PBI Powder Processing to Performance Parts

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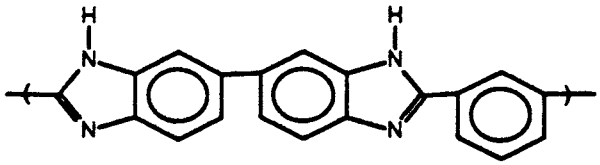
SYNOPSIS

A new route ("direct forming") was developed for forming dense PBI shapes from PBI powder. The new process affords the possibility of automated PBI powder shaping ("cold compaction") and densification in batches of multiple parts by a "powder-assisted hot isostatic pressing" process. Direct forming is a more productive alternative to hot compression molding. Two developments enable PBI direct forming: (1) the discovery that PBI powders that are porous and plasticized with moisture can be shaped by compaction at ambient temperatures (cold-compacted), and (2) a finding that cold-compacted shapes can be densified in large batches by a powder-assisted hot isostatic pressing. The porous PBI powder is formed from PBI in solution by a spray-precipitation process. When plasticized with moisture, this powder is cold-compactible to PBI shapes with densities up to 94% of that of ultimate density of PBI. These shapes, which have sufficient strength to be handled, are then further consolidated via powder-assisted hot isostatic pressing to shapes with excellent thermal and mechanical properties and densities of about 99% of the ultimate.

INTRODUCTION

The general chemistry of polybenzimidazoles was reviewed by Neuse.[1] PBI™ is the acronym and trade mark for poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] (**1**):



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The technology of PBI synthesis via a first-stage melt polymerization and a second-stage solid-state heat treatment to increase molecular weight was described by Powers and Serad[2] and by Buckley et al.[3] The product from the second stage is a dense powder with an inherent viscosity, η_{inh} = 0.8 dL/g and a shardlike morphology that can be thought of as "melt-derived" PBI. The majority of this powder is dissolved in *N,N*-dimethylacetamide (DMAc) and spun into fiber that is marketed by the Hoechst Celanese PBI business unit (Charlotte, NC).

Hot Compression-molding Processes

Ward et al.[4] demonstrated that three-dimensional shapes (billets) could be fabricated from the melt-derived PBI powders by simultaneously heating and pressing. This hot compression-molding (hcm) approach is convenient for fabrication of small numbers of specimens but is not efficient for commercial production.

An alternative hcm process was devised that separates the heating and pressing steps and thereby utilizes the expensive press more efficiently. In this approach, powder is briefly pressed in a billet mold (a cylinder with movable end pieces) in an unheated uniaxial press. The end pieces are clamped in place to maintain pressure on the powder and the mold is moved to an oven for heating. The clamped mold and contents are heated in an oven to temperatures above the PBI glass transition temperature, T_g (~ 425°C, dry), for a period of 5–10 h, then cooled and opened. The billet that results can be cut and

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machined to produce parts with intricate shapes. This technology was used to establish a separate business unit, PBI Performance Parts (Houston), to market PBI parts under the trade name Celazole™.

Both versions of the hcm process were initially based on a 100 mesh powder fraction that was isolated from the solid-state reactor product. This powder has a lower molecular weight, η_{inh} = 0.6 dL/g, than that of the main fraction. Molded PBI specimens exhibit a valuable set of properties that include high T_g (425°C, dry); high tensile, flexural, and compression strengths; and retention of these properties to elevated temperatures.

Fabrication of parts by either hcm process is labor intensive because they rely on machining to produce the final shape. In addition, they use low molecular weight PBI fractions and are not readily adapted to fabrication of particulate-filled composites.

Direct-forming Process

The direct-forming process described here was developed to reduce fabrication costs and enable the processing of large numbers of parts. Direct forming (df) refers to a combination of powder-shaping and densification steps that leads directly to the desired shape with a minimal need for machining.

Shape forming can be conducted on standard automated presses for shaping. These presses typically operate at high speeds at ambient temperatures; hence, they require free-flowing powders that can be consolidated into shapes at room temperature (cold-compacted). Some PBI powders, particularly the melt-derived powders from the solid-state synthesis reactor, are not cold-compactible. These do not form a cohesive powder compact under available pressures at ambient temperatures.

Hughes and Kurschus[5] found that PBI powders having porous particles and a moisture content can be cold-compacted. Chen and Tucker[6] and Hughes and Kurschus[7,8] showed that these powders can be fabricated by a spray-precipitation process. Spray-precipitated powders can be fabricated that (1) have a rounded particle shape that affords free-flowing powders, (2) have adequate bulk density to minimize the stroke of a press required for their compaction to a specified density, and (3) are based on a higher molecular weight (η_{inh} = 0.8 dL/g) polymer. Finally, spray-precipitated powders can be fabricated with dispersed filler particles.

Once formed, the compacted powder shapes must be slowly dried, then heated and pressed to develop ultimate densities and mechanical properties. Since the intricacy of the cold-compacted shape must be faithfully retained during this densification step, pressure must be applied isostatically to all external surfaces of the shape. In principle, the pressure could be applied via gas, liquid, or solid contact with the shape. Gas-assisted hot isostatic pressing (hip'ng) approaches are widely used to consolidate metal or ceramic powder compacts when their densities are very high (> 95% of the ultimate). When part densities are this high, the internal porosity of the compacted shape is not well connected to the external surface, so gas pressure at the surface of the shape causes a consolidation at softening or sintering temperatures. However, it has not been practical to design automatic press tooling to operate at the high pressures required to produce compacted PBI densities with adequate densities for gas-assisted hip'ng.

In another approach, the internal porosity in a compact shape can be sealed off from the applied gas pressure with a gas-impermeable barrier. This was accomplished with a low melting glass deposit,[9] but this is tedious. Finally, Alvarez and Andres[10] developed another approach: powder-assisted hip'ng. The formation of cold-compactible PBI powders, their shaping by cold compaction, and their densification by powder-assisted hip'ng is described below.

EXPERIMENTAL

Spray-precipitated Powder

Porous PBI powders were formed from PBI solutions in DMAc solvent (typically, 12 wt % PBI) by spraying into a water mist where PBI particles precipitate instantly. A unit for this purpose is shown schematically in Figure 1. The PBI solution was fed to and sprayed with an air nozzle through a 100 μm-diameter orifice (supplied by Spraying Systems, Inc., Wheaton, IL, fluid cap #2050 and air cap #64). PBI/DMAc solutions (viscosity ~ 700 cP) were supplied at a pressure of 100 psig to the nozzle via a Zenith Co. gear pump (Model 1B) at a rate of 50 cc/min. Nitrogen was supplied to the air side of the nozzle at 80 psig. This combination produced a uniform spray pattern with a round cross section that projected down into the spray unit for a distance of about 2 m. Water was sprayed into the unit from the side through four nozzles (spray setup #16, fluid cap 2050, air cap 67-6-20-70°). The water spray was directed to intersect the PBI solution spray. The diameter and height of the unit were designed to minimize the violence with which the sprayed fluids

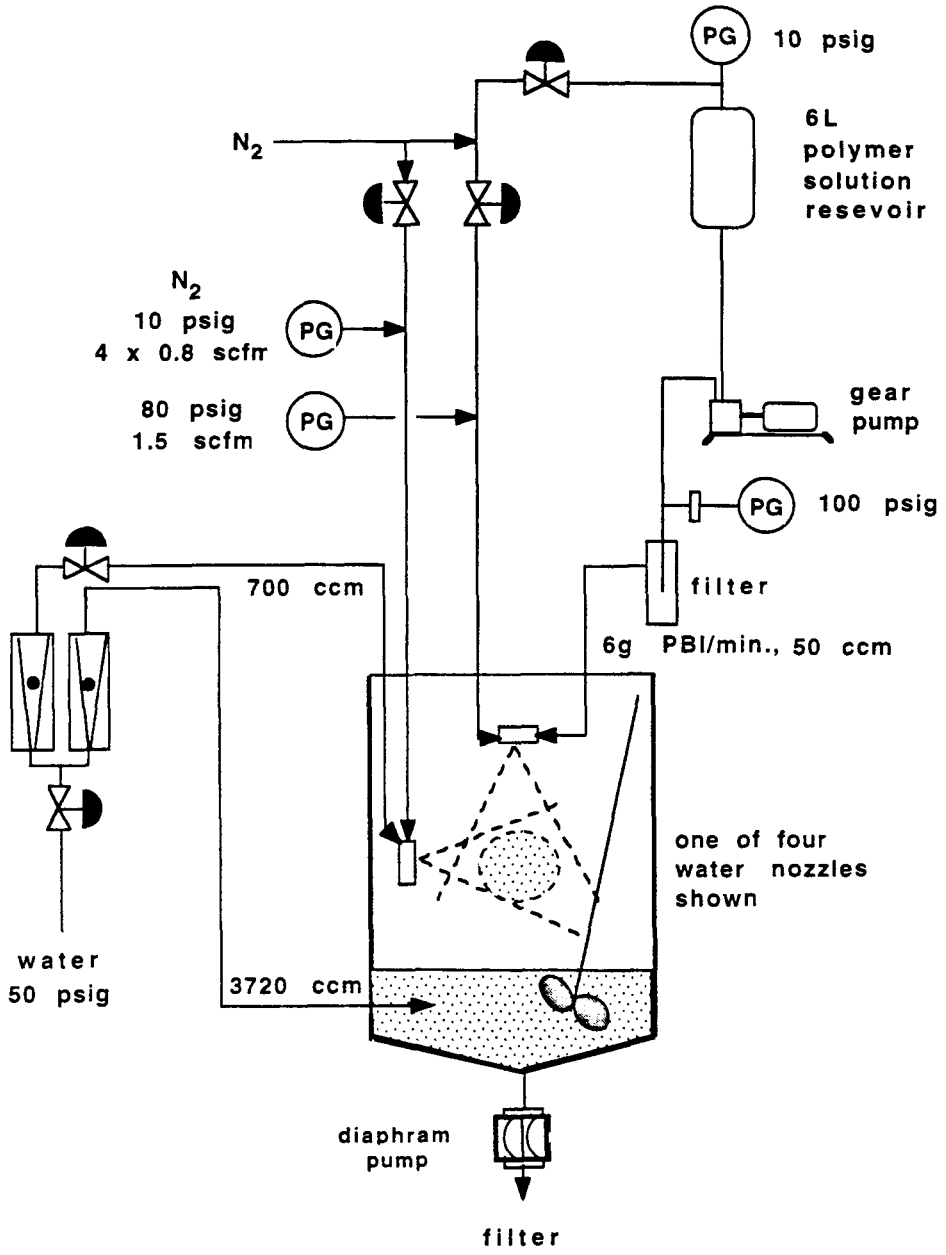

Figure 1 Spray-precipitation reactor schematic.

meet. This promotes the formation of rounded vs. fibrillar particles. Water was supplied to the nozzles at a rate of 175 cc/min per nozzle at 50 psig. An additional 3720 cc/min of water was fed directly to the base of the unit to maintain the DMAc concentration there at < 1 wt %.

The precipitated powder accumulated as a slurry of rigid, porous PBI particles in a DMAc/water solution at the base of the spray unit that could be recovered by filtration or centrifugation. Typically, the recovered wet powder contained about 8 wt % PBI that was saturated with residual DMAc/water solution. DMAc remaining in the powder was extracted by soaking the powder in boiling water. DMAc levels of less than 0.1 wt % were achieved after two extractions, each lasting several hours. Filled PBI powders were prepared by spraying slurries of filler particles in solutions of PBI (12 wt %) in DMAc.

The surface area, porosity, pore-size distribution, and morphology were characterized by standard methods. In addition, two properties, bulk density and angle of repose, were measured.

The angle of repose,[11a] i.e., the angle from a hor-

izontal plane to the free surface of a pile of powder, was used to characterize the fluidity of the powder. Good fluidity is required to assure that the powder will flow freely and predictably from feed hoppers to molds in automatic presses. Low values indicate good fluidity; high values indicate a nonoptimal particle-size distribution or the presence in the distribution of platy or fibrillar particles. The angle of repose of the spray-precipitated powder is low (33°), indicating a free-flowing powder.

Bulk density,[11b] i.e., the ratio of the mass of a powder bed to the volume of the bed, including the inter- and intraparticle void volumes, was measured to define the extent of the compression the powder will undergo when pressed to its ultimate density. This was used to calculate the required height of molds and stroke lengths to fully compress powder in the molds. Powders with a high bulk density can be shaped in shorter molds with shorter piston strokes.

The bulk density of spray-precipitated powder is lower than that of the melt-derived powder due to its porosity, but is within an acceptable range for use with standard presses and molds. The density of cold-compacted powders was measured by immersion in Hg.[12]

Cold Compaction

PBI powders with desired moisture contents were fabricated by moisturizing dry powders or by drying wet powders. Moisturizing was accomplished in humidity chambers at constant temperatures in the range from 30 to 80°C and at constant relative humidity levels in the range 30–80%. Drying was accomplished in vacuum dryers. Moisture content was measured via Karl Fisher titration or by weight loss on a moisture balance (Denver Instruments, Inc., Model IT-100).

The cold compactibility of PBI powders was evaluated by pressing compacted powder flexural test bars between free-floating dies at 20–25°C at pressures from 3 to 60 kpsi. Suitable test bars were fabricated in a mold that was designed for testing the strength of compacted metal powders (ASTM B 312). The 1.25 in. long by 0.5 in. wide cavity was filled with sufficient powder so that the compacted powder was $\frac{1}{4}$ in. thick.

Rupture strengths and densities increased with increasing moisture content and increasing applied pressure. Densities up to 94% of the ultimate and strengths in the range 500–900 psi were achieved at moisture contents 8–14 wt % at applied pressures from 15 to 59 kpsi. These densities and strengths are adequate for handling the parts.

Before hip'ng, moisture that was added to aid cold compaction was removed from the cold-compacted PBI shapes. This was done in a N_2-purged oven whose temperature was increased slowly to vaporize the moisture slowly enough to permit it to diffuse from the shape without forming defects. Shapes

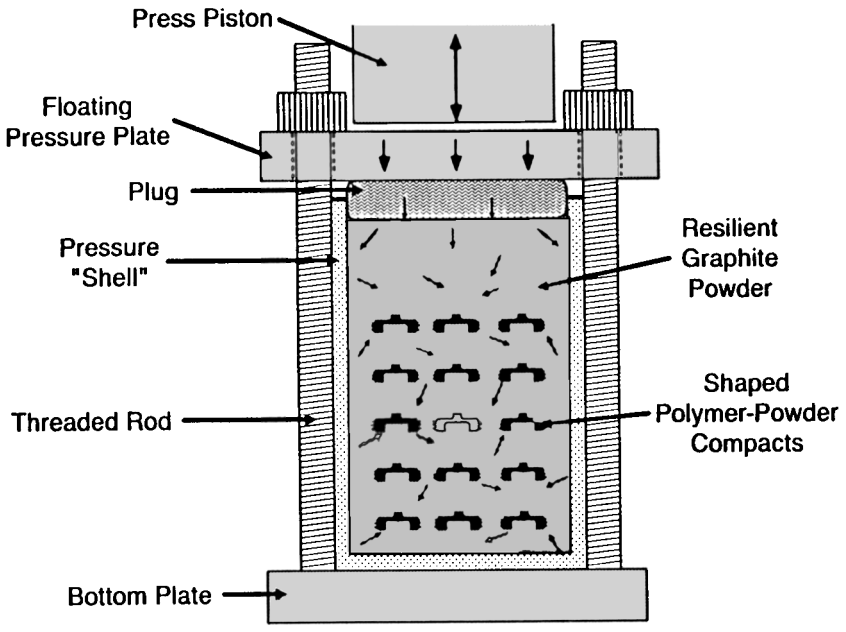

Figure 2 Pressure vessel and clamp assembly for powder-assisted hip'ng.

Table I Unfilled PBI Powder Properties

	Melt-derived	Spray-precipitated
Particle morphology	Dense, shardlike	Open porous, rounded
Mean particle size[a] (μm)	95	140
Polymer inherent viscosity[b] (dL/g)	0.55	0.77
Surface area[c] (m^2/g)	0.3	55
Porosity[d] (cc/g)	0.03	1
Pore radius range[d] (angle)	20–120	20–600
Skeletal density[e] (g/cc)	1.4	1.4
Bulk density[f] (g/cc)	0.3	0.12
Angle of repose[g] (deg)	43	33
Cold compactibility		
Dry (< 1 wt % moisture)	No	No
Humidified (> 6 wt % moisture)	No	Yes

[a] Light scattering particle size analysis.
[b] 1 wt % solution in DMAc at 30°C.
[c] BET single-point N_2 adsorption.
[d] Hg intrusion porosimetry.
[e] He pycnometry.
[f] ASTM # D 1895-89.
[g] Injection method, Ref. 13, p. 130.

(disks and cylinders) having at least one dimension that was 5 mm thick or less were dried by increasing the temperature from ambient to 200°C at 0.05°C/min.

Powder-assisted Hot Isostatic Pressing

The cold-compacted shapes have a relatively low density and strength due to poor particle-to-particle

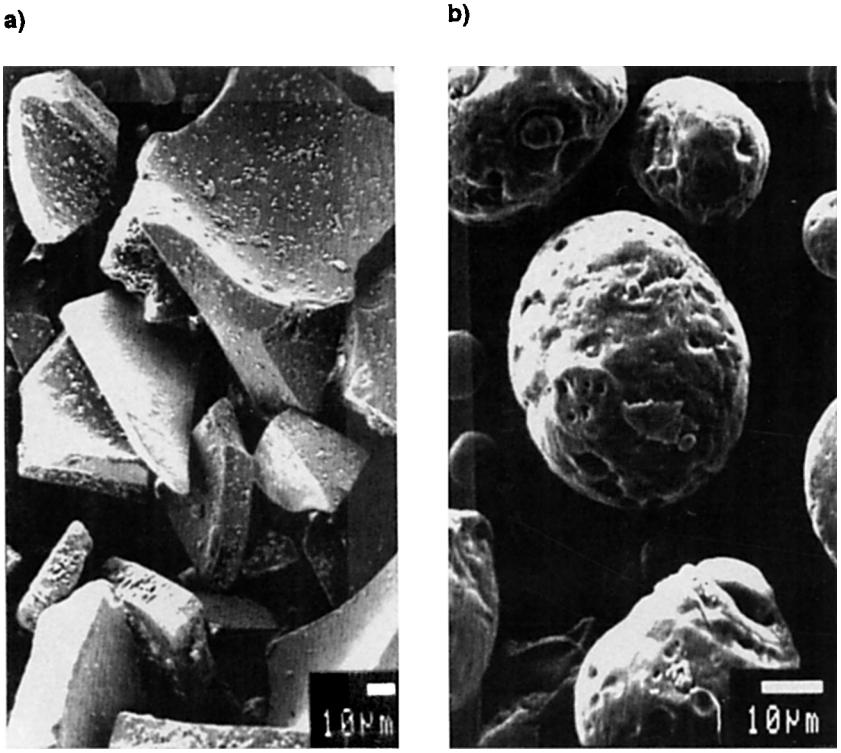

Figure 3 PBI powder particle morphology: (a) melt-derived powder, shardlike shape; (b) spray-precipitated powder, rounded shape.

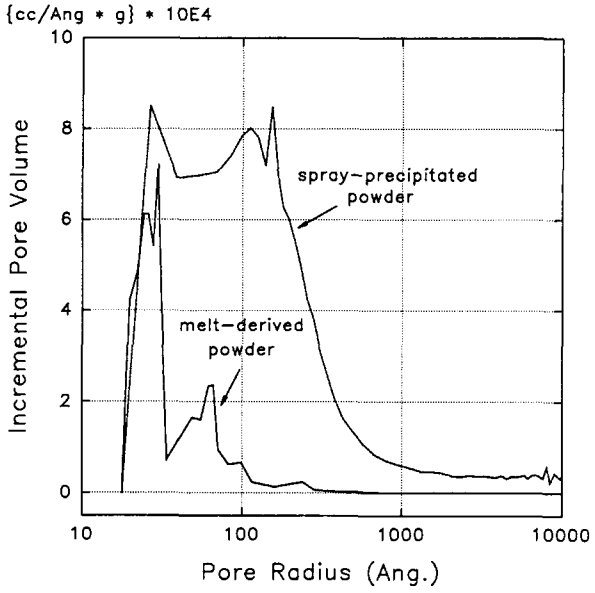

Figure 4 Porosity of PBI powders: (a) melt-derived; (b) spray-precipitated.

polymer entanglement and residual inter- and intraparticle voids. Ultimate densities and mechanical properties were developed by sequentially isostatically pressing and heating the shapes to fuse the particles and eliminate their individual identities. An apparatus for this is shown schematically in Figure 2. The apparatus consists of a pressure vessel with a movable piston that can be filled with cold-compacted shapes distributed in a powder bed.

The pressure vessel can be pressurized in a press at ambient temperature and then transferred to an oven for heating. The applied pressure can be maintained on the powder bed and shapes after the vessel is removed from the press by tightening the bolts on threaded rods that clamp the movable piston in place.

The powder bed converts the uniaxial force of the piston of the press to an omni-directional force in the powder bed. A resilient graphite powder (Superior Graphite, resilient graphite powder, 9400™ grade) was used. With resilient powders, it is possible to maintain the applied pressure in the clamped vessel even though small changes in vessel dimension may occur during thermal cycling. The designated powder is stable at PBI hip'ng temperatures and has a resilience of 35–42%. Resilience is here defined as the percentage increase in the volume of compacted powder after release of a 10 kpsi compacting pressure.

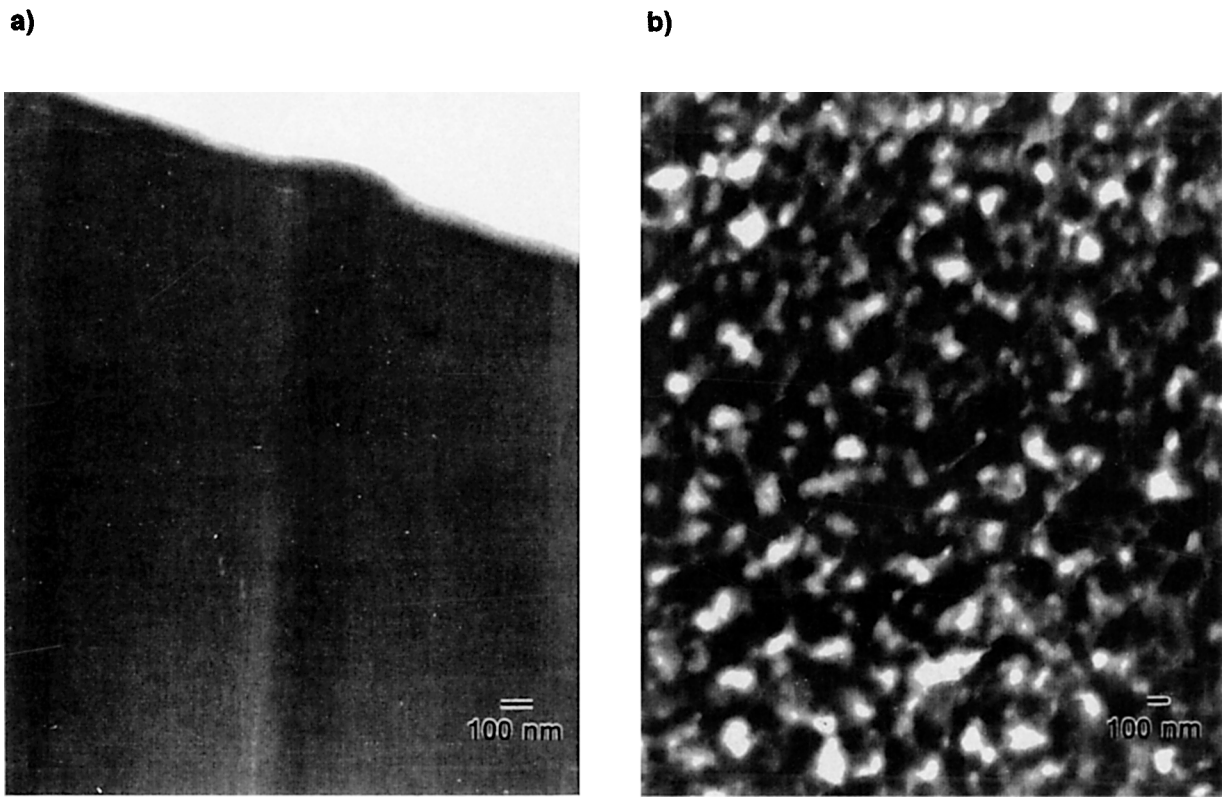

Figure 5 Transmission electron micrographs of PBI particle cross sections: (a) melt-derived; (b) spray-precipitated.

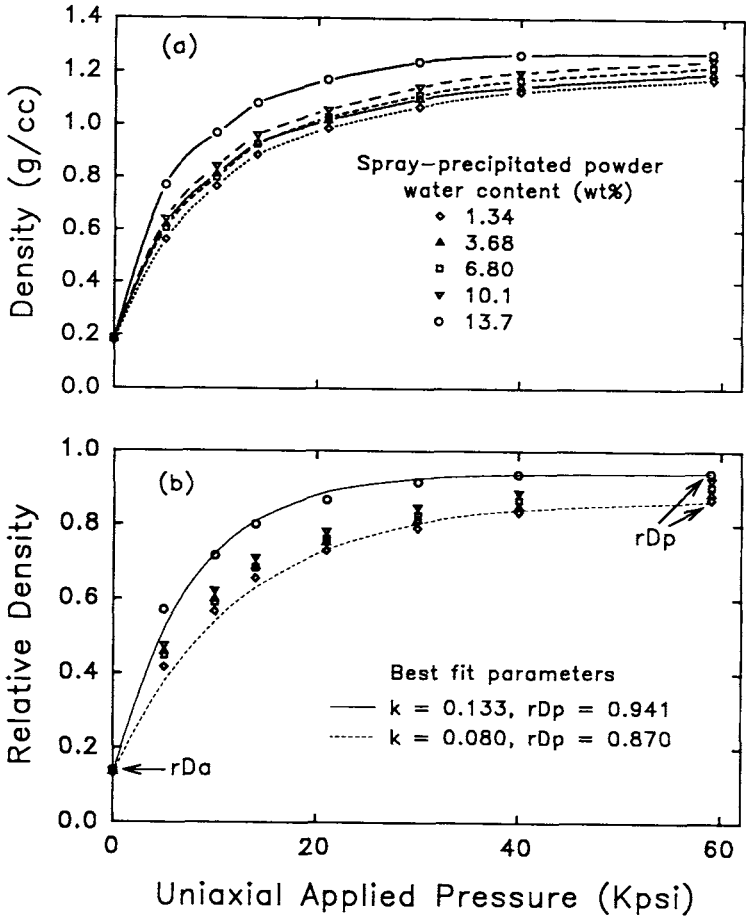

Figure 6 Effect of water content on compressibility: (a) density vs. pressure; (b) relative density vs. pressure.

A steel cylinder (3.5 in. inside diameter, 7.0 in. outside diameter, 12 in. high) was used as a pressure vessel in laboratory work. An oven capable of 500°C was used to heat the mold. A hydraulic press (Hydraulic Component Service, Houston) with capability of applying a 100 ton total force on rams that could be separated to a maximum clearance of 36 in. was used. The press was able to generate pressures up to 10 kpsi on the shapes in the pressure vessel.

In a typical operation, the pressure vessel was loaded with the compacted shapes, each carefully positioned within the graphite powder bed. The contents of the pressure vessel were then pressed with unheated rams to 1–3 kpsi for 15 min. The piston of the pressure vessel was then bolted in place and the apparatus was transferred to an oven for heating. After several hours at 425–500°C, the vessel was allowed to cool. The molded specimens were recovered by opening the pressure vessel and sifting the molded parts from the graphite powder.

Tensile and flexural bar shapes were machined from simple molded panels (4 in. square by $\frac{1}{8}$ in. thick. These panels were made in a 4 in.-square steel mold with a 2 in.-deep cavity. The panels were hot compression-molded using the same heat treatment as used for isostatic pressing.

RESULTS AND DISCUSSION

Powder Comparison

Selected properties of melt-derived and spray-precipitated powders are compared in Table I. The shardlike and rounded shapes of each are shown in the scanning electron micrograph images in Figure 3(a) and (b).

The distribution of pore volume in pores of increasing radii in melt-derived and spray-precipitated powders is compared in Figure 4. The spray-precipitated powder exhibits a large connected porosity (0.9 cc/g) and a high internal surface area (55 m^2/g). By contrast, the melt-derived powder has lit-

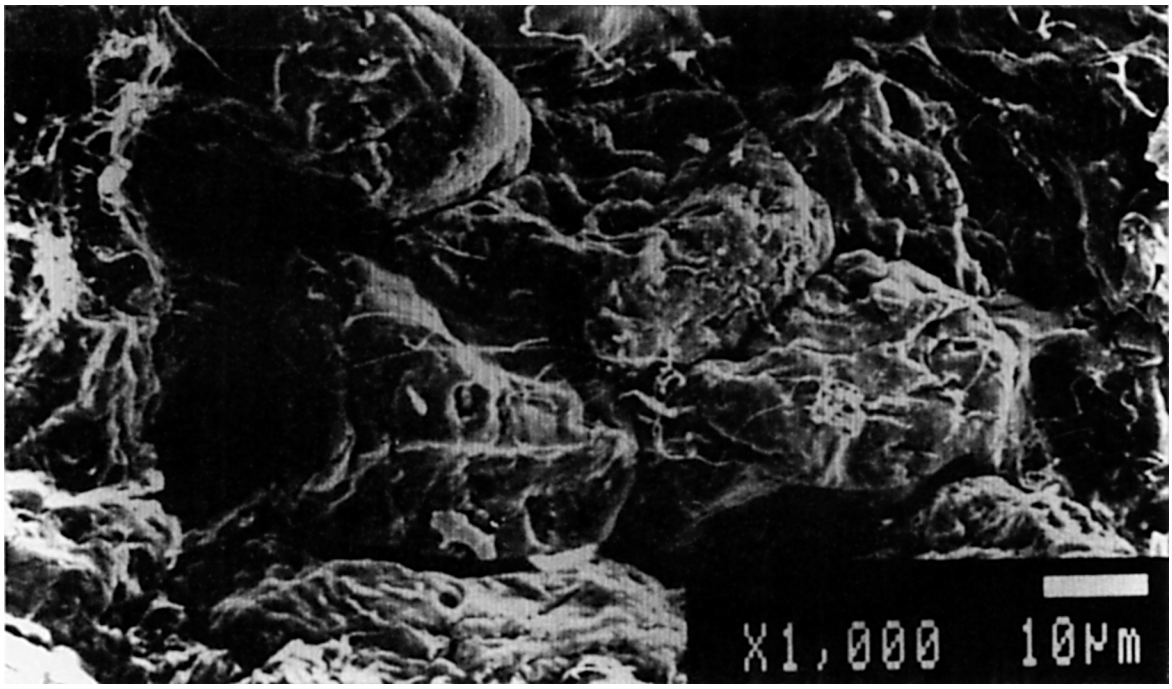

Figure 7 Shape of spray-precipitated PBI particles at the fracture surface of a cold-compacted shape. Scanning electron micrograph.

tle porosity (0.02 cc/g) and a low surface area (0.3 m^2/g).

Transmission electron micrographs of melt-derived and spray-quenched PBI particles are presented in Figure 5. The TEM image of the melt-derived PBI particle is uniform and featureless. The TEM image of the spray-precipitated particle shows a density variation on the 100 nm scale that corresponds to the porosity seen by Hg intrusion.

Moisture Sorption

All forms of PBI sorb moisture in humid atmospheres. Melt-derived powders sorb up to 12 wt %, whereas spray-precipitated powders sorb up to about 15 wt % under comparable conditions of temperature and humidity. A moisture-activated transition can be detected by DMA at subambient temperatures in PBI with sorbed moisture contents but not in dry PBI. The plastisizing effect that water has on PBI that enables cold compaction is believed due to this moisture-activated transition.

Cold Compaction

PBI powders are not readily cold-compactible. Melt-derived PBI powders could not be cold-compacted either in the dry or moisturized state. Spray-precipitated powders could also not be cold-compacted when dry, but these powders can be cold-compacted when moisturized. The densities that can be achieved when moisturized powders are cold-compacted is a function both of the moisture content and the applied pressure. The densities (D) and relative densities (rD) of spray-precipitated PBI powder compacts are plotted as functions of the uniaxial pressures used to compact the powder and the moisture content of the powder in Figure 6(a) and (b). Powders having moisture contents from 1.3 to 13.7 wt % could be cold-compacted. If the moisture content of the PBI powder was lower than ~ 5 wt %, laminar cracks perpendicular to the pressing axis form in the compacted shapes on releasing the compacting pressure. Figure 7 is an SEM image of a fracture surface of a cold-compacted (50 kpsi), spray-precipitated powder compact.

The bulk densities, Db, of spray-precipitated PBI powders were all about 0.18 g/cc, or 13% of the ultimate density of PBI (1.35 g/cc) as measured by He pycnometry, regardless of the moisture content.

The powders with high water contents are more readily compacted to high densities. Powder compacts exhibited densities that approach plateau densities (Dp) as the compacting pressure (P) increases. These plateau densities were less than the skeletal density of PBI. The highest Dp was observed

in the compacted shapes formed from a powder with the highest moisture content (13.7 wt %) at the highest applied pressure (59 kpsi). This density was 1.27 g/cc or 94% of the ultimate density of PBI. The plateau densities of compacted shapes with lower moisture contents were somewhat lower.

The Halldin/Shah function[13] for the compressibility of polymer powders, [eq. (1)] adequately summarizes the relative density vs. pressure relationship for shapes formed from spray-precipitated PBI powders with various water contents:

$$rD = rDp - \{rDp - rDb\}e^{(-kP)} \qquad (1)$$

where rD = ratio of an observed density to the ultimate density of PBI (= 1.35 g/cc), rDp = relative plateau density, rDb = relative bulk density, k = compressibility parameter, and P = applied pressure (Kpsi).

The relative densities of compacts formed from powders with 1.34 and 13.7 wt % water contents were fit with eq. (1). The result is plotted in Figure 6(b). The parameters, k and rDp, were highest (0.133 and 0.94) for the shape with the highest water content and somewhat lower (0.080 and 0.87) for the shape with lowest water content. For comparison, Halldin and Shah[13] reported k and rDp parameters for 10 polymer powders, including PE, PVC, PMMA, and PI. The compressibilities ranged from k = 0.01 to 0.11 and relative plateau densities ranged from 0.76 to 0.91. The comparison indicates that the moisturized, spray-precipitated PBI powders are readily cold-compactible.

Filled, Spray-Precipitated Powders

An important benefit of the spray-precipitation approach to PBI powder fabrication is that filled PBI powders can be made that are cold-compactible and moldable by hcm or df processing. This leads to particulate-filled molded PBI specimens that have tailored properties. For example, solid lubricants, e.g., graphite particles, when dispersed in molded PBI confer low wear and friction properties at the surface of the shapes.[14] Other fillers can be added. For example, hollow glass balloons can be dispersed to lower density and thermal conductivity.[15]

Cold-compactible-filled PBI powders were made with the spray-precipitation process by spraying slurries of the filler powder dispersed in the PBI/DMAc solutions. This approach led to composite powders with better df properties than those of powders with similar compositions prepared by blending powders. In spray-precipitated composite

Table II Molded PBI Materials: Process Conditions and Properties

PBI Powder Type	Filler	Molding Conditions				Density (g/cc)	Tensile Properties			Compression Strength (Kpsi)	Izod Impact Strength (Unnotched) (ft lb/in.)
		Process[a]	Temp (°C)	Pressure (Kpsi)	Time (h)		Strength (Kpsi)	Elong. (%)	Modulus (Mpsi)		
Melt-derived	None	hcm	462	3.00	0.50	1.278	22.9	3.0	0.850	57	6.7
	None	hcm	463	3.00	4.00	1.276	27.1	3.8	0.830		9
Spray-precipitated	None	hcm	461	3.00	0.50	1.285	26.5	3.5	0.857		9.8
	None	hcm	460	2.00	2.00	1.280	27.8	3.7	0.870	60	
	None	hcm	463	3.00	4.00	1.277	31.3	4.4	0.836		15.2
Spray-precipitated	None	df	463	1.00	4.00[b]	1.300	32	5.0	0.950		

[a] hcm = hot compression-molded to panel shape, machined to final test shape. df = direct-formed: cold-compacted and hip'd to billet shape, machined to final test shape.
[b] Approximate time and temperature; actual conditions vary with vessel size.

powders, the filler particles are more intimately mixed with PBI, even encapsulated by PBI.

Slurries could be sprayed continuously as long as the filler particle diameter is less than $\sim \frac{1}{5}$ of the nozzle orifice diameter. Filler particles with a maximum dimension $< 20\ \mu m$ were typically chosen for use with nozzles having an orifice diameters of $100\ \mu m$.

Molded PBI Properties, Unfilled

The properties achieved when melt-derived and spray-precipitated powders are shaped by hcm and df processing, respectively, are summarized in Table II. Higher density, strength, and elongation properties were achievable in specimens formed from spray-precipitated powder than from melt-derived powder, whether by hcm or df processing. The higher strength of specimens formed from spray-precipitated powder is attributed to (1) the higher PBI molecular weight of the polymer used and (2) the greater uniformity (monophasic character) of the molded specimens produced.

PBI is present in molded specimens as an X-ray amorphous material. Molded PBI specimens have identical broad X-ray diffraction patterns over the range $2\theta = 5$–$60°$ whether fabricated from melt-derived or spray-precipitated powders or fabricated by hcm or df processing.[16]

The morphologies of molded specimens formed from melt-derived and spray-precipitated PBI powders were examined by optical microscopy (slightly defocused). Images of polished cross sections of typical examples of each are presented in Figure 8. The specimen formed from a spray-precipitated powder is homogeneous, whereas that from a melt-derived powder is not. Outlines of remnants of the original melt-derived PBI particles can be seen in the melt-derived specimen. In this case, the duration of molding (30 min) was adequate to fuse particles but did not produce a monophasic molded PBI. The size and quantity of particle remnants can be reduced with longer molding times.

There is no trace of original particles in the optical micrograph of the specimen formed from the spray-precipitated powder. PBI in the porous, spray-

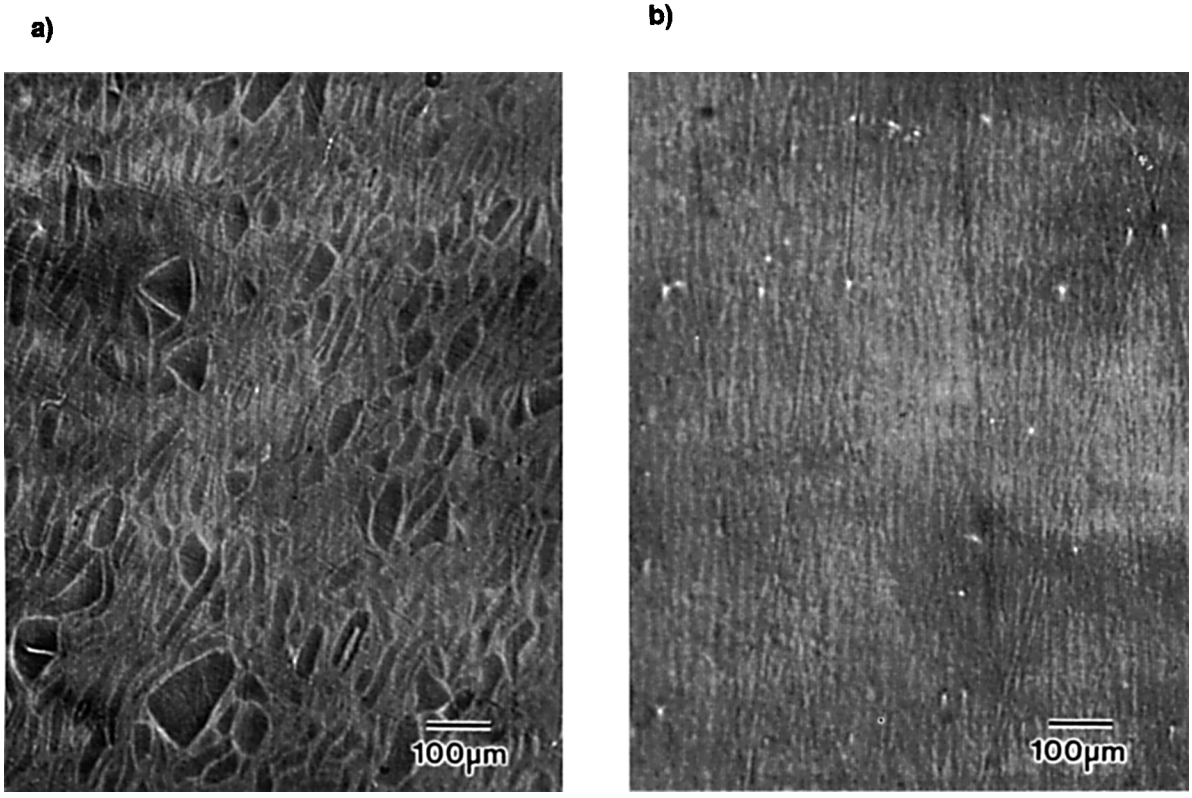

Figure 8 Morphology of hot compression-molded PBI specimens. Optical micrographs of polished cross sections of molded specimens formed from (a) melt-derived PBI powder and (b) spray-precipitated PBI powder.

Table III Glass Bubble-filled PBI Composites: Process Conditions and Properties

Glass Bubble Content (Vol %)	Hot Compression Molding[a]			Density (g/cc)	Tensile Properties			Compression Strength (Kpsi)	Thermal Conductivity[b] W/cm K at 25°C
	Temp (°C)	Pressure (Kpsi)	Time (h)		Strength (Kpsi)	Elong. (%)	Modulus (Mpsi)		
0	463	2.00	1.00	1.280	27.8	3.7	0.870	60	0.00327
10	460	3.00	2.00	1.248	18.4	2.4	0.860	47	—
19	460	2.00	2.00	1.201	20.9	3.1	0.860	44	0.00387
35	460	2.00	2.00	1.154	15.2	2.2	0.930	39	—
48	460	0.50	2.00	0.940	8.8	1.8	0.730	33	0.00290
70	460	0.50	2.00	0.810	4.1	1.4	0.640	24	0.00251

[a] PBI composite powders fabricated by spray-precipitation. Hot compression-molded to panel shape, machined to final test shape.
[b] Thermophysical Properties Research Laboratory, Purdue University.
[c] 3M Scotchlite S-60 glass bubbles, density = 0.6 g/cc, 100 mesh (160 μm max diameter), resistant to ~ 10 Kpsi isostatic pressure.

precipitated particle form fuses more readily than in the melt-derived particle form. The more intimate packing that results when the porous particle is compacted and the greater amount of finely distributed void volume that is probably still present in the cold-compacted shapes may account for the more facile particle fusion. Additionally, the spray-precipitated polymer itself may have a higher free volume than that of the melt-derived polymer.

Melt-derived polymer is formed by relatively slow solidification at high temperatures, i.e., by cooling from PBI melt-polymerization temperatures. This appears to afford an opportunity for polymer chain–chain packing that would result in polymer with a lower free volume and a lower driving energy for particle–particle fusion under molding conditions.

Spray-precipitated polymer is formed instantaneously at temperatures that are significantly below the T_g of PBI. Under these conditions, there appears to be little opportunity for efficient polymer chain–chain packing. A high free-volume content can be anticipated. Elimination of this free volume under hcm or df conditions could provide an additional driving energy for particle–particle fusion.

Molded PBI Properties, Glass Bubble-Filled

PBI powders having a broad range of glass-bubble contents were fabricated by the spray-precipitation approach and shaped by hot compression molding. Fabrication conditions and properties are given in Table III. The density and mechanical properties decline with increasing glass bubble content, but adequate properties are retained to significant filler levels. The thermal conductivity decreases slightly.

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