

# Tough, Transparent Heat- and Flame-Resistant Thermoplastics via Silicone Block-Modified Bisphenol Fluorenone Polycarbonate\*

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## Synopsis

Bisphenol fluorenone carbonate-dimethylsiloxane block polymers have been synthesized by interfacial condensation of phosgene with various mixtures of BPF-encapped silicone oligomers and free BPF or its monosodium salt. The multisequence block polymers described here contain 7% to 27% silicone consisting of blocks of number-average degree of polymerization 10 to 40. Cast films are clear and colorless. Two glass temperatures are evident in each resin, one at about  $-100^{\circ}\text{C}$  for the silicone microdomains and one at temperatures as high as  $275^{\circ}\text{C}$  for the polycarbonate matrix. While BPF polycarbonate is brittle, block polymers with as little as 10% silicone yield by shear deformation before breaking. Ultimate elongations are increased by preorientation at silicone contents above 15%. At temperatures far removed from BPF carbonate domain  $T_g$ 's, both modulus and yield stress decrease with increasing silicone content, independent of block length, in a manner rationalized quantitatively by hard phase-soft phase continuum models. Ultimate tensile elongation, impact toughness, and plane strain stress intensity factors increase with silicone content, through a stress whitening mechanism. At higher silicone contents, shear deformation enhances tensile elongation and impact toughness. Heat distortion temperatures of  $200^{\circ}\text{C}$  or more are achieved. Flame resistance exceeds that of any known nonhalogenated resin. The resins are extrudable and injection moldable with only minor changes in color, transparency, and strength properties. Resins with 15% to 20% silicone can have a balance of properties that makes them attractive as tough, transparent heat- and flame-resistant engineering plastics.

## INTRODUCTION

Current aircraft canopies are limited to use at ambient temperatures less than about  $125^{\circ}\text{C}$ . The basic source of this limitation is the thermomechanical behavior of the sheet material. This behavior reflects primarily the glass temperature of the resin involved— $100^{\circ}\text{C}$  in the case of poly(methyl methacrylate) and  $150^{\circ}\text{C}$  in the case of the polycarbonate of bisphenol acetone. The use of other higher temperature resins available on a commercial or developmental basis has been ruled out due to failure in each case to meet one or more of the various requirements, color, UV resistance, toughness, and ease of fabrication. Thus,

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almost all crystalline plastics have poor clarity. And generally, glassy polymers having  $T_g$ 's higher than that of BPA polycarbonate are too brittle.

This paper deals with the development of a family of transparent thermoplastics having sufficient heat resistance *and* toughness to meet many advanced canopy applications. In addition, the flammability characteristics of these resins suggest their attractiveness for uses where flame resistance and low smoke production are important characteristics.

Technically, the impetus for this work came from the aforesaid knowledge of the brittleness limitations of high temperature glassy plastics and the discovery of the effect on impact toughness of BPA polycarbonate of the introduction of short dimethylsiloxane blocks.<sup>1,2</sup> These multisequence block copolymers contain microdomains of silicone blocks and of polycarbonate blocks. Two  $T_g$ 's are evident, one for the silicone domains in the neighborhood of  $-100^\circ\text{C}$  and one for the polycarbonate domains at temperatures somewhat below the  $T_g$  of high molecular weight homopolycarbonate.<sup>3</sup> When made properly, these resins are all as clear as BPA polycarbonate itself. Although poly(dimethylsiloxane) and BPA polycarbonate have different refractive indices, the small sizes of the silicone blocks result in silicone domains that are much too small (e.g., 40 Å) to cause appreciable light scattering. The stiffness and strength of these resins decrease with increasing silicone content; at 25% silicone, for example, these are reduced by 50% from the corresponding quantities for the homopolymer. While  $\frac{1}{8}$ -in.-thick BPA polycarbonate exhibits an abrupt ductile-brittle transition in notched Izod impact toughness at about  $-10^\circ\text{C}$ , the 25% silicone block polymer remains very tough down to  $-105^\circ\text{C}$ . Thus, the considerably increased low temperature toughness in this resin suggested that silicone block introduction into high  $T_g$  resins that are brittle at room temperature might augment their toughness considerably without damaging clarity or heat resistance severely.

The polycarbonate of bisphenol fluorenone (BPF) can be made by rather standard condensation polymerizations.<sup>4</sup> It was initially reported to have an exceptionally high  $T_g$ .<sup>4</sup> The lack of aliphatic hydrogens in the homopolymer was expected to confer good thermal and thermo-oxidative stability up to about  $420^\circ\text{C}$  where  $\text{CO}_2$  evolution begins (*vide infra*). The similarity of the polymerization chemistry to that for BPA polycarbonate made the formation of the BPF carbonate silicone block polymers appear feasible using chemistry similar to that for the corresponding BPA block polymers.

## RESIN SYNTHESIS AND ISOLATION

In the course of this program, we have synthesized high molecular weight BPF polycarbonate and BPF carbonate-silicone block polymers of a range of silicone contents.<sup>5,6</sup> Silicone block lengths have ranged from 10 to 30 on a number-average basis. The synthesis is an interfacial copolycondensation of phosgene with BPF admixed with a preformed siloxane oligomer each end of which is capped with BPF. The reaction is carried out in a mixture of chloroform and aqueous caustic at pH 9.7. Following neutralization and washing, the polymer is precipitated by pouring the chloroform layer into an excess of a nonsolvent. Although 5% of the BPF is converted to BPF carbonate cyclic side products during the reaction, this unwanted material is left behind in solution if the proper nonsolvent is used in the precipitation (e.g., acetone).

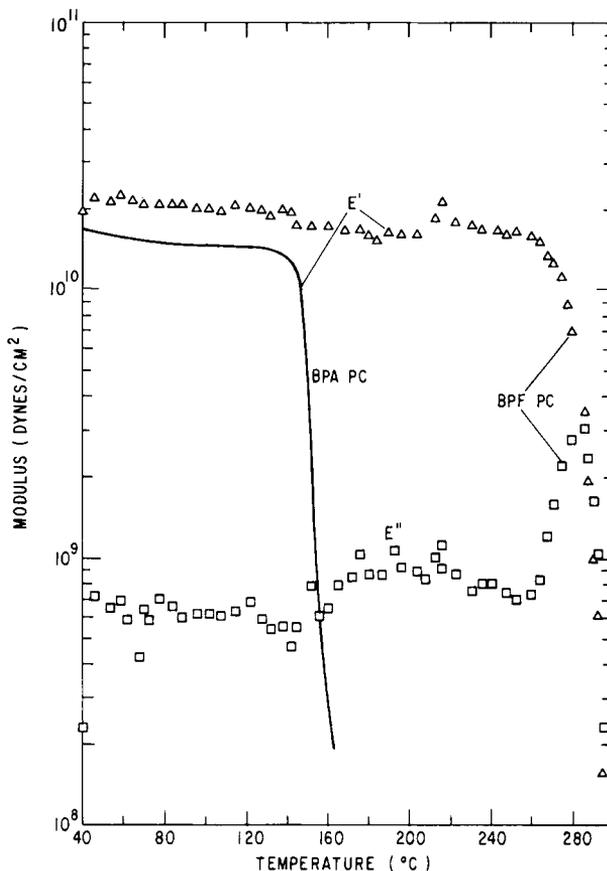


Fig. 1. Temperature dependence of dynamic storage  $E'$  and loss moduli  $E''$  at 110 Hz for BPF polycarbonate.

Intrinsic viscosities of the resins produced have ranged as high as 2.0 dl/g. Values of 0.7 dl/g appear to be sufficient, however, to achieve maximum strengths and elongations. At this viscosity, osmotic molecular weights of polymers containing less than 25% silicone are in the range of 25,000 to 40,000.

Resin synthesis was scaled up in three stages from 10 g to 3 lb per run with a 90% yield. The large resin batches were redissolved in chloroform after isolation and then steam precipitated; the granular product had a rather uniform particle size (e.g., 2 mm) which aids substantially in controlling melt extrusion. Three-lb runs were routinely made, cleaned up, steam precipitated, and dried at the rate of one batch per man week. Films cast from these resins had excellent clarity and barely detectable color by visual inspection.

### VISCOELASTIC BEHAVIOR

The viscoelastic behavior of the BPF and BPA block polymer families are very similar except for two basic factors: First, the  $T_g$  of BPF polycarbonate is 275°C compared to 150°C for the BPA analog (Fig. 1); second, the elastic modulus of the first is 410,000 psi compared to 340,000 psi for the latter (Fig. 2). Related differences are seen in the block polymers.

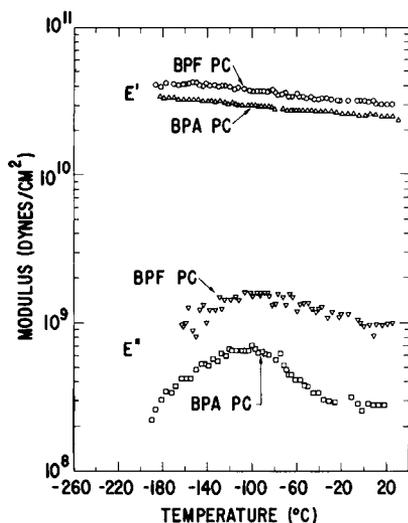


Fig. 2. Temperature dependence of  $E'$  and  $E''$  at 110 Hz for BPA polycarbonate and BPF polycarbonate.

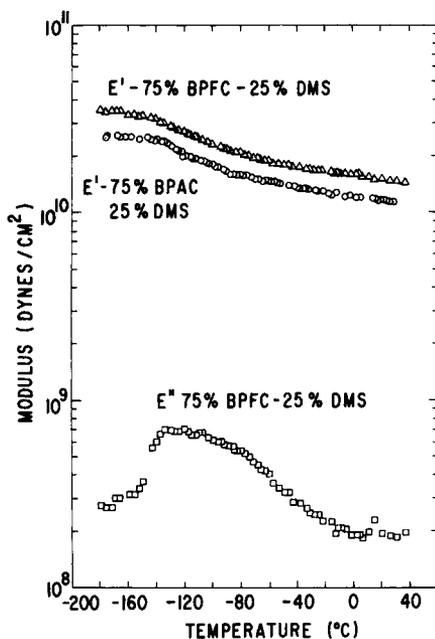


Fig. 3. Plot of  $E'$  and  $E''$  at 110 Hz and low temperatures for one BPF carbonate-silicone block polymer.  $E'$  for BPA carbonate-silicone block polymer of same wt-% silicone shown for comparison.

Each homopolymer exhibits a broad  $\beta$  relaxation that is centered at roughly  $-100^\circ\text{C}$  at 110 Hz (Fig. 2). Each silicone block polymer exhibits additional relaxation in the same temperature range due to the glass-to-rubber relaxation of the silicone domains. For resins of 15% silicone or more, this relaxation is stronger than the polycarbonate  $\beta$  relaxation (Fig. 3).

At elevated temperatures, block polymers of the same polycarbonate content differ significantly in terms of the temperatures of their polycarbonate domain

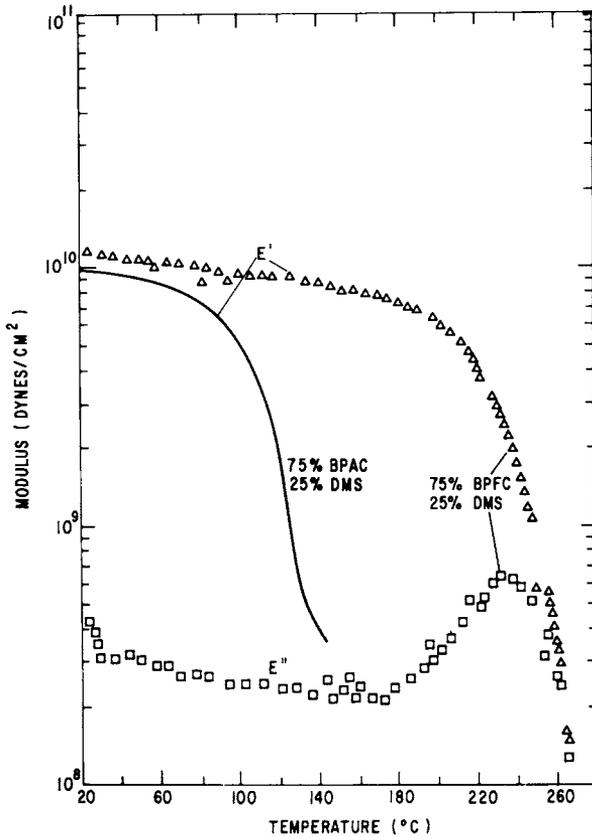


Fig. 4. Plot of  $E'$  and  $E''$  at 110 Hz and high temperatures. Same block polymers as in Fig. 3.

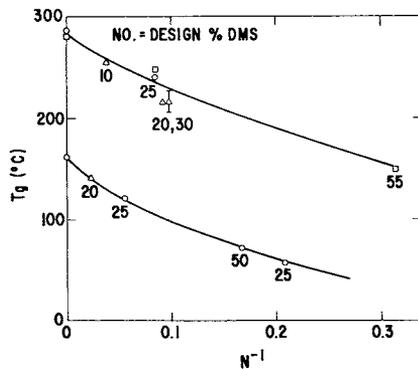


Fig. 5. Dependence of polycarbonate domain  $T_g$  on reciprocal number-average degree of polymerization  $N^{-1}$  of polycarbonate block. Upper line: BPFC-silicone family. Lower line: BPAC-silicone family. Circles: dynamic mechanical  $E''$  or middle of  $E'$  dispersion. Squares: differential scanning calorimetry. Triangles: TOA thermo-optical analysis.<sup>14</sup>

$\alpha$  relaxations (Fig. 4). When the two families of resins are compared on the basis of polycarbonate block degree of polymerization, it is seen that these upper temperature relaxations differ only because the  $T_g$ 's of the homopolymers differ (Fig. 5). The reduction in the temperature of this relaxation with decreasing

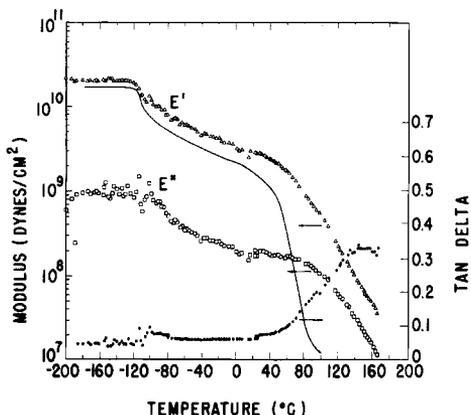


Fig. 6. Temperature dependence of  $E'$ ,  $E''$ , and  $\tan \delta$  for block polymer designed to be: 45% BPF carbonate (3.9 units/block)–55% silicone (20 units/block). Solid line: storage modulus of 50% BPA carbonate (6 units/block)–50% silicone (20 units/block).

block length is attributed<sup>3</sup> to a block junction concentration effect analogous to the chain end effect seen in the  $T_g$ 's of homopolymers: the ends of each polycarbonate block appear to possess essentially the same degree of mobility as possessed by the ends of a homopolymer molecule due to the fact that the molecular mobility of the attached silicone moieties is so high.

The upper relaxations of BPA and BPF block polymers of the same *weight* or *volume fraction* polycarbonate and the same silicone block length differ by a lesser amount (Fig. 6) because the degrees of polymerization of their respective polycarbonate blocks differ (in turn due to the different bisphenol carbonate molecular weights—376 vs. 254).

At intermediate temperatures where the silicone domains are rubbery, elastic moduli vary with BPF carbonate content in a way that can be rationalized in terms of hard phase–soft phase continuum models.<sup>7–12</sup> Thus, resins of about 50% BPF carbonate are leathery at room temperature (Fig. 6), while those of about 35% BPF polycarbonate are thermoplastic elastomers. Resins useful as engineering thermoplastics should have moduli of about 250,000 psi or more. This requirement restricts the amount of silicone that can be usefully incorporated in the BPF carbonate plastics to about 22% (*vide infra*).

## ULTIMATE TENSILE PROPERTIES OF CAST FILMS

Thoroughly dried cast films of BPF polycarbonate craze and then fracture in a brittle manner at 11,000–12,000 psi. The material is brittle enough that compression moldings made in unlubricated steel dies fracture during cooling. The homopolymer is ductile in low-speed tensile tests only at temperatures above 235°C (Fig. 7). Cast films containing residual chloroform (the casting solvent) fail in a ductile manner. Extrapolation of yield stresses of cast films to zero residual solvent gives a yield stress of 14,000 psi for the thoroughly dry polymer at 25°C.

Cast films of resins containing from 8–9% to 27% silicone are ductile from room temperature upward, although they break almost immediately upon neck formation. Yield stresses are dependent on temperature in the same way, quali-

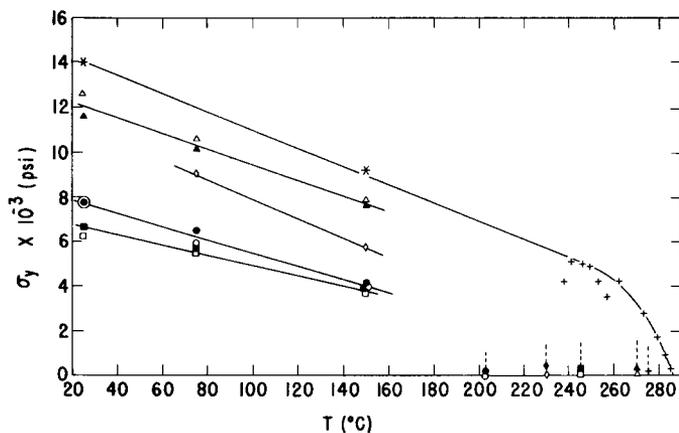


Fig. 7. Temperature dependence of yield stress for several resins + BPF polycarbonate molded bars. Asterisks: BPFPC films (value at 25°C extrapolated from values of films containing residual casting solvent). Circles: 23% silicone, 14.3 unit silicone block length. Triangles: 7% silicone, 8 unit silicone block length. Diamonds: 16% silicone, 8 unit silicone block length. Squares: 27% silicone, 23.5 unit silicone block length. Dashed vertical lines at right indicate corresponding polycarbonate domain  $T_g$ 's.

tatively as is that for the homopolycarbonate (Fig. 7). Yield stresses at a given temperature, in the range well below the range of polycarbonate domain  $T_g$ 's, are dependent only the silicone content of the resin essentially. The actual dependence can be rationalized by assuming that the only effect of the silicone domains is to cause stress concentrations on the microscopic level, the polycarbonate domains responding to local stress in a way unchanged from the way the homopolycarbonate responds to stress on a macroscopic level. Thus, the reduction in yield stress with silicone incorporation is predictable from the same hard phase-soft phase continuum models that rationalize the dependence of modulus on silicone content. In Figure 8, yield stresses of various resins obtained at 25° and 75°C are plotted versus silicone content. The solid lines are generated from the Halpin-Tsai equation for the modulus of a hard continuum phase containing spherical inclusions of negligible modulus.<sup>7,8</sup> The yield stress of the homopolymer at the particular temperature of test is the only experimental parameter used, and there are no adjustable parameters in the original equation.

The neck is a zone of shear deformation essentially, although some stress whitening is evident therein. Plastic strain in the neck, as determined from post-test measurements of the cross-sectional area in the neck, is about 80%—similar to that in BPA polycarbonate. In the BPF block polymers, however, fracture occurs at a total specimen elongation of 9% to 13% or so, independent of silicone content or block length. (By contrast, the corresponding BPA family sustains specimen elongations above 100%.) The fracture initiates in the middle of the neck generally.

Hot stretching can have a marked effect on subsequent tensile elongation. Thus, films of several resins including the homopolymer were subjected to dead loading for different lengths of time at temperatures slightly above their respective polycarbonate  $T_g$ 's. At the appointed times the film jigs were removed from the air ovens in order that the films cool quickly while under the stretching loads. The degrees of hot elongation attainable by this procedure increased

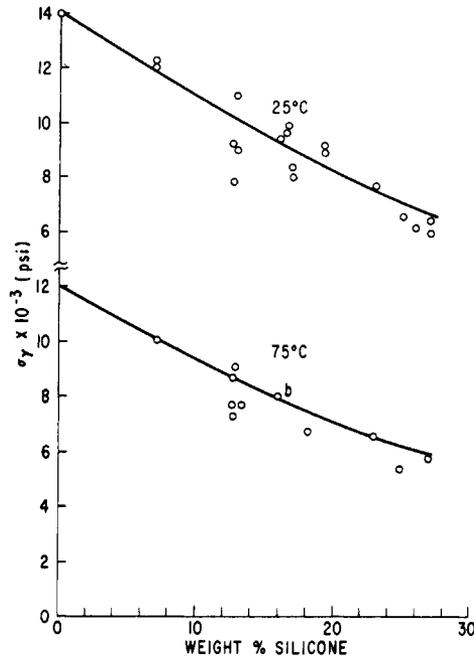


Fig. 8. Dependence of yield stress on silicone contents of several BPFC-silicone block polymers at 23° and 75°C. Solid lines: predictions based on Halpin-Tsai equation for moduli of two-phase composite and experimental yield stresses of homopolycarbonate.

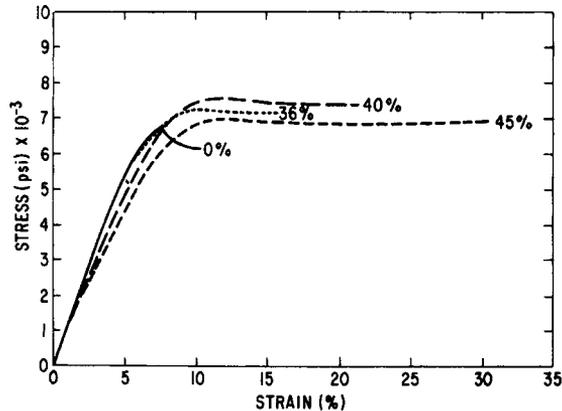


Fig. 9. Room-temperature stress-strain curves for BPFC-silicone block polymer of 25% silicone, 35.8 unit silicone block length.

substantially with silicone content, the homopolycarbonate being completely refractory in this regard while a resin of 25 wt-% silicone was drawn to elongations as high as 45%. In subsequent room temperature tensile tests (Fig. 9), specimens were found to elongate more the greater the degree of hot stretching. Although the yield stress of the preoriented films was somewhat higher, the plastic strain in the neck was substantially reduced and the stress whitening and crazing eliminated entirely. Thus, preorientation reduces true stress in the neck by increasing cross-sectional area and also eliminates potential sites of crack initi-

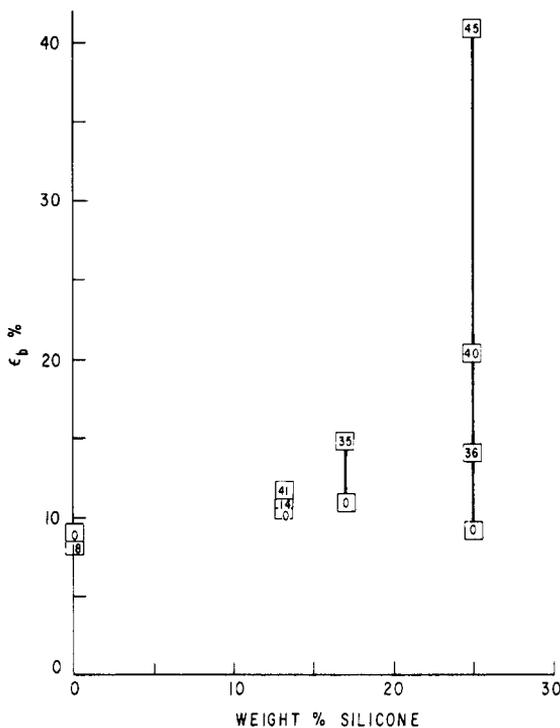


Fig. 10. Ultimate elongation  $\epsilon_b$  at 23°C vs. silicone content of films hot stretched to the percentages indicated in the data symbols.

ation. One or both of these changes appears responsible for the substantial increases in neck stability, fraction of test section drawn out, and thus total elongation.

On the basis of limited experimentation, it appears that both the ability to hot stretch successfully to a given elongation and the effectiveness of a given degree of hot stretching in increasing ultimate elongation in subsequent room-temperature tensile tests increase with silicone content. In Figure 10, average ultimate elongation is displayed versus silicone content: the number inside each datum square is the percent hot stretch in the specimens giving that elongation. Only above 15% silicone do the elongations begin to be susceptible to improvement by this process.

### MODULUS, FRACTURE TOUGHNESS, AND NOTCHED IMPACT STRENGTH

Three kinds of toughness measurements have been made using sections of extrudate and injection-molded specimens, all  $\frac{1}{8}$ -in thick. First, standard notched Izod tests have been conducted. Second, the plane strain-stress intensity factor  $K_{Ic}$  has been determined using single-edge notch,  $\frac{1}{2}$ -in.-wide specimens. Third, a ball impact puncture test that gives puncture energies has been used (section below).

In each  $K_{Ic}$  specimen, a small cut was sawn into the side and a crack induced at the base of the cut by fatigue flexing. The specimens were then pin loaded

to failure. Because the length  $a$  of the crack constituted a significant fraction of the specimen width  $w$ , the stress intensity factor was calculated as<sup>13</sup>

$$K_{Ic} = \sigma_b a^{1/2} \left[ 7.59 - 32 \frac{a}{w} + 117 \frac{a^2}{w^2} \right] \quad (1)$$

where  $\sigma_b$  is the breaking stress. Strain energy release rates were also calculated as

$$G_{Ic} = K_{Ic}^2/E \quad (2)$$

where  $E$  is the elastic modulus. Elastic moduli were measured in 3-point flexure according to ASTM test D790 on the same specimens prior to notching.

Whereas BPF polycarbonate fracture surfaces are clear and smooth, copolymers containing as little as 8% or 9% silicone show stress whitening, presumably due to a cavitation process like crazing. The extent of whitening is greater at 15% than at 10% silicone, but changes little with increasing silicone content thereafter. No evidence of shear deformation was apparent in these specimens. In tensile tests, however, a measure of necking can be seen above 10% silicone; shear deformation increases extensively only above 20% silicone, however.

In Figure 11, several mechanical properties are displayed versus silicone content. Modulus is reduced to 250,000 psi, the approximate limit for an engineering material by about 20% silicone incorporation. Over the range of 10% to 20% silicone  $K_{Ic}$ , notched Izod impact energy and ultimate tensile elongation are essentially constant. Nominal tensile elongation is constant in this range and only begins to rise rapidly at silicone contents above 20%.

Two conclusions can be inferred from Figure 11 and associated failure morphologies. First, a silicone content of 15% appears to be optimum: toughness is as good as that of stretched acrylic and modulus is acceptable at this point, while the increase in silicone content necessary to bring any increase in ductility from that at this silicone level is great enough to reduce modulus below the acceptable level.

Second, there are three failure regimes evident: (a) homopolycarbonate is highly brittle, failure occurring in a manner superficially reminiscent of "crystal" polystyrene, and the same is probably true of all resins having much less than 7–8% silicone; (b) a first regime of toughness exists between about 8% and 20% silicone in which the function of the silicone is simply that of inducing stress whitening, which we infer to be a crazing phenomenon; (c) a second regime of toughness begins at 20% silicone more or less (depending on stress configuration) that involves the onset of shear flow in addition to stress whitening.

### BALL IMPACT PUNCTURE ENERGIES

These regimes of ductility are also evident in ball impact puncture tests on injection-molded square  $2\frac{1}{2}$  in.  $\times$   $2\frac{1}{2}$  in. in area by  $\frac{1}{8}$ -in. thick. The test used consisted of driving a ram at constant rate through a plaque mounted in a holder on a load cell. The best machine was an MTS closed loop hydraulic tester. The ram used was a steel cylinder 2 cm in diameter with a hemispherical head of the same diameter. The ram was driven at 6000 in./min through the plaque to a fixed depth (1 in.) below the bottom surface of the plaque each time. The hole edge had a radius of 0.001 in. Force displacement data were recorded via a Nicollet

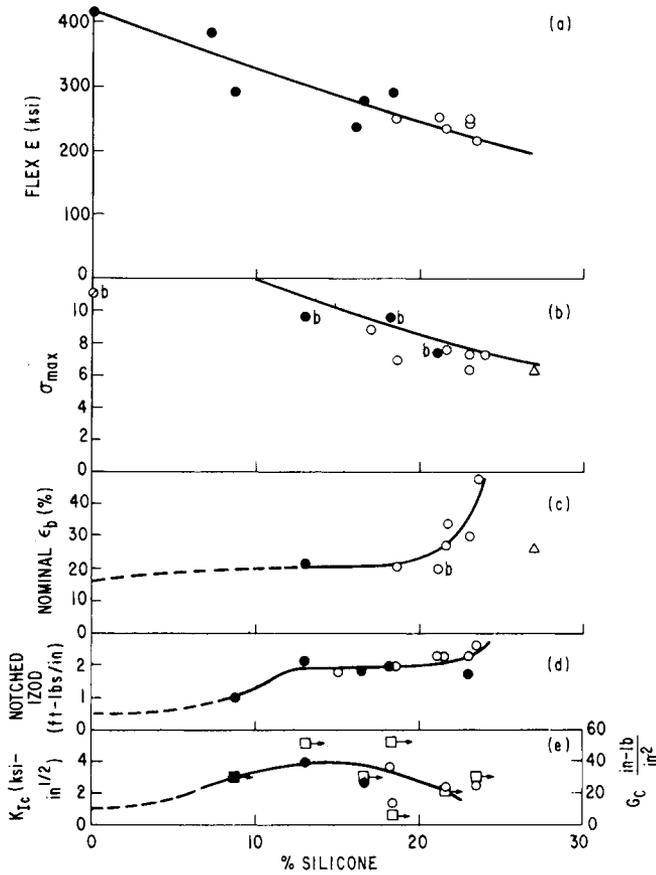


Fig. 11. Dependence on silicone content of several room-temperature mechanical properties of molding and extrudates of BPF polycarbonate and its block polymers. (a) Flex modulus; line: Halpin-Tsai equation. (b) Yield stress; line: Halpin-Tsai equation. (c) Nominal ultimate elongation (exceeds gauge elongation by 10% to 15% due to shoulder effects). (d) Notched Izod impact energy. (e) Stress intensity factor  $K_{Ic}$  and strain energy release rate  $G_{Ic}$ . (●) Compression molding; (○) bar extrudate; (△) ribbon extrudate with longer gauge section; (□→)  $G_{Ic}$  datum corresponding to  $K_{Ic}$  value at same silicone content; (b) brittle failure.

digital oscilloscope and integrated appropriately to yield impact puncture energies. Thus, like the Izod test but unlike the Gardner dropping ball test, this procedure gives a failure energy for each specimen tested.

This test was conducted on four block polymers and also specimens of Acrylite poly(methyl methacrylate) and Lexan BPA polycarbonate for reference purposes. Puncture energies (Table I) ranged from 2.4 ft-lb for PMMA to 126 ft-lb for BPA polycarbonate. The BPF block polymers gave energies from 5 ft-lb at 18% to 26 ft-lb at 23% silicone. These energies varied also with the quality of the molding used. The failures were completely brittle (2–5 ft-lb) to semibrittle with stress whitening (~10 ft-lb) to largely ductile with a little stress whitening (26 ft-lb) to completely ductile with no stress whitening (125 ft-lb). Force displacement traces and associated failure morphologies for these four types of failure are shown in Figure 12.

Impact energy and fracture morphology also varied from specimen to specimen

TABLE I  
Ball Impact Puncture Energies on  $1/8$ -in. Plaques<sup>a</sup>

Resin	Injection shot no.	Ram speed, in./min	Plaque thickness, in.	Energy, ft-lb
10053-129B-3	23	6000	0.126	6.82
(24% Silicone)	24	6000	0.128	6.07
10053-132C	60	6.0	0.125	10.71
(24% Silicone)	64	6000	0.125	10.86
	73	6000	0.137	26.24
10053-136C	49	6000	0.124	8.99
(21% Silicone)	50	6000	0.125	7.96
10053-151	4	6000	0.123	4.73
(18% Silicone)	5	6000	0.122	4.93
PMMA (Acrylite)		6000	0.120	2.38
Lexan BPA polycarbonate	Extruded Sheet	6000	0.126	125.9

<sup>a</sup> Ram driven 1.0 in. below position of lower face of plaque each time at rate listed above. Punch: 2 cm diam. with hemispherical nose. Hole in support plate: 4 cm diam.

of a given block polymer, depending on molding conditions. Thus, for the resin of 23% silicone, a relatively low melt temperature gave 10 ft-lb while a higher temperature gave 26 ft-lb. The lower temperature conditions appear to result in poor knitting of skin and core of the plaque, and delamination of these occurs on impact.

These differences in molding quality reflect the very limited amounts of material available for perfecting molding conditions so far. We expect that larger amounts of resin would enable further optimization of molding conditions and bring about higher impact puncture energies generally.

### TEMPERATURE RESISTANCE OF EXTRUDATES AND MOLDINGS

While the modulus, strength, and toughness at low temperatures depend primarily on silicone content independent of block length, the heat resistance depends primarily on the softening temperature of the polycarbonate domain. This temperature is in turn dependent on the BPF polycarbonate block length and independent of silicone content.

Yield stress and ultimate elongation of several melt-processed block polymers have been determined versus temperature to 200°C or above. Yield stress shows the same temperature dependence as for cast films of similar silicone contents and block lengths. For several resins of 15% to 24% silicone, yield stress is 2000 psi or greater at 200°C (Fig. 13). Although the block lengths of these resins are such as to lead to average polycarbonate  $T_g$ 's of 225° to 250°C, yield stress drops rapidly toward zero at roughly 210°C. Ultimate elongation for these block polymers (Fig. 14) rises gradually from room temperature to 150°C; the temperature dependence increases abruptly at that point. This abrupt change in temperature dependence occurs at a temperature coincident with the onset of the polycarbonate domain  $\alpha$  relaxation, which has a much greater breadth on the temperature scale (Fig. 4) than does that for the high molecular weight ho-

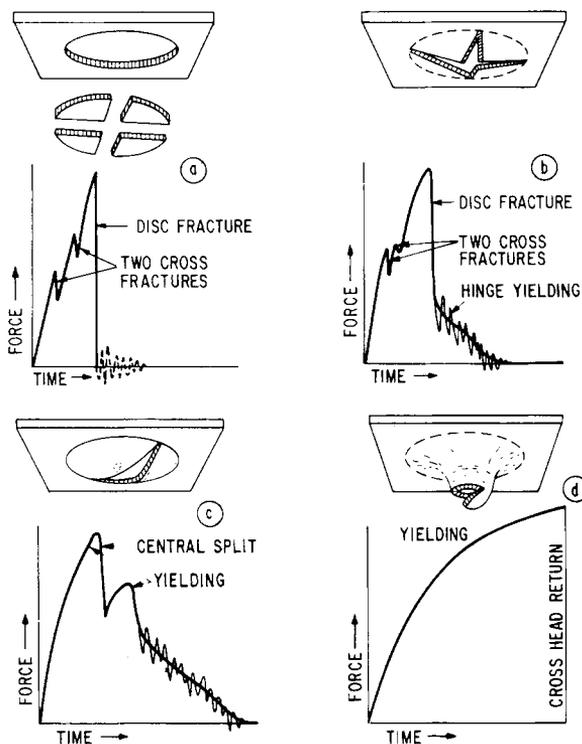


Fig. 12. Ball impact puncture morphologies and associated force-time traces for plastics of varying ductility. (a) Completely "brittle" fracture into four separate quadrants (ca. 2-5 ft-lb). (b) Brittle fracture except for lower surface "hinges" that attach quadrants to disc circumference (ca. 10 ft-lb). (c) Single cross-disk crack with gross shear deformation and some stress whitening (26 ft-lb). (d) Only shear deformation (125 ft-lb). Oscillations at ends of load time trace arise from ringing of load cell washer.

mopolymer (Fig. 1). Part of this great breadth probably arises from the polycarbonate block size distribution; because the synthesis is a polycondensation, the block size distribution should be random roughly. If so, it seems likely that a segregation of blocks into domains of differing average block size occurs: viewed in terms of the  $N^{-1}$  dependence of  $T_g$  (Fig. 5), such a segregation would give rise to a significant dispersion of domain  $T_g$ 's and thus to the spreading out of the  $E''$  versus  $T$  curve. A loss of shear resistance and yield stress for a fraction of the polycarbonate matrix would also be expected at a temperature well below the temperature of the center of the  $E''$  peak. The change in the temperature dependence of ductility at 150°C is therefore attributed to the softening of microregions of the polycarbonate matrix having the lowest values of  $N^{-1}$ .

These results suggest that changes in synthesis procedures leading to broader block length distributions could bring increased ductility at low temperature with little or no sacrifice of heat resistance.

ASTM heat deflection temperatures at 264 psi have also been determined on several melt processed block polymers of 17% to 24% silicone. Results are summarized in Table II. Heat deflection temperatures exceed 200°C except for two resins (129B3 and 129B-5) which had been contaminated during steam precipitation with an organic impurity that we believe acted as a plasticizer.

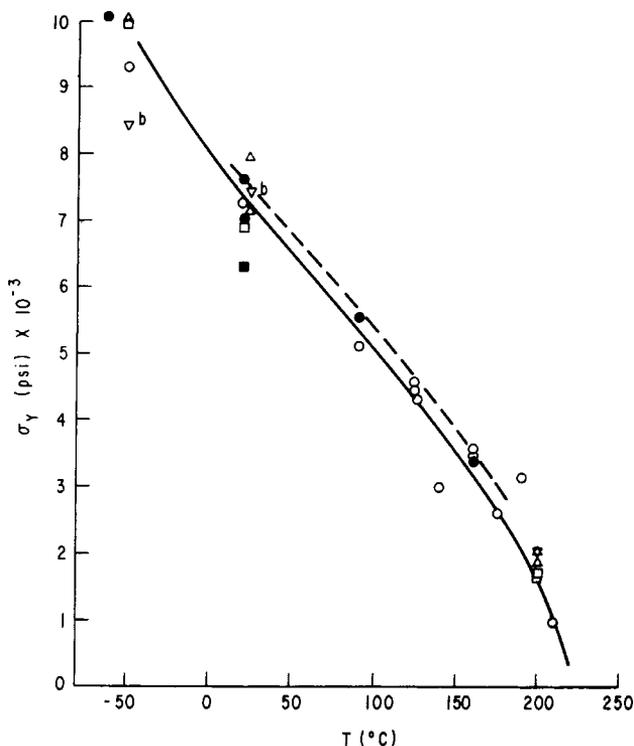


Fig. 13. Tensile yield stress vs. temperature for several BPFc-silicone block polymers, all containing silicone blocks of number-average degree of polymerization 18.8. Silicone contents: (●) 23.0%; (■) 23.8%; (○) 24%; (Δ) 21%; (□) 18.5%; (▽) 21%; (b) brittle failure datum.

## FLAMMABILITY

**Oxygen Index.** The Fennimore-Martin limiting oxygen index (ASTM Test No. D2863-70) has been determined on  $\frac{1}{8}$  in.  $\times$   $\frac{1}{2}$  in.  $\times$   $2\frac{1}{2}$  in. specimens of the homopolycarbonate and four of the block polymers (Table III). Indices for the block polymers are far higher than those of any other transparent nonhalogenated plastic known to us. In this test, all of the BPF resins char rapidly and extensively; little smoke is produced and no dripping occurs.

Curiously, the indices of the block polymers appear to be higher than that of BPF polycarbonate in spite of the fact that homopoly(dimethylsiloxane) has a much lower oxygen index (Table III). The mechanism of this synergism (if indeed it is real) is unclear. However, the mechanism very likely involves the extent of char formation and the ability of the char to insulate the underlying resin. Correlation of residues from thermogravimetric analyses with oxygen index is ambiguous. The difficulty lies in the choice of atmosphere for the TGA run. Thermogravimetric analyses run in air give amounts of black residue at 700°C that appear to increase linearly with silicone content. TGA's run in nitrogen, however, give amounts of residue that decrease gradually with silicone content. Which of these trends is relevant to the oxygen index depends on the oxygen content of the atmosphere at the surface of the OI specimen. Since the burning of organic solids is thought to involve a thermal decomposition and volatilization of the decomposition products the inner part of the oxygen index

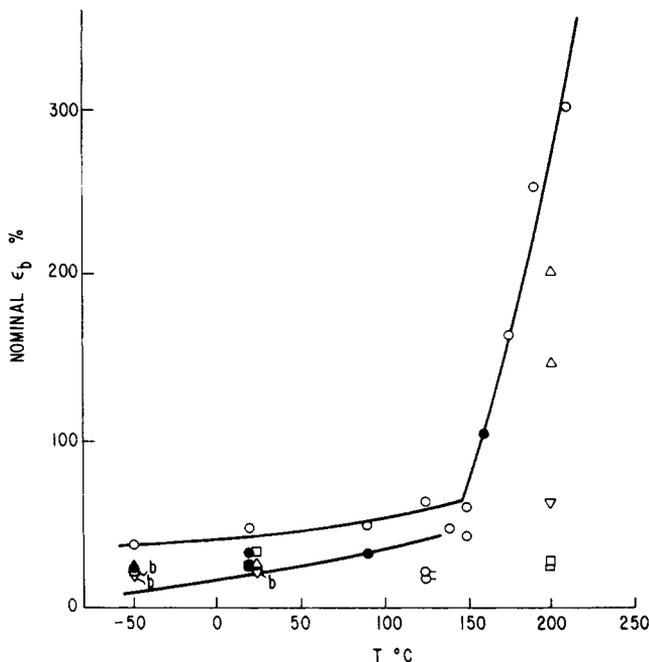


Fig. 14. Nominal ultimate elongation vs. temperature for several extruded block polymers. Nominal elongations exceed gauge elongations by 10% to 15%. Same symbols as in Fig. 13; (O) indicates sections of extrudate that were compression flattened.

test flame should constitute a reducing atmosphere. If true, the TGA's run in nitrogen should be more relevant ones and the tempting positive correlation of air-TGA residue with silicone content irrelevant.

**Flame-out Time.** A test designed to assess the resistance to burning over a flame that arises from another source is as follows. A  $\frac{1}{8}$  in.  $\times$   $\frac{1}{2}$  in.  $\times$   $2\frac{1}{2}$  in. bar of plastic is gripped at one end by tongs and held vertically with the lower end in a Bunsen burner flame. After 10 sec in the flame, it is removed and the time for the flame to extinguish is measured. When the flame is extinguished, the specimen is immediately returned to the flame for another 10 sec, then removed, and the flame-out time again determined. Times are measured with a stopwatch. Any tendency to drip is also noted. The test is like, but not identical to, the U.L. Bulletin 94 test.

Flame-out times are 1 to 3 sec generally for the block polymers, but greater than 30 sec for BPA polycarbonate and poly(methyl methacrylate) (Table III).

TABLE II  
Heat Deflection Temperatures of Injection-Molded Block Polymers by  
ASTM D648 at 264 psi

Resin	Silicone, wt.-%	Temp., °C
10053-129B3	24	187
10053-129B5	23	184
10053-132C	24	208
10053-136C	21 ca.	204
10053-151	18	214
10053-152	21	208

TABLE III  
Flammability Characteristics of BPF Polycarbonate,  
BPF Carbonate-Dimethylsiloxane Block Polymers, and Some Commercial Resins

Resin	Silicone, wt-%	Limiting oxygen index	Burning characteristics in oxygen index test	Residue (TGA 700°C) (air)	Flame-out times, sec <sup>a</sup>	
					1st	2nd
BPF polycarbonate	0	40	rapid charring low smoke no drip	2	—	—
10053-129B	23	48-49	rapid charring low smoke no drip	16.5	2	3
10053-132C	24	49.1-50.2	rapid charring low smoke no drip	17.0	1	3
10053-136C	21	49.8-50.3	rapid charring low smoke no drip	15.5	1	3
10053-151	16	50.3-51.1	rapid charring low smoke no drip	10	1	5
BPA polycarbonate	0	30	little char dripping smoke	0		>30
Poly(methyl- methacrylate)	0	ca. 18		0		>30
Poly(dimethyl- siloxane) (SE-30)	100	ca. 22		11	—	—

<sup>a</sup> Explanation of test: a single  $\frac{1}{8}$  in.  $\times$   $\frac{1}{2}$  in.  $\times$   $2\frac{1}{2}$  in. bar held vertical in Bunsen burner flame for 10 sec and removed; time for flame to extinguish then measured. Specimen returned immediately to flame for 10 sec and removed; time for flame to extinguish measured again.

## MELT PROCESSING

BPF polycarbonate and the silicone block polymers have been compression molded, extruded, and injection molded with varying degrees of success. Compression molding, carried out at 320° to 360°C, has been least successful, particularly with the block polymers. Because of the low degree of melt shear inherent in compression molding and the high melt viscosities of these resins, air bubbles are often entrapped and frequently sections are not well knitted internally.

Extrusion studies have been carried out with a Brabender  $\frac{3}{4}$ -in.-diameter extruder to which dies of various geometries have been attached. One pound of BPF polycarbonate was dried at 125°C overnight and then extruded at 350° to 370°C through a ribbon die of cross section 1 in. by  $\frac{1}{16}$  in. using a 1:1 compression screw. The extrudate was clear and light yellow. Most sections contained tiny bubbles thought to arise from entrapped air.

Several of the block polymers have been extruded. The largest and best extrusions have most recently been made with a bar die of cross section  $\frac{1}{8}$  in. by  $\frac{3}{4}$  in. A 2:1 compression screw appeared to help considerably in providing the necessary shearing of the resin and in backing out the air.

Best results were obtained when large amounts of a dried resin (i.e., 1 lb or more) were available in the form of free-flowing steam-precipitated granules. Resins were "starve-fed" to the extruder hopper using controlled flow-rate feeders until steady-state extrusion conditions developed. Feed rate could then be raised to a flood condition. Barrel and die temperatures of 335° to 360°C worked well, and screw speeds from 10 to 120 rpm were used. In most cases, a stream of air was directed at the emerging extrudate to quench it and thereby suppress die swell.

Torque increased with screw speed, but wide variations were seen from resin to resin not only in the shape of the torque-speed curve but even in the ease of establishing a steady torque at a given speed. Temperature changes of 10° or 20° seemed to have little effect on torque.

On several occasions, a run was stopped and the extruder screw pulled from the barrel. Frequently, a compacted mass of granules was found in the last two or three flights of the compression section of the screw. Each of the flights of the pumping section of the screw would be found mostly empty, but a cap of resin more or less well fused would be found covering the screw torpedo.

Finally, it was found that the steam-precipitated granules (each of which is a weak aggregate of fibrous particles) processed much more easily than the same granules after acetone treatment (which swells the granules; upon drying, they shrink and harden considerably).

On the basis of these observations, it seems clear that the torque characteristics were primarily determined by the processes going on in the compression section of the screw where resin is softened by the heat generated through internal friction effects rather than by external heat. Modifications in screw design should eventually bring a substantial improvement in the ease and quality of extrusions.

The extrudate varied considerably in quality. When conditions were optimized, however, clear bubble-free sections several yards long were extruded. In 1/8-in.-thick sections, the extrudates of some resins were golden yellow to straw color. Color intensity in a given run varied noticeably with barrel temperature and screw speed, which controls residence time. Residual color is believed to arise from impurities largely; with further development, extrudate color should be as good as that of commercial BPA polycarbonate sheet. Theoretically, thermal stability and oxidation resistance of the BPF residue are high compared to the BPA residue, since BPF contains no aliphatic hydrogens.

Injection molding trials were carried out on some of the block polymers using a 45-ton Battenfeld reciprocating screw machine having a shot size of 3/4 oz. The mold used has a rotatable valve at the sprue that allows the runners to one, two, or three mold cavities to be open. From these cavities, Izod bars, ASTM heat distortion bars, and 2-in. × 2-in. plaques, all 1/8-in. thick are obtained, respectively. A total of about 10 lb of several resins was available in various forms (chopped extrudate, steam precipitated granules, etc.).

Conditions were optimized quickly enough to be able to fill any two of the three cavities at once (filling all three would have required a greater shot size). With the last of the moldings, splay was entirely eliminated, and well-knit, golden-yellow clear moldings resulted. Barrel temperatures in the range of 330° to 345°C, injection pressures of 1300° to 1500 psi, and a hold time (residence time of resin in barrel) of 25 sec gave these results.

TABLE IV  
Properties of Selected Resins

	BPF poly-carbonate	BPFC block polymer #1	BPFC block polymer #2	BPA poly-carbonate
Silicone content, wt-%	0	18.5	21	0
BPFC block degree of polymerization	10 <sup>2</sup>	16	14	—
Flex modulus, psi	410,000	250,000	245,000	340,000
Tensile strength, psi	11,000b <sup>d</sup>	6,900y <sup>e</sup>	7,400y	9,000y
Nominal ultimate elongation, %	≤18	21	24	110
Izod impact strength, ft-lb/in. notch	0.2 <sup>a</sup>	1.9	2.3	16
K <sub>IC</sub> , psi-in. <sup>1/2</sup>	<1000 <sup>a</sup>	1500–3500	2300	1000–3500 <sup>b</sup>
Heat deflection temp., °C, at 264 psi	280 <sup>a</sup>	214	208	135
Temp. for strength = 1000 psi, °C	280	216	210	150
Limiting oxygen index	40 <sup>c</sup>	50 <sup>c</sup>	50 <sup>c</sup>	30 <sup>c</sup>
Ease of grinding and polishing	same			
Extrusion temp, °C	370	340	340	260
Injection molding temp., °C	>370	330	335	280

<sup>a</sup> Estimated value based on other observations.

<sup>b</sup> High value applied only to low crack velocities.

<sup>c</sup> No flame retardants added.

<sup>d</sup> b = Brittle.

<sup>e</sup> y = Yields before fracture.

## CONCLUSIONS

This development program has demonstrated the feasibility of converting suitable high-temperature, brittle resins to melt-processable plastics having a sufficiently good balance of stiffness, strength, toughness, and heat resistance to qualify as high temperature engineering plastics of high transparency. A comparison of selected properties of one of these block polymers with the properties of BPF polycarbonate and BPA polycarbonate is made in Table IV.

The major improvement over the base resin comes about through effects of the rubbery domains on stress-induced cavitation phenomena in the matrix (i.e., crazing and the craze breakdown). Superficially, this action is similar to that of toughening in resins containing much larger conventional rubber particles, in that stress whitening is involved. Since the silicone domains in these block polymers are smaller than the filaments of the craze in a homopolymer while conventional rubber particles are very much larger than these filaments, the details of the stress-whitening processes involved are undoubtedly different in the two cases. Whatever the mechanism, the toughening action becomes great enough with increasing silicone content to delay fracture to the point that shear deformation can occur extensively.

Finally, it is worth reiterating that the two independent molecular characteristics of the block polymers tend to influence different properties: while polycarbonate block length dominates in the fixing of the softening temperature, composition seems to control all mechanical properties at low temperatures

rather independently of block length. The looseness of the coupling between these cause-and-effect relationships brings great flexibility to the design of optimally tailored resins.

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