

PBI (Polybenzimidazole): Synthesis, Properties and Applications

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ABSTRACT *PBI (polybenzimidazole) is a thermally stable high performance polymer. In a variety of forms, e.g. fibers, neat resin and composites, PBI finds use in a wide range of high temperature applications. The synthesis of PBI, and properties, and applications of fiber and molded resin are discussed. Also included are recent developments in composite fabrication technology and PBI composite applications in carbon/carbon composites.*

1. INTRODUCTION

Poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole], referred to throughout this article as PBI, is well known for its outstanding thermal stability and chemical resistance [1]. PBI is a thermoplastic; it has the highest T_g , 435°C (815°F), of any commercially available polymer. It does not burn, contribute fuel to flames or produce much smoke. These attributes are a consequence of the inherent chemical stability of the benzimidazole functionality found in the polymer backbone (Figure 1).

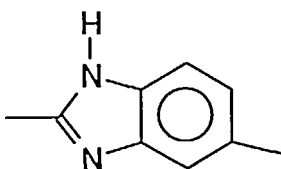


Figure 1. Benzimidazole functionality found in the polymer backbone.

Polybenzimidazoles have been reported in the literature since the early 1960s [2]. While being well-known for their excellent thermo-oxidative stability, PBIs were thought to be intractable 'brick-dusts'. However, in the last few years [3] work at Hoechst Celanese has demonstrated that (i) PBI can be made at high molecular weight, (ii) PBI is moldable and (iii) advantage can be taken from PBI's solubility in dimethylacetamide (DMAc) allowing for the facile preparation of PBI matrix resin composites containing continuous fiber reinforcement.

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1.1 Background

PBI is prepared from the polycondensation of tetraaminobiphenyl, TAB, with diphenylisophthalate, DPIP. The reaction scheme is shown in Figure 2. Two possible mechanisms have been proposed. One mechanism postulates the existence of a polyamic acid as a primary intermediate, which then undergoes dehydration and cyclization to the imidazole. The second mechanism postulates the existence of a Schiff's base intermediate that cyclizes to a benzimidazoline which subsequently eliminates phenol upon forming the imidazole [4].

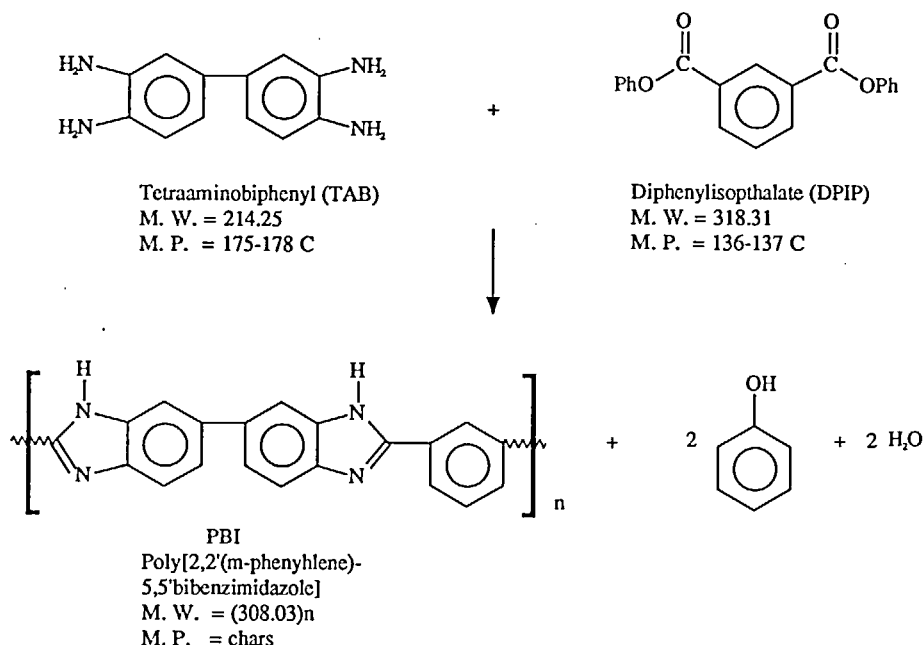


Figure 2. Synthesis of PBI.

Poly [2,2'-(*m*-phenylene)-5,5'-bibenzimidazole], PBI is the only commercially available polybenzimidazole and is made at Hoechst Celanese's Rock Hill facility (South Carolina, USA). The commercial polymerization occurs in two stages, both of which are carried out in an inert atmosphere. In the first stage, the DPIP melts and solubilizes the TAB. As the temperature rises, polymerization begins and phenol and water are generated. The evolution of the condensation by-products causes the formation of a friable foam. In the second stage, the foam is crushed and the polymer molecular weight is advanced in the solid state [3].

2. PBI FIBER AND ITS APPLICATIONS

The fiber is dry spun from a ~25% solution of PBI in DMAc. Addition of a small percentage of lithium chloride lengthens the solution's shelf life from days to months. The solution is prepared under pressure at temperatures above the boiling point of DMAc. Particulates are removed by filtration and the solution is then extruded into a heated nitrogen atmosphere where the majority of solvent evaporates. The residual

solvent and lithium chloride are extracted from the fiber by washing in water. Following the wash, the fiber is dried, drawn to increase strength and then treated with sulfuric acid. Sulfonation of PBI reduces the flame shrinkage of the drawn fiber from >50% to <10% [5]. Finally, the fiber is crimped and cut, providing a material with conventional textile processing characteristics. An outline of this process is shown in Figure 3; the boxed items are accessible for alternative processing, as will be described later.

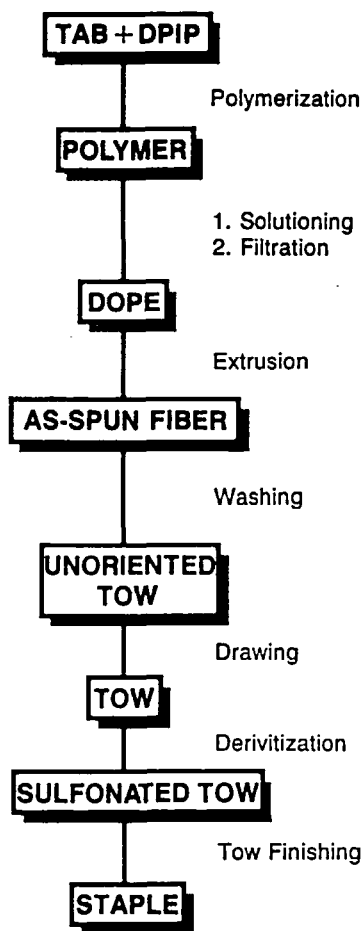


Figure 3. Materials available from Hoechst Celanese's fiber process.

The physical properties of PBI fiber are summarized in Table 1. This array of properties enables PBI to be processed on conventional staple fiber textile equipment: PBI's hydrophilicity results in a high equilibrium moisture content in the fiber, i.e. ~15%. This coupled with a low modulus contributes to PBI's comfort in industrial apparel applications.

With a limiting oxygen index of ~40%, PBI will not support burning in air. It therefore releases little or no offgases up to its decomposition temperature of 580°C. PBI fabrics will not melt or drip, and they retain dimensional stability to high temperatures and heat fluxes. Even charred PBI fabrics retain integrity and flexibility with little shrinkage. The thermal oxidative stability of PBI is shown in Table 2. Table

Table 1. Physical Properties of PBI Staple Fiber

PROPERTY	UNITS	TYPICAL VALUE
DPF	denier	1.5
	dtex	1.7
Tenacity	g/d	2.7
	dN/tex	2.4
Breaking elongation	%	28.5
Initial modulus	g/d	32.0
	dN/tex	28.0
Crimp	per in.	11.0
	per mm	0.4
	%	28.0
Finish	%	0.6
Specific gravity		1.43
Moisture regain at 68°F (20°C), 65% RH	%	15.0
Boiling-water shrinkage	%	<1.0
Hot-air shrinkage at 400°F (205°C)	%	<1.0
Specific heat	BTU/lb °F	0.3
Limiting oxygen index	%	>41.0
Surface area resistivity at 70°F (21°C), 65% RH	ohms/cm ²	1 × 10 ¹⁰
Color		gold
Standard cut lengths*	in.	1.5, 2.0, 3.0
	mm	38, 50, 76
Thermal Conductivity	BTU/h ft °F	0.022

*Other cut length may also be available.

Table 2. Thermal-oxidative Stability of PBI Fiber

Temperature (°F/°C)	Time (useful life)
1110/600	3–5 s
840/450	5 min
750/400	1 h
625/330	24 h
570/300	1 week

3 shows that PBI fiber has excellent resistance to inorganic acids and bases, even at elevated temperatures. In addition, it retains its strength when exposed to a broad range of organic chemicals and solvents as shown in Table 4.

PBI's unique combination of thermal, chemical and textile properties make it a candidate for many applications in severe environments [6]. PBI can be used in 100% form or it can be blended with other fibers, e.g. glass, FR cellulose or aramids. Some of the current textile applications include firefighters' protective apparel, aluminized crash rescue gear, industrial workers' apparel, aircraft fire blocking layers and wall fabrics, and suits for racing car drivers [7].

Table 3. Tensile Strength after Immersion in Inorganic Acids and Bases

Compound	Concentration (%)	Temperature (°F/°C)	Time (h)	Tensile strength retained (%)
Sulfuric acid	50	85/29	144	90
	50	160/71	24	90
Hydrochloric acid	35	85/29	144	95
	10	160/71	24	90
Nitric acid	70	85/29	144	100
	10	160/71	48	90
Sodium hydroxide	10	85/29	144	95
	10	200/93	2	65
Potassium hydroxide	10	77/25	24	88

Table 4. Tensile Strength of PBI Fibers after Immersion in Organic Chemicals

Compound	Tensile strength retained* (%)
Acetic acid	100
Methanol	100
Perchloroethylene	100
Dimethylacetamide	100
Dimethylformamide	100
Dimethylsulfoxide	100
Kerosene	100
Acetone	100
Gasoline	100

*All exposures at 86°F (30°C) for 168 h.

3. MOLDED PBI RESIN: CELAZOLE®

PBI resin, trademarked Celazole®, is molded via a proprietary sintering process that was jointly developed by Hoechst Celanese (North Carolina, USA) and Alpha Precision Plastics, Inc. (Houston, Texas, USA) [8]. Celazole is molded in a variety of stock shapes or directly molded into finished articles. The data shown in Table 5 describes the room temperature mechanical properties of molded, unfilled Celazole resin.

Molded PBI has the highest compressive strength, 58 ksi, of any available, unfilled resin. Other mechanical properties such as a tensile strength of 23 ksi, a flexural strength of 32 ksi, a ductile compressive failure mode (see Figure 4) and the relatively low density of 1.3 g/cm³, make the material an excellent candidate for high strength, low weight applications. Thermal and electrical properties are also listed in Table 6. Notable among these is the heat deflection temperature (at 264 psi) of 435°C (815°F) which is the highest value known for any available thermoplastic resin [1].

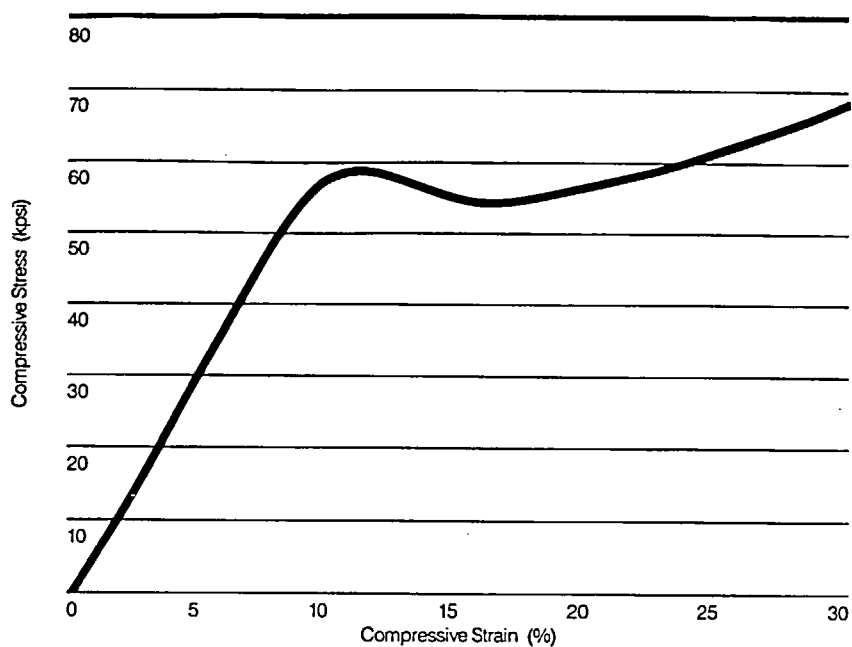


Figure 4. Typical compression stress-strain curve for Celazole PBI.

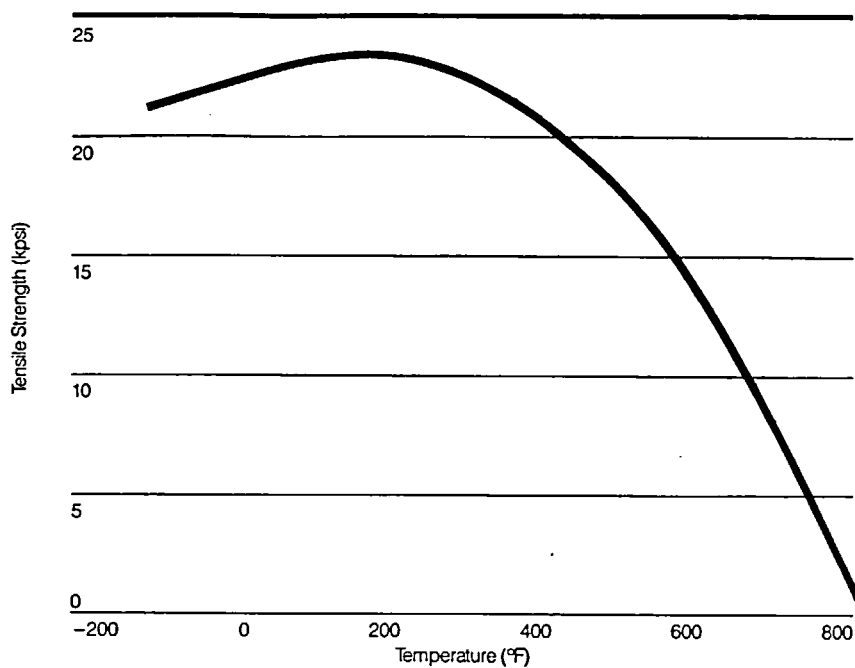


Figure 5. Celazole PBI; compressive strength versus temperature.

Table 5. Room Temperature Mechanical Properties of Molded, Unfilled PBI

Property	ASTM method	English value	Metric value
Tensile strength	D638	23000 psi	160 MPa
Elongation	D638	3%	3%
Tensile modulus	D638	850 ksi	5.9 GPa
Tensile fatigue, % of stress to failure at 1×10^6 cycles, 1 Hz		35% (8.1 ksi)	35% (56 MPa)
Flexural strength	D790	32000 psi	220 MPa
Flexural modulus	D790	950 kpsi	6.5 GPa
Compressive strength at yield (12% strain)	D695	58000 psi	400 MPa
at 10% strain		50000 psi	340 MPa
Compressive Modulus	D695	900 ksi	6.2 GPa
Izod impact strength notched	D256	0.5 ft-lb/in.	30 J/m
unnotched		11 ft-lb/in.	590 J/m
Poisson's ratio		0.34	0.34
Special gravity		1.3	1.3
Hardness			
Rockwell K	D785	115	115
Rockwell M	D785	> 125	> 125
Shore D	D2240	99	99
Water absorption 24 h at 73°F		0.4%	0.4%
Tribological Properties	D3708		
Static Friction Coefficient versus C1018 steel			0.27
Dynamic Friction Coefficient versus C1018 steel			0.19
Wear factor (K) (100 h test) at $PV=50000$ ($P=1000$ psi, $V=50$ ft/min)			29
Total wear (mils) (100 h test)			14.4

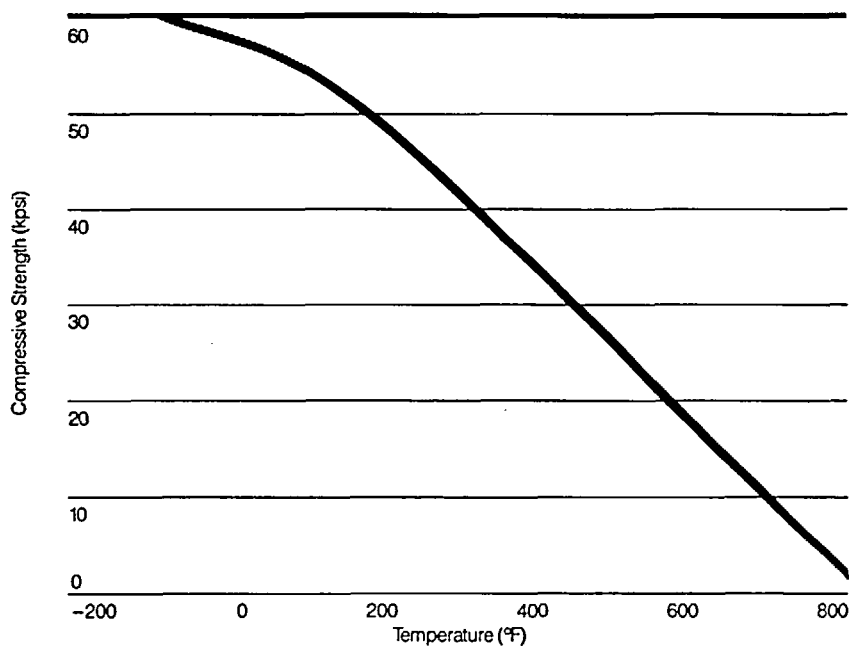
The Composite Materials Research Group at the University of Wyoming has tested mechanical properties of Celazole parts over a 1000°F (538°C) temperature range. Tensile tests evaluated included ASTM D 638 type V micro tensile bars at temperature after a 5-min dwell time. As shown in Figure 5, Celazole maintains significant tensile properties up to 700°F (371°C). In addition, compression tests were run on ASTM D695 compression billets, 0.5 in. in diameter and 1 in. long. Specimens were equilibrated for 15 min and were tested at temperature. As Figure 6 shows, Celazole maintains significant compressive strength to 700°F (371°C) and shows no embrittlement to -100°F (-73°C).

Isothermal strength and weight retention tests were performed on compression billets 0.5 in. in diameter and 1 in. long. As shown in Figures 7 and 8, samples exposed to air at 500°F (260°C) for up to 500 h or 600–700°F (316–371°C) for up to 100 h exhibit no weight loss or compressive strength change. In fact, molded PBI resin has been subjected to 1400°F (760°C) for 3 min with no significant change in structural dimensions or properties.

Sintered PBI exhibits excellent chemical resistance as defined by retention of tensile strength and dimensional stability. In hot aqueous environments, Celazole experiences

Table 6. Thermal and Electrical Properties of Unfilled Molded Celazole

Property	ASTM method	SI value	English value
Heat deflection temperature, 264 psi	D648	708K	815°F (435°C)
Glass transition temperature	DMA	700K	800°F (427°C)
Coefficient of linear thermal expansion			
75–300°F	TMA	23 $\mu\text{m}/\text{m K}$	13 ppm/°F
390–570°F	TMA	33 $\mu\text{m}/\text{m K}$	18 ppm/°F
Limiting oxygen index	D2863	58%	58%
Dielectric strength	D149	20.9 kv/mm	550 V/mil
Volume resistivity	D257	8×10^{14} ohm-cm	8×10^{14} ohm-cm
Dissipation factor	D150		
1 kHz		0.000	
10 kHz		0.003	
0.1 MHz		0.034	
Dielectric constant	D150		
1 kHz		3.3	
10 kHz		3.3	
0.1 MHz		3.2	
Arc resistance	D495	186 s	186 s

**Figure 6.** Celazole PBI: compressive strength versus temperature.

some loss of hardness, and tensile and compressive strength and modulus. However, original properties are restored after drying suggesting that hydrolytic degradation does not occur [9].

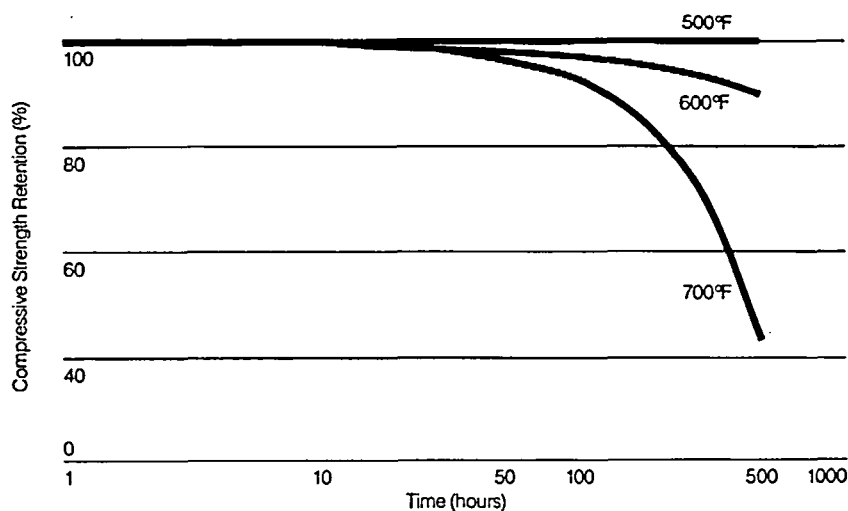


Figure 7. Isothermal compressive strength retention at 10% strain in air.

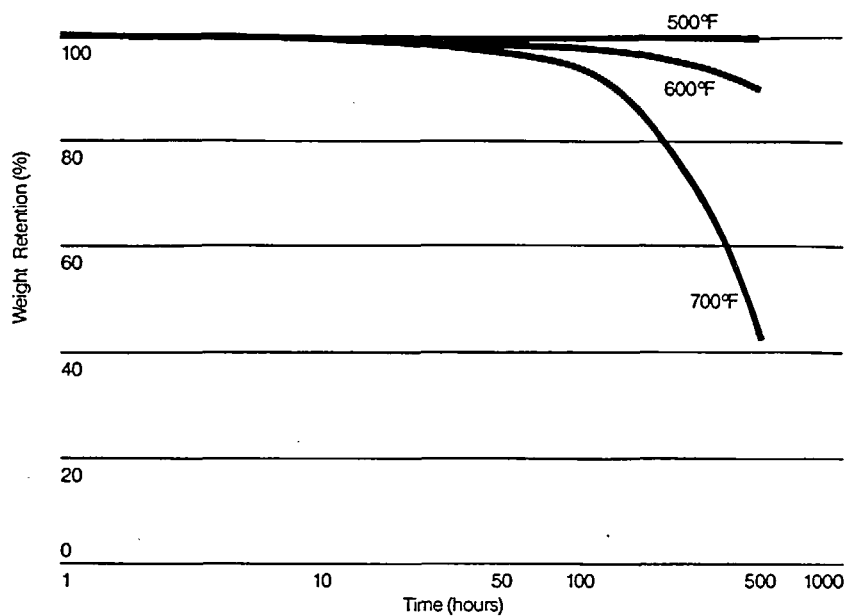


Figure 8. Isothermal weight loss in air.

Celazole parts are currently being evaluated for the chemical process and oil recovery industries where the key demands are thermal stability and chemical resistance. In these areas, Celazole has been successfully used in demanding sealing applications such as valve seats, stem seals, hydraulic seals and backup rings. Additional consideration is being given in the aerospace industry where advantage is taken from Celazole's high strength and short-term high temperature resistance. In the industrial sector, Celazole is used as a thermal and electrical insulator where high

dimensional stability as well as retention of electrical properties at high temperature is important [10].

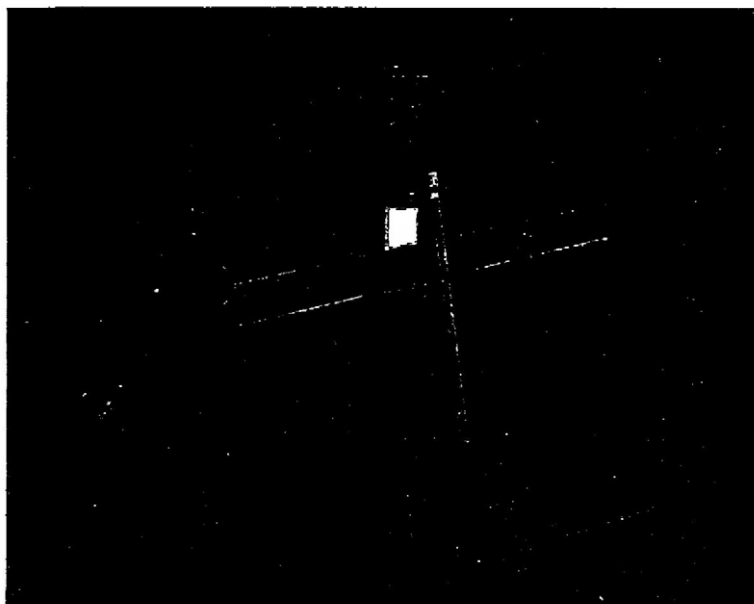


Figure 9. PBI composite parts.

4. PBI MATRIX RESIN FOR CONTINUOUS FILAMENT COMPOSITES

PBI is also available for use as a matrix resin in advanced fiber composite applications. The resin is available as a 45% solution of 0.2–0.3 IV PBI, molecular weight (weight average) of 12 000 to 20 000, in DMAc. The viscosity of these solutions, 3–6000 poise, permits facile prepregging to standard resin contents of 35–40%. The ~30% residual DMAc gives the prepregs excellent room temperature drape and tack allowing the fabrication of complex shapes (Figure 9).

PBI prepregs have been produced using a variety of continuous fiber substrates, e.g. graphite, quartz and ceramic, on a variety of forms, e.g. fabric, tow and tape. These

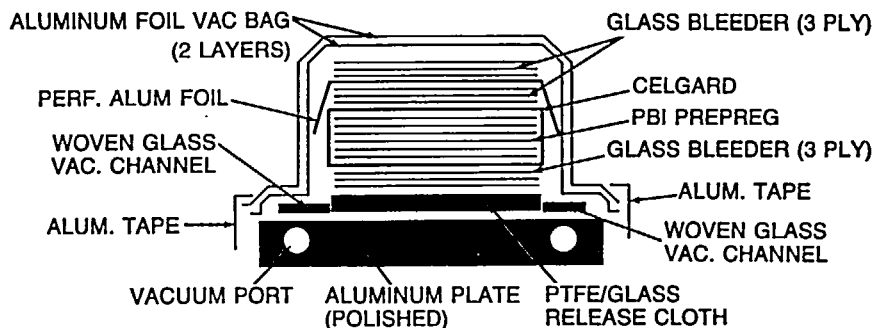


Figure 10. Layup for PBI matrix resin prepregs in compression molding.

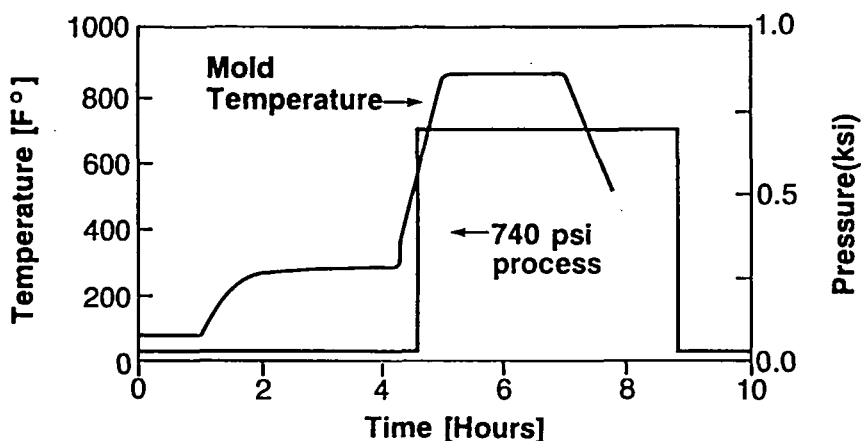


Figure 11. Hoechst Celanese PBI matrix resin prepreg molding conditions.

materials are commercially available from YLA Inc. of Concord, California, USA. Processing can be accomplished by compression molding, autoclave processing, filament winding and Thermo-claveTM techniques. The preform fabrication and curing process is well established. The PBI matrix prepreg layup and conditions for compression molding are shown in Figures 10 and 11, respectively.

PBI composites offer the same high temperature performance that other forms of PBI exhibit. These properties, coupled with the structural property enhancements expected from continuous fiber reinforcement, make PBI attractive for high temperature structural and ablative applications. Typical physical properties of PBI matrix laminates are shown in Table 7. Table 8 shows the excellent strength retention at high temperature of PBI matrix resin/Celion G30-500 8HS, 35% resin content, six-ply laminates [11].

Table 7. Typical Composite Laminate Properties

Density (g/cm ³)	Flexural		Tensile		SBS
	Strength (ksi)	Modulus (Msi)	Strength (ksi)	Modulus (Msi)	Strength (ksi)
1.5	130	7-9	100	9-10	7-10

Note: all CelionTM G30-500, 3 K, 8 harness satin.

Table 8. Properties of PBI/Graphite Composite Panels after High Temperature Exposure

Temperature (°F/°C)	Test/dwell	Flexural strength (ksi)	Flexural modulus (Msi)	Shear strength (ksi)
77/25	—	125	6.5	8.4
550/288	Hot/15 min	110	6.4	8.3
700/371	Hot/15 min	95	6.2	7.1
1300/704	Cold/5 min	20	4.3	2.1
1800/982	Cold/5 min	8	2.8	1.0

PBI resin is under evaluation for a variety of high performance end-uses where high specific strength and ultra-high temperature stability is a requirement. Aerospace applications include tactical missile structures, e.g. nose cones, radomes, fins, nozzles and casings. Additional applications are high speed projectiles, aircraft brake assemblies and radiation-resistant structures.

5. PBI AS A MATRIX RESIN PRECURSOR FOR CARBON/CARBON COMPOSITES

The attributes of PBI that make it an intriguing candidate as a precursor resin in carbon/carbon composites have been known for over 20 years. Efforts in this direction were hampered due to processing difficulties. However, with the demonstrated viability of PBI as a matrix resin just described, it is a natural extension to investigate these composites as precursors for carbon/carbon composites.

The chemically inherent characteristics of PBI give it excellent potential as a carbon matrix precursor. PBI has a very high carbon content of 78% and a carbon or char yield of 75%, and so has a pyrolysis efficiency of 95%. Therefore, during pyrolysis minimal polymeric carbon is released and the matrix remains dimensionally stable. Additionally, PBI is fully aromatic and has a high molecular weight, and therefore graphitizes easily. In fact, work at Celanese in the 1970s showed that PBI fiber could be rapidly converted to graphitic fiber [12]. X-ray diffraction results indicate that graphitized PBI is highly oriented and essentially pure carbon.



Figure 12. Microstructures of densified composite.

Microscopic examination of carbonized laminates show periodic microcracks which traverse the fiber bundles (Figure 12). These microcracks offer an avenue for impregnation with additional matrix and appear similar to microcracks observed in phenolic laminates. Furthermore, polarized light microscopy indicates that PBI has a

greater affinity for graphitization than do phenolics. Physical testing of twice reimpregnated/carbonized (i.e. heated in N₂ to 815°C (1499°F)) laminates show flex strengths similar to phenolics, low porosity, <4% and density of >1.6 g/cm³. See Table 9 for details.

Table 9. Properties of Densified T-300/PBI Composite Panel

	Density	Flexural strength (ksi)	Open porosity (%)
As-cured	1.5	33	<5
First carbonization*	1.46	9	17
CVI carbon	1.54	29	8
Reimpregnation with Code 88A	1.60	43	4

*Note: carbonization done at 815°C (1499°F).

Our preliminary results indicate a significant potential for PBI/carbon fiber composites as precursors for carbon/carbon composites both in structural and ablative capacities. With a commercial facility already on line, PBI is an attractive alternative to low char yield phenolics and other 'developmental' high char resins.

6. CONCLUSIONS

While PBI has been known for 25 years, from a development point of view it is still a new polymer. The above work, conducted at Hoechst Celanese, has demonstrated that processing of 'brick dusts' is not only possible, but commercially useful, and intriguing new developments in the applications arena can be expected in the years to come.

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