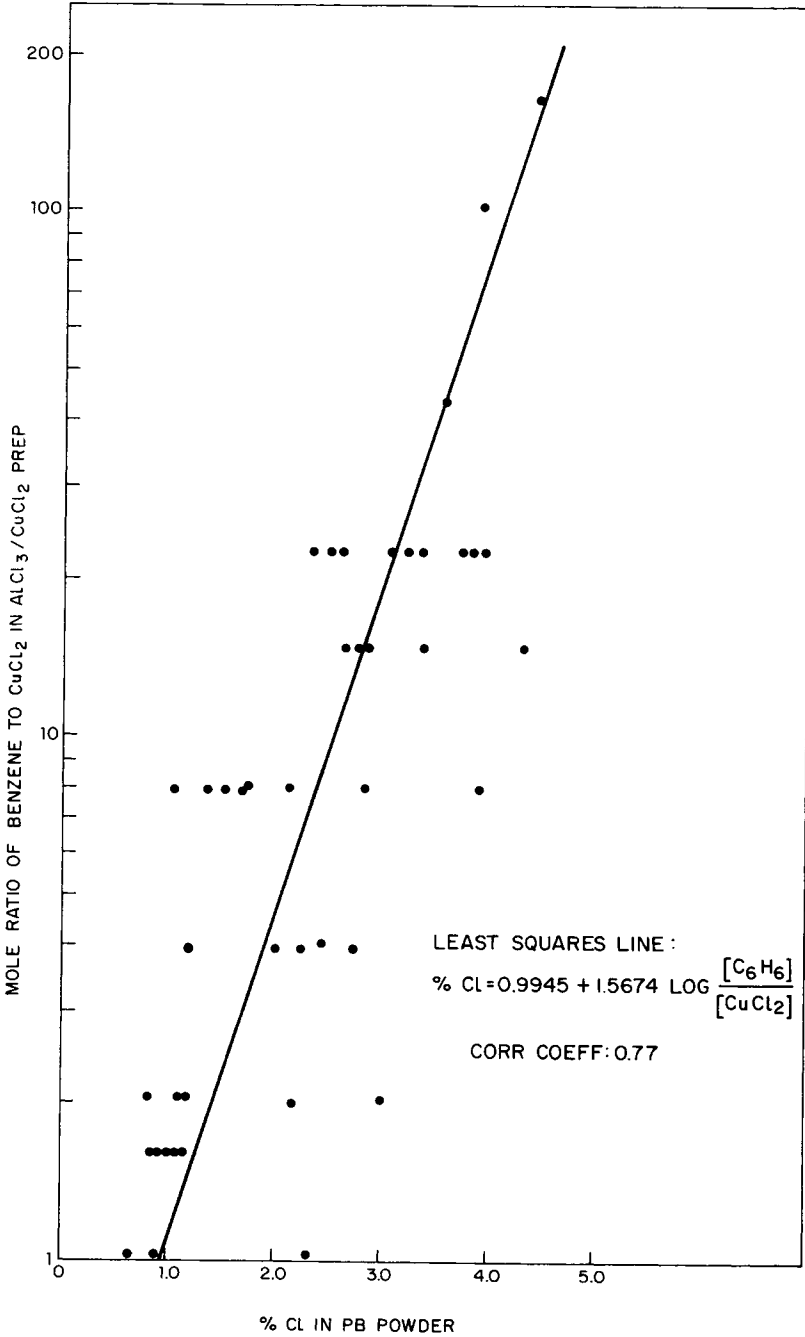


Fig. 12. Effect of dilution with benzene on the Cl content of PB powder in the $\text{CuCl}_2\text{-AlCl}_3$ preparation.

(preheated at $275^\circ/17$ hr) improved green strength of 12.3 MPa (1.750 psi) to 24.2 MPa (3440 psi). Elongation at break also increased from 0.6% to 1.7% on sintering. Best results are obtained for powders that approach theoretical purity, for example, partly unchlorinated powders respond poorly to the sintering process

because of loss of HCl (here, too much hydrogen is bad, the converse of too much chlorine in PB powders). We believe that aromatic polymers similar to PB and PCPB will respond to sintering in a like manner.

The author is indebted to Professor C. S. Marvel for a sample of PB prepared by polymerization of cyclohexadiene.

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