Properties of Fabricated Poly-*p*-phenylene

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Synopsis

Mechanical properties of fabricated poly-*p*-phenylene (PB) parts are compared to those of commercial polyimide. PB showed excellent retention of strength and stiffness at high temperature. Results of environmental exposure and properties of some PB composites are included. In general, PB parts have properties between those of commercial polyimide and carbon graphite.

INTRODUCTION

Fabrication of poly-*p*-phenylene (PB) by powder-forming techniques has been described.[1] In this paper, we compare PB sintered parts with those of a commercially available polyimide (SP-1). Emphasis has been placed on environmental testing at elevated temperatures. Properties of some PB composites and literature data on fabricated graphite parts are discussed. Properties of molded, unsintered PB parts have been reviewed.[2]

EXPERIMENTAL

General Property Comparison

A general comparison of properties reported for carbon graphite and SP-1 with those we measured for fabricated PB (Table I) shows that PB has properties that fall between these competitive materials. Strength, modulus, elongation at break, and coefficient of friction (air) of PB fall at intermediate values, while PB has a lower density. The modulus of PB parts can be raised by forming composites (Table II), but this lowers strength and elongation and increases density. Also, the inherent lubricities of the composite components may conflict; we measured a coefficient of friction of the 85 PB/15 graphite composite of 0.17 μF (28,500 PV, air).

High-Temperature Properties

Since PB has no known T_g or T_m, we were especially interested in measuring mechanical properties at unusually high temperatures. Flexural modulus (Fig. 1) and strength (Fig. 2) were determined on nonstandard "matchsticks" between room temperature and 800°C. Retention of half the strength at >650° and half the modulus at >800° is unusual for linear polymers. We were able to measure strength in tension on microtensile bars (nonstandard ASTM D1708), and powder-metallurgy bars (standard ASTM E8) as high as 500° and 316°, respectively (Fig. 3). Retention of tensile strength is consistent with the

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TABLE I
Properties of Graphite, Poly-*p*-phenylene, and SP-1 Polyimide[a]

Property	Carbon graphite[b]	PB	SP-1[c]
Tensile Strength			
MPa	5–32	35	91
psi	700–4500	5000	13,000
Elongation at break,			
%	0.07–0.21	1.4	7–9
Flexural modulus			
MPa	3,700–19,700	3900	3200
kpsi	530–2800	555	450
Apparent density, g/cc	1.51–1.93	1.1–1.2	1.43
Notched Izod Impact			
cm-kg/cm	very low	1.1–1.4	5.4
ft-lb/in.	very low	0.20–0.25	1.0
Hardness	25–100	24.6; 23.9	45–58
Type	Shore "S"	KHN; Vickers	Rockwell "E"
Coefficient of friction, μF (air)	0.03–0.26	0.08–0.12 (28,000 PV)	0.29 (25,000 PV)

[a] Graphite and SP-1 Polyimide parts were fabricated using techniques similar to those used in forming PB, e.g. direct-forming by compaction followed by free sintering (see ref. 1). The properties for SP-1 reported here are those found (for direct-forming/free-sintering) in the direction perpendicular to the axis of compression.
[b] From reference 3.
[c] From reference 4.

TABLE II
Properties of PB Composites[a]

Weight-% composition	Sintered density, g/cc	Tensile strength, MPa (psi)	Absolute elongation, %	Tensile modulus, MPa (kpsi)
85 PB/15 Graphite[b]	1.26	39 (5600)	0.89	5800 (830)
50 PB/50 Ni[c]	2.13	26 (3700)	0.53	5900 (840)
70 PB/30 Ni[c]	1.64	21 (3000)	0.53	4800 (680)
85 PB/15 Soft glass	1.25	23 (3300)	0.58	5600 (800)
7 PB/1 Al[d] (vol/vol)	1.72	32 (4500)	0.58	9800 (1400)

[a] Composites were prepared by wet mixing powders (ethanol/water), drying, compacting the blends at 420 MPa (30 Tsi), and sintering at 587°/2 hr.
[b] Dixon microfine graphite
[c] Mond 123 nickel.
[d] Reynolds 200 atomized aluminum.

"matchstick" studies. A comparison of PB high-temperature toughness with that of SP-1 polyimide[4] and SP-1/graphite composites[4] (Fig. 4) points out the differences in the various materials. PB retains toughness over a wide range of temperatures but is inherently less tough. The toughness of carbon graphite parts (only 0.004–0.07 MPa-cm/cm, 0.6–10 psi-in./in. at room temperature) would probably be retained at even higher temperatures.

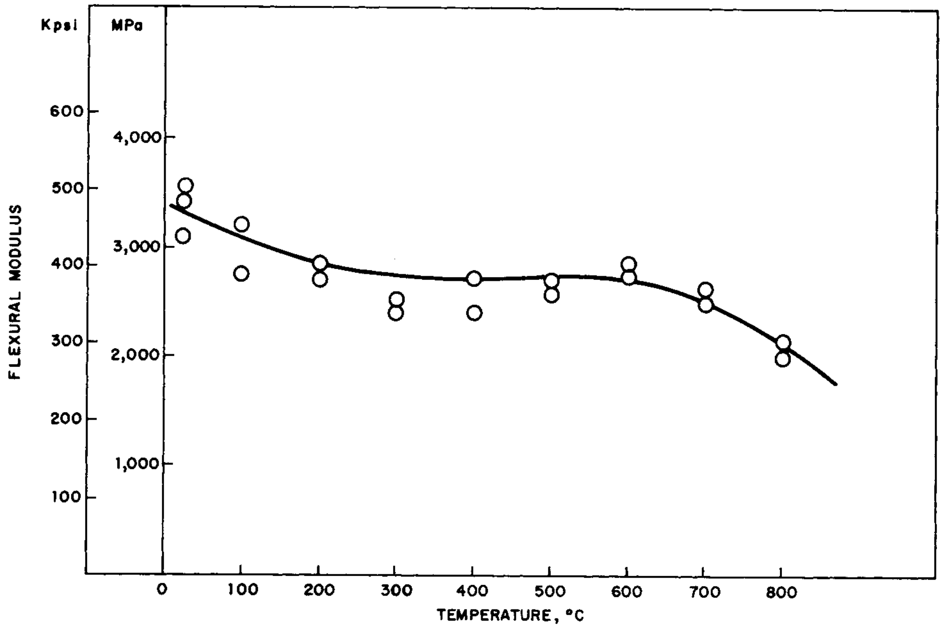

Fig. 1. Variation of flexural modulus with temperature for fabricated poly-*p*-phenylene.

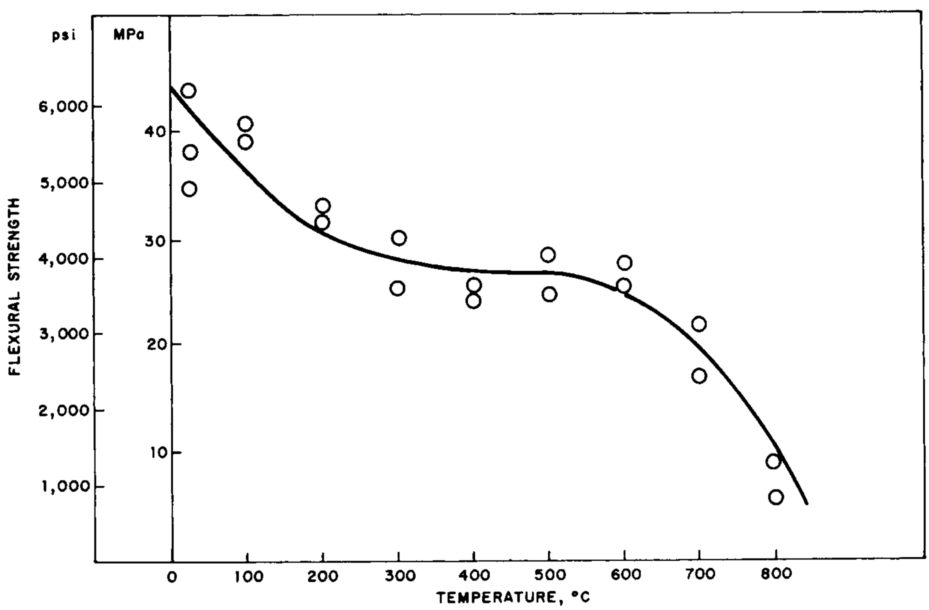

Fig. 2. Variation of flexural strength with temperature for fabricated poly-*p*-phenylene.

Air-Aging Studies

Samples of SP-1 polyimide E8 tensile bars (slightly different properties than reported in Table I because laboratory "direct forming" employed) were compared to PB E8 bars in air-oven aging studies. Properties were measured after aging at both room temperature and at 316°C (Table III). The measurement at 316° did not employ an external extensomer, so that elongations and moduli

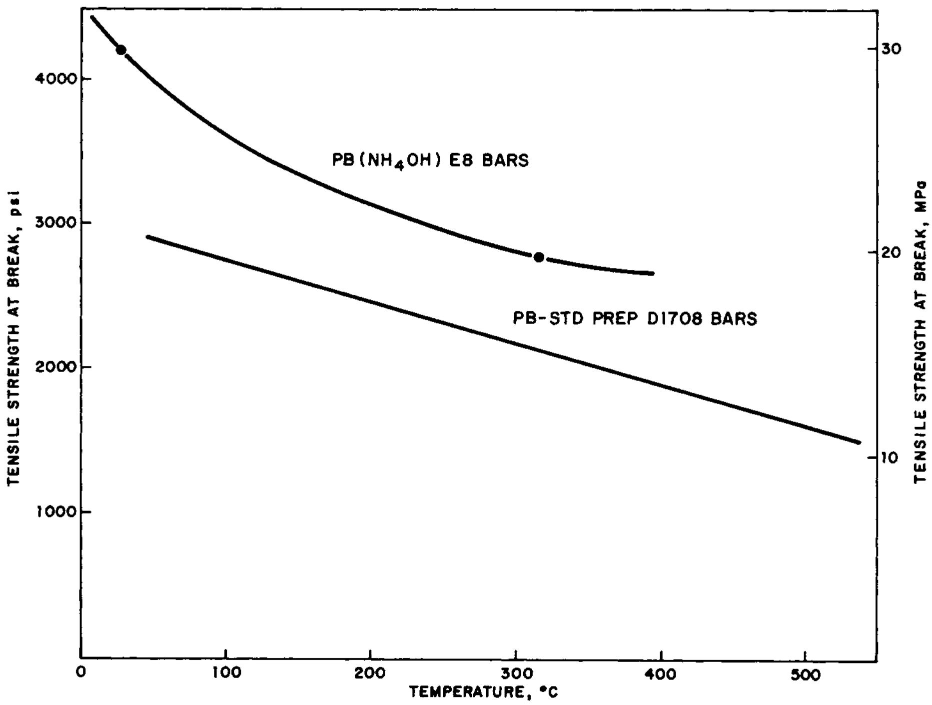

Fig. 3. Tensile strength vs temperature.

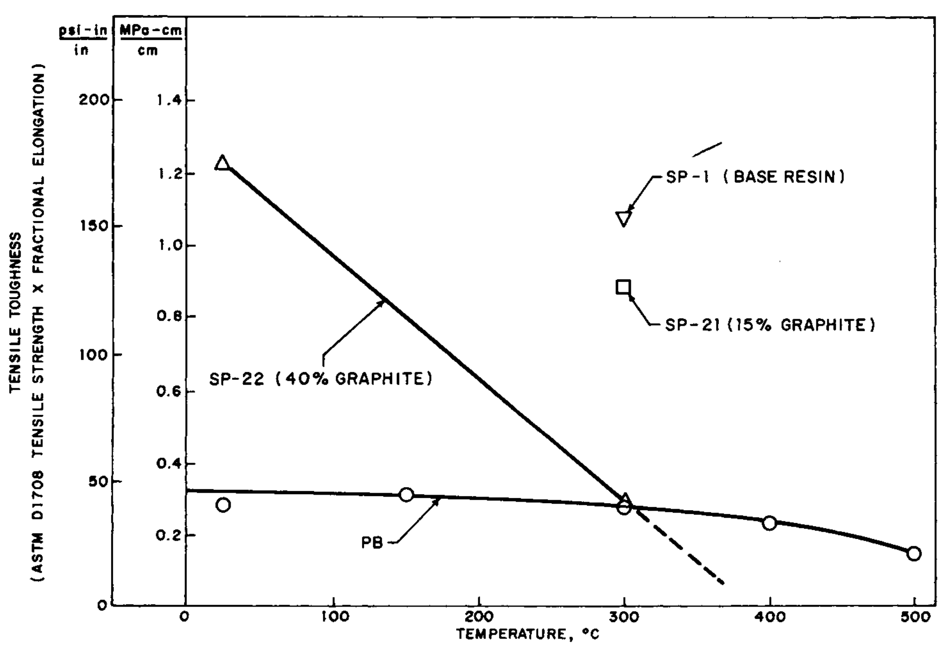

Fig. 4. Tensile toughness vs temperature for fabricated poly-*p*-phenylene, polyimide, and polyimide/graphite.

TABLE III
Air Aging of PB and SP-1 Resins

Resin	Air aging	Measurement temp., °C	Weight loss, %	Tensile strength, MPa (psi)	Elongation, %	Tensile modulus, MPa (kpsi)
SP-1[a,b]	none	RT	none	79 (11,200)[b]	6.5[a]	2,700 (387)[b,e]
SP-1[b]	none	316	none	25 (3,600)	4.1[d]	1,100 (150)[d]
PB[c]	none	RT	none	34 (4,900)	1.3[e]	3,700 (523)[e]
PB[c]	none	316	none	19 (2,700)	1.4[d]	1,800 (250)[d]
SP-1[b]	316°C for 500 hr	RT	2.37	44 (6,300)	1.9[e]	3,300 (473)[e]
SP-1[b]	316°C for 500 hr	316	2.37	18 (2,500)	1.5[d]	1,500 (209)[d]
PB[c]	316°C for 500 hr	RT	5.43	22 (3,100)	0.7[e]	4,100 (587)[e]
PB[c]	316°C for 500 hr	316	5.43	12 (1,600)	0.9[d]	2,000 (278)[d]
SP-1[b]	400°C for 42 hr	RT	3.23	46 (6,500)	1.9[e]	3,300 (467)[e]
SP-1[b]	400°C for 42 hr	316	3.23	11 (1,500)	1.0[d]	1,200 (174)[d]
PB[c]	400°C for 42 hr	RT	9.36	15 (2,100)	0.5[e]	3,700 (529)[e]
PB[c]	400°C for 42 hr	316	9.36	not determined		

[a] Reference 4.
[b] Measured this study.
[c] Powder from $CuCl_2$-$AlCl_3$ prep., further treated with NH_4OH for 8 hr at 275°; compacted at 140 MPa (10 Tsi) and sintered at 590° for 1 hr.
[d] Relative.
[e] Absolute.

TABLE IV
Hydrolytic Stability of PB Objects[a] When Treated with Steam at 260°C

Time treated, hr	Apparent density, g/cc	Tensile strength, MPa (psi)	Absolute elongation, %	Tensile modulus, MPa (kpsi)
Start	1.05 ± 0.05	23 (3,300)	0.94	3,250 (462)
24	1.16 ± 0.04	24 (3,400)	0.89	3,450 (490)
168	1.18 ± 0.06	29 (4,100)	1.11	4,100 (584)
700	1.17 ± 0.06	26 (3,700)	0.94	3,870 (550)

[a] Powder from $CuCl_2$–$AlCl_3$, further treated with NH_4OH for 8 hr at 275°; compacted at 140 MPa (10 Tsi) and sintered at 590° for 1 hr.

are only relative, while data measured at room temperature were standard ASTM E8 and so gave absolute values for elongation and modulus. In general, PB retains properties about as well as SP-1 but has poorer values to start with. Weight loss, surprisingly high for PB, is undoubtedly due to impurities introduced during synthesis,[5] which catalyze oxidation and are not removed on fabrication.[1]

Hydrolytic Stability

Formed E8 tensile bars of PB were heated in an autoclave with saturated steam at 260° for various times. Bars were removed and tensile properties determined at room temperature (Table IV). The increase in apparent density is probably due to water-filling voids. The tensile strength and elongation of SP-1 are reduced to 45% and 35% of their original values after 500 hr in boiling water[4]; no tests were made at 260° as severe hydrolysis is likely to occur for polyimides under these conditions.

CONCLUSIONS

Fabricated PB parts, in general, show properties between those of carbon graphite and polyimide. Retention of properties at high temperature is excellent. Weight loss on high-temperature air aging was higher than expected, but high-temperature hydrolytic stability is outstanding. Properties might be improved if purer sources of PB powder can be developed.

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