Macromolecules

Volume 5, Number 4 July–August 1972

Swelling, Crazing, and Cracking of an Aromatic Copolyether–Sulfone in Organic Media

R. P. Kambour,* E. E. Romagosa, and C. L. Gruner

Polymer Chemistry Branch, Chemical Laboratory, General Electric Corporate Research and Development, Schenectady, New York. *Received March 30, 1972*

ABSTRACT: The critical flexural strain ϵ_c for crazing or cracking has been determined for compression-molded bars of an aromatic copolyether-sulfone in air and in 40 different small-molecule organic liquids. Measurements of degree of swelling of the polymer by 39 liquids have been also made and the resultant lowered glass temperature has been measured in 30 cases. Plasticization is responsible for the lowering of ϵ_c from its value in air to the minimum observed. As expected, maximum degree of swelling occurs in agents having values of solubility parameter δ close to that of the polymer. However, over a very broad range of δ swelling can be sufficient to lower T_g and ϵ_c markedly from their dry-state values. The broad susceptibility to limited swelling is a general characteristic of glassy polymers of high T_g caused by the excess free energy of the glassy state.

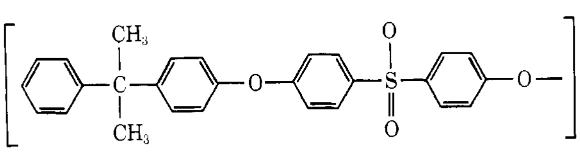
In a previous study,[1] critical strains were reported for crazing of poly(2,6-dimethyl-1,4-phenylene oxide) in contact with a wide spectrum of organic agents. The critical strain was shown to be reduced in proportion to the reduction of T_g through plasticization. Since degree of plasticization depends primarily on degree of swelling and the latter depends primarily on the solubility parameters of polymer and swelling agent, a correlation was found between crazing resistance in a given agent and its solubility parameter δ. Specifically, critical strain was found to be reduced to a minimum at the same position on the δ spectrum where swelling reached a maximum. Moreover, this value of δ coincided with that for the polymer as calculated using Small's group contribution method.

For a variety of reasons it is of interest to explore how well these simple correlations hold for the solvent crazing of other glassy polymers. Is the reduction in critical strain exclusively a function of the ease of flow of the glass? How well does δ act as a correlating parameter for the limited swelling of other glassy polymers in a wider variety of organic agents? Conversely, do entropic factors, specifically those relating to molecular size effects, play a negligible role in the swelling of other polymers by small organic molecules, as seems to be true for poly(phenylene oxide)? Finally, how does the solvent crazing susceptibility profile of a given polymer differ from the profile of poly(phenylene oxide)? Is the profile simply shifted on the δ spectrum to the extent that the δ's for the two polymers are different? Or does the profile *shape* differ as well?

With these questions as a background, we have conducted an extensive study of the swelling and crazing characteristics of polysulfone—another glassy polymer of substantially higher solubility parameter but of physical characteristics similar to those of poly(phenylene oxide): high T_g, high crazing resistance in air, and a yield stress of 10,000 psi, roughly.

Experimental Section

(A) **Materials.** The resin, obtained from the Westlake Plastics Co., was an alternating copolyether, poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene), often referred to simply as polysulfone. The repeat unit in the chain is shown in I. The as-received resin is said to have a $\bar{M}_n$ of 25,000 on the basis of viscosity measurements. $\bar{M}_w/\bar{M}_n$ should be 2.1–2.2.[2] Resin density is 1.24 g/cc and its T_g is 186°C as determined here by scanning calorimetry.



I

Before molding into sheets for crazing studies, the resin pellets were held 4 hours or more at 125° in a circulating air oven to drive off moisture. Sheets 0.04–0.05-in. thick were compression molded between aluminum foils at about 210°. After 5 min under pressure at this temperature, the press was cooled over a 5-min interval to 180° and the sheets were then removed. They exhibited first-order birefringent colors, as was true for the poly(arylene oxide) sheets that were used in the previous study of solvent crazing resistance. In neither case were attempts made to remove the birefringence by annealing.

Bars for crazing were cut from the sheets and their edges milled smooth. They were washed in soapy water, rinsed, dried with paper towels, and then handled only with gloves or tongs prior to being strained.

(B) **Critical Strains.** Values of critical strain ϵ_c were determined with Bergen elliptical strain jigs (Figure 1).[3] These afford con-

---

[1] G. A. Bernier and R. P. Kambour, *Macromolecules*, **1**, 393 (1968).

[2] See R. N. Johnson, A. G. Farnham, R. A. Clendinning, W. F. Hale, and C. N. Merriam, *J. Polym. Sci., Part A-1*, **5**, 2375 (1967), for molecular weight characteristics of these resins.

[3] R. L. Bergen, Jr., *SPE J.*, **18** (6), 667 (1962).

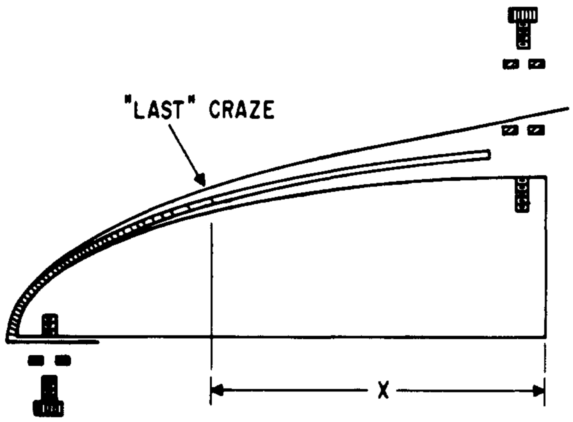


Figure 1. Bergen elliptical strain jig.

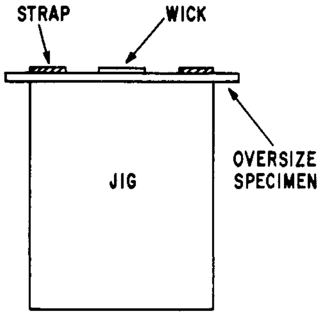


Figure 2. Cross section of jig with oversize specimen and wick, designed to prevent edge initiation of crazes or cracks.

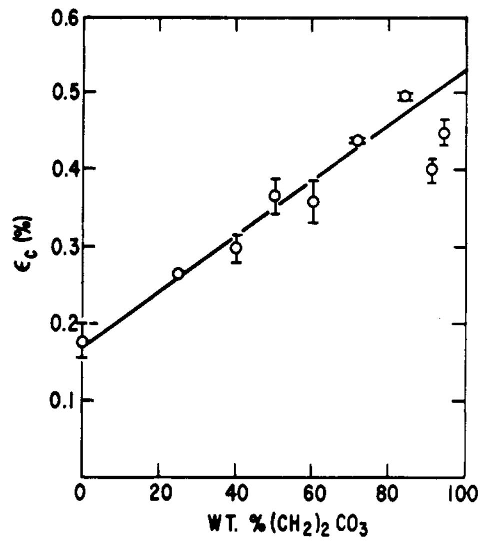


Figure 3. Critical strains for crazing or cracking in propylene carbonate and its mixtures with ethylene carbonate.

siderable savings in time and materials by contrast with the three-point bending jigs used in the poly(phenylene oxide) study. These savings arise from the variation in strain along the length of each specimen when strapped down to the curved surface of the jig. Heavy crazing or cracking usually occurs in the areas under higher strain but becomes more sparse with distance along the bar and does not occur in areas of low strain. Each specimen thus yields a value of critical strain, so that only two or three specimens are needed to determine a reasonably precise value of ϵ_c.

The major difficulty with the use of jigs onto which specimens are strapped before immersion in a test fluid arises from edge effects. Specimens cut from sheets often exhibit substantially lower resistance to crack growth from the cut edges than to crack initiation on the molded faces. This problem can be avoided by the use of a narrow wick of cloth or filter paper. The wick is laid along the center of the specimen and saturated with the test fluid which is applied with an eye dropper. Crazes and cracks tend to initiate under the wick but not at the bar edges. Even with this precaution, edge initiation can result if cracks initiating at the wick early in the test propagate as far as the straps. Liquid can then travel from these large cracks up under the straps by capillary action and cause preferential edge initiation at parts of the specimen under lower strains. The use of specimens cut wider than the jig obviates this problem, however, since both edges of an oversized specimen can be located out beyond the jig edges. A diagram of the jig, oversized specimen, straps, and wick, all in cross section, is shown in Figure 2.

With one of the agents, ethylene carbonate, a value of critical strain at room temperature could not be obtained directly since the material melts at 37°. The addition of propylene carbonate in small amounts is enough to prevent ethylene carbonate liquid from freezing at room temperature for periods of a day or more. (Wicks could not be used with the supercooled solutions because of nucleation of crystallization. However, droplets of these solutions could be placed on the glassy polymer surface at various positions without crystallization and ϵ_c's determined by noting which droplets caused crazing and which did not.) Critical strains were, therefore, determined over the entire composition range of these mixtures in order to get an extrapolated value for pure ethylene carbonate. Results are shown in Figure 3.

(C) Solubilities of the Agents in the Polymer. Sorption studies were conducted at room temperature (23–24°) on 0.001-in. thick films of the resin exposed to the saturated vapor of each liquid. The films had been cast from methylene chloride solution and dried *in vacuo* at elevated temperatures. Pieces of film were suspended in stoppered test tubes or screw cap jars containing a few milliliters of the test liquids. The films were removed intermittently for weighing over periods of time ranging up to 18 months. Sorption kinetics were usually complex. We report here only $S_{w,max}$, the maximum weight increase per unit weight of film, and $S_{v,max}$, the corresponding volume of liquid absorbed per unit volume of dry polymer.

(D) Glass Temperatures of Plasticized Films. At the end of the exposure to the saturated vapors, the glass temperatures of many of the swollen specimens were determined calorimetrically using a Perkin-Elmer DSC IB differential scanning calorimeter. Each specimen was quickly compressed into pellets which were immediately sealed in DSC volatile sample pans. Scanning rate was 20°/min. In each case enough material was available for two separate runs. The average of the two is reported here. In one case, propylene carbonate swollen film, the glass transition was determined by TOA, thermooptical analysis;[4] since this method gives a T_g roughly 10° higher than that from DSC, the value recorded herein is 10° lower than the TOA value actually determined.

Results

All experimental data and relevant physical properties of the 40 agents used in this study are summarized in Table I.

$S_{v,max}$ is plotted *vs.* δ, the solubility parameter of the test agent, in Figure 4. The peak in solubility behavior here suggests that δ = 10–11 for polysulfone. This value is consistent with the value 10.7–10.8 calculated by Small's group contribution method. In this calculation we used a value of the sulfone group contribution calculated from the heats of vaporization of tetramethylene sulfone and dimethyl sulfone. By contrast, the calculated value of δ for poly(dimethylphenylene oxide) is 8.6 and its susceptibility to swelling tends to peak at this point (dotted line in Figure 4). (Par-

---

[4] A. R. Shultz and B. M. Gendron, *J. Appl. Polym. Sci.*, **16**, 461 (1972).

TABLE I

	δ,[a–c] (cal/cm^3)$^{1/2}$	ρ_s,[d] g/cm^3	$S_v \times 10^2$, cm^3/cm^3	T_g, °C	ϵ_c, %
Dodecamethylpentasiloxane	5.34	0.88	3.95	139–144	1.64
Perfluoromethylcyclohexane	6.0	1.788	11.4	87–102	1.16
Hexamethyldisiloxane	6.0	0.762	5.2	101–124	1.47
n-Pentane	7.02	0.626	20.2	104–111	0.94
n-Hexane	7.27	0.660	7.0	100	0.97
$C_2F_3Cl_3$ (Freon 113)	7.3	1.358	20.9	94–117	1.09
n-Heptane	7.50	0.684	2.9	106–108	0.89
n-Octane	7.54	0.703	1.6	121–137	0.97
Isoamyl butyrate	7.8	0.872	10.7	60–61	0.44
Methylcyclohexane	7.8	0.769	3.52	132	0.99
Cyclohexane	8.19	0.779	5.22	75–80	1.01
n-Butyl acetate	8.69	0.883	26.5	38–58	0.17
Methyl ethyl ketone	9.45	0.805	36.4	−14 to −7	0.12
Methyl acetate	9.46	0.933	48.5	21–37	0.15
Acetone	9.62	0.789	50.1	1	0.14
Methyl formate	9.93	0.974	35.6		0.17
Nitrobenzene	10.0	1.204	83.8	−48 to −32	0.21
Cyclopentanone	10.53	0.949	99.5		0.20
Allyl cyanide	10.54	0.833	37.5		0.20
Triethylene glycol	10.7	1.11	0.5	140–143	0.63
N,N-Dimethylacetamide	10.8	0.937	29.8		0.15
1-Pentanol	11.12	0.814	8.53	101–108	0.81
Dioxolane	11.33	1.060	51.0		0.17
Sulfolane	11.3[e]				0.49
2-Propanol	11.44	0.789	5.52	59–81	0.77
Methylene iodide	11.8	3.33	25.0		0.16
Acetonitrile	12.11	0.786	20.1	37–39	0.40
1-Propanol	12.18	0.804	8.18	83–85	0.85
Dimethyl sulfoxide	12.0	1.101	24.3	55–56	0.10
N,N-Dimethylformamide	11.79	0.949	67.6	−4 to −1	
Benzyl alcohol	12.05	1.042	38.7	7–11	0.14
Ethanol	12.78	0.789	8.63	83–88	1.00
γ-Butyrolactone	12.87	1.129	38.9		0.17
Propylene 1,2-carbonate	13.3	1.20	18.3	43–60	0.18
β-Propiolactone	13.3	1.146	34.4		0.20
Methanol	14.50	0.791	5.80	68–91	0.99
Propylene glycol	14.99	1.036	3.59	113–118	1.06
Ethylene carbonate	14.7				~0.45
N-Methylformamide	16.1	1.011	16.1	60–64	0.43
Ethylene glycol	17.05	1.109	2.46	113–121	1.32
Formamide	19.2	1.133	2.52	109–110	1.35

[a] K. L. Hoy, *J. Paint Technol.*, **42,** 76 (1970) (preferential source). [b] H. Burrell and B. Immergut, "Polymer Handbook," J. Brandrup and E. H. Immergut, Ed., Interscience, New York, N. Y., 1966, pp IV-341–IV-357. [c] See ref 1. [d] "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1969. [e] Calculated by Small's method. See footnote *b*.

tially chlorinated aliphatic liquids are the best solvents for both polymers, but these agents were used in neither study.)

Polysulfone is susceptible to limited degrees of swelling at least (2.5–20%) over the entire spectrum of liquids. Heavy swelling (greater than 25%) is generally confined to non-hydrogen-bonded liquids in the δ range 8.0–12 or 13, a spread of 4.0–5.0 in δ. Monohydric and dihydric aliphatic alcohols are all strikingly less soluble than non-hydrogen-bonded liquids of similar solubility parameters. By contrast, poly(dimethylphenylene oxide) exhibits a tendency to swell to greater than 20% over a smaller δ range, roughly 2.5, centered at $\delta = 8.6$.

Two other differences between the resins are apparent. First, considerably more scatter of swelling data from the swelling envelope is evident for polysulfone than was seen for poly(phenylene oxide). In particular, the larger hydrocarbons and the aliphatic alcohols fall substantially below the polysulfone envelope. Second, the polysulfone swelling envelope appears to be higher in general than that of poly(phenylene oxide), taking into account the difference in δ's of the two polymers. This latter observation must be tempered by noting that the lists of agents used in the two studies are not identical. Most importantly, a much larger number of aprotic polar liquids was used in the current study.

The T_g's of the swollen films are plotted *vs.* $S_{v,\max}$ in Figure 5. The lowering of T_g per unit volume absorbed is greatest for low degrees of absorption. The shape is qualitatively reminiscent of the T_g *vs.* concentration curve obtained when a single plasticizer is added in varying amounts to a resin. However, when expressions such as the Kelly–Bueche equation[5] are applied here,[6] no single curve can be found that will

---

(5) F. N. Kelley and F. J. Bueche, *J. Polym. Sci.*, **50,** 549 (1961).

(6) The curve in Figure 5 is calculated from the Kelley–Bueche equation using for the solvent $T_{g,s}$ = 100°K and for the polymer a change in expansion coefficient $\Delta\alpha_p = 3.78 \times 10^{-4}$ °C^{-1}, a value for bisphenol-A polycarbonate obtained by F. P. Price. The latter is used as a good approximation to $\Delta\alpha_p$ for polysulfone, which is not known. The expansion coefficient for the solvent α_s is assigned a representative value of 1.2×10^{-3} °C^{-1}.

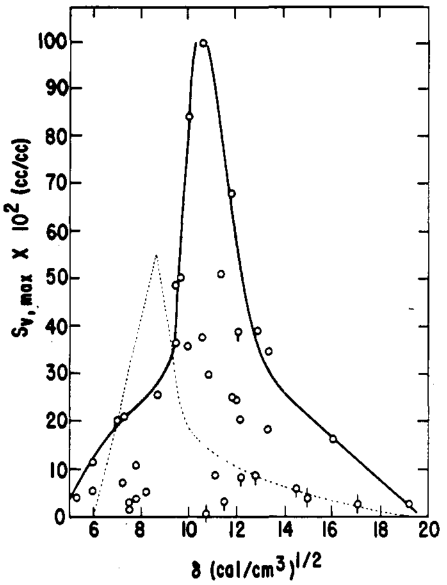


Figure 4. Volume solubility $S_{v,max}$ of saturated vapors in polymer *vs.* δ. Solid line is a swelling envelope drawn to reflect uppermost points largely. Broken line is envelope for poly(2,6-diemthyl-1,4-phenylene oxide) from ref 1. Single tab, monohydric alcohol; double tab, dihydric alcohol.

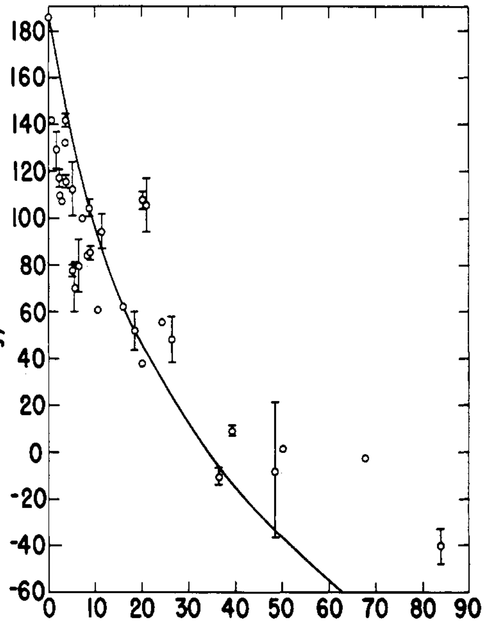


Figure 5. T_g of swollen polymer film *vs.* volume solubility S_v. Line is from Kelley–Bueche equation with solvent T_g = 100°K, solvent $\alpha_s = 1.2 \times 10^{-3}$ deg^{-1}, and polymer $\Delta\alpha = 3.78 \times 10^{-4}$ deg^{-1}.

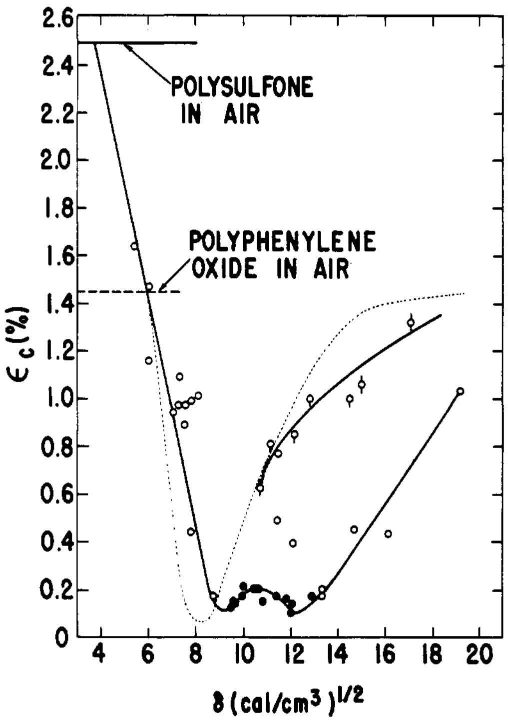


Figure 6. Critical strain ϵ_c for crazing or cracking of polysulfone *vs.* δ of liquid organic agent: (open points) crazing agents; (closed points) cracking agents; (single tab) monohydric alcohol; (double tab) dihydric alcohol; (dotted line) profile of ϵ_c *vs.* δ for solvent crazing and cracking of poly(2,6-dimethyl-1,4-phenylene oxide).

run through the band of data satisfactorily: with increasing swelling, T_g drops too steeply at low degrees of swelling and not steeply enough at high degrees for a single curve to fit. Following Braun and Kovacs,[7] we suppose that this departure reflects how the degree of ideality of mixing varies across the solvent spectrum. Those agents that are the poorest swelling agents presumably exhibit the greatest volume of mixing in addition to the greatest endothermal heat of mixing. Therefore, they should add the greatest increment of free volume and thus the greatest T_g drop per unit of swelling.

It can also be seen from Figure 5 that agents swelling polysulfone to 0.25 or 0.30 cause the DSC T_g to be lowered to the vicinity of 30°. Because of measurement rate effects, this corresponds roughly to a dilatometric T_g of 20–25° or less, which is the laboratory ambient. In turn, this is the degree of swelling at the junction of the "spike" and the broad section of the swelling envelope (Figure 4) where the profile has a width of about 3.5 units on the δ scale. Thus, with the exception of aliphatic alcohols, organic agents in the range 8.5 or 9–12 or 12.5 lower the T_g of polysulfone to room temperature or below. The significance of these general swelling characteristics for the environmental strength of the polymer will now become evident.

In Figure 6, ϵ_c, the critical strain for crazing or cracking, is displayed *vs.* δ for 40 of the agents of this study. The least-soluble agents, lying at each end of the δ spectrum, produce a decrease of 30–50% in ϵ_c as a result of the large reduction of T_g per unit swelling that poor swelling agents bring about. Agents lying between δ = 8.5 and 13.3 (alcohols excepted) produce cracks instead of crazes. In this range, crazes are not stable because it is in just this range that swelling is great enough to lower T_g to ambient or below (see Table I). The same kind of relationship between the onset of cracking and the reduction of T_g to ambient temperature was previously observed with poly(phenylene oxide). The nonzero minimum value in ϵ_c (~0.15%) is presumed to be due to other processes that compete with cracking as modes of stress relaxation. The volume increase from swelling is probably one of these, and the other is homogeneous stress relaxation of the swollen material. We suspect that these competing modes become so

---

[7] G. Braun and A. J. Kovacs, "Proceedings of the International Conference on the Physics of Non-Crystalline Solids," J. A. Prins, Ed., North Holland Publishing Co., Amsterdam, 1965, p 303.

pronounced with the best swelling agents as to cause the small peak in ϵ_c at $\delta \simeq 10.5$. (We have seen similar effects with other polymers, notably polystyrene.)

The crazing effectiveness of liquids of high δ is clearly not correlated well by solubility parameter, just as their solubility behavior is not. The monohydric and dihydric aliphatic alcohols lie in a well-correlated class by themselves, but the other liquids are rather scattered in both crazing and swelling behavior. This failure of δ to correlate crazing and swelling at high values of δ stands in marked contrast to the behavior of poly(phenylene oxide). Sources of this failure will be the subject of another paper.

In Figure 7, ϵ_c is plotted *vs.* T_g of the swollen films. The coordinates of the left-hand end of the curve are fixed by ϵ_c and T_g of the dry polymer. ϵ_c then drops in an approximately linear fashion with T_g and reaches its minimum value (and the transformation from crazing to cracking) at 30–50° roughly. Moreover, the alcohol data are scattered among the other points at random verifying that, once swelling differences are taken into account, alcohols behave no differently than non-hydrogen-bonded agents. The near-linearity of the ϵ_c *vs.* T_g relationship down to 50° or less indicates that ϵ_c for crazing of polysulfone is dominated by the ease of flow of the glass under stress, whether or not a small-molecule organic agent is present. Moreover, competitive modes of stress relaxation are of negligible importance down to a T_g of 50° roughly. Similar behavior was observed in poly(phenylene oxide), although the data supporting this conclusion were much less numerous.

Discussion

It is clear that the primary role of solvents in the crazing of polysulfone and poly(phenylene oxide) is one of plasticization. By comparison with polymers of lower T_g that will be discussed elsewhere, the competition from homogeneous swelling or creep as modes of reducing stress is minor in both materials except at high degrees of swelling. The T_g's of the two polymers are rather similar (189 *vs.* 210°), and thus the degree of swelling required to lower T_g to ambient is about the same for the two ($S_v \sim 0.25$).

The differences in crazing and cracking susceptibilities of the two resins seen in Figure 6 are thus caused wholly by differences in susceptibilities to swelling—more particularly to swelling characteristics between 0 and 0.25 cm³/cm³. The *maximum* susceptibility to swelling of polysulfone occurs as expected at a δ 2.5 or 3 units higher than in poly(phenylene oxide). However, the swelling envelope at low degrees of swelling is broader in polysulfone, and this breadth largely counteracts the difference in δ on the low-δ side of the swelling envelope. As a consequence, the low-δ side of the polysulfone crazing envelope lies only one δ unit to the right of that for poly(phenylene oxide) at low critical strains.

The great breadth of the base of the swelling envelope for each of the two polymers is probably a general characteristic of absorption in glassy polymers of high T_g. The most likely source of the broadening of the envelope for *glassy* solutions (*i.e.*, for those cases where T_g has not been reduced below ambient temperature) is the excess free energy of the glassy polymer, $\Delta F_{g,\mathrm{l}}$. It is well known that glasses exhibit greater enthalpies and entropies than do their fictitious counterparts, the same materials in the equilibrium liquid state. The reduction of polymer T_g by swelling brings a corresponding reduction in the excess free energy. Thus, the potential for reduction of T_g toward the ambient temperature by plasticization produces a driving force for swelling that adds to whatever is the driving force for mixing of swelling agent and *liquid* polymer.

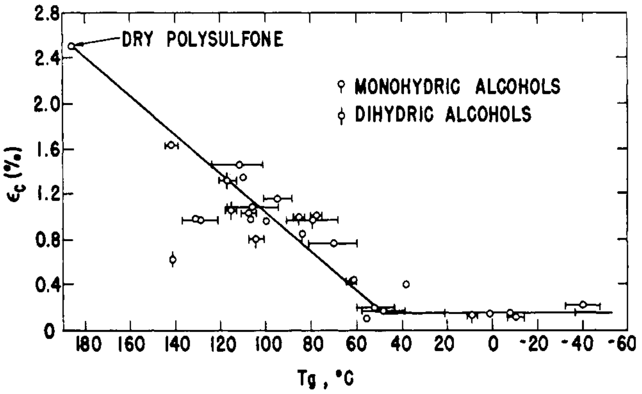


Figure 7. Critical strain ϵ_c for crazing or cracking of polymer bar *vs.* T_g of solvent-equilibrated polymer film.

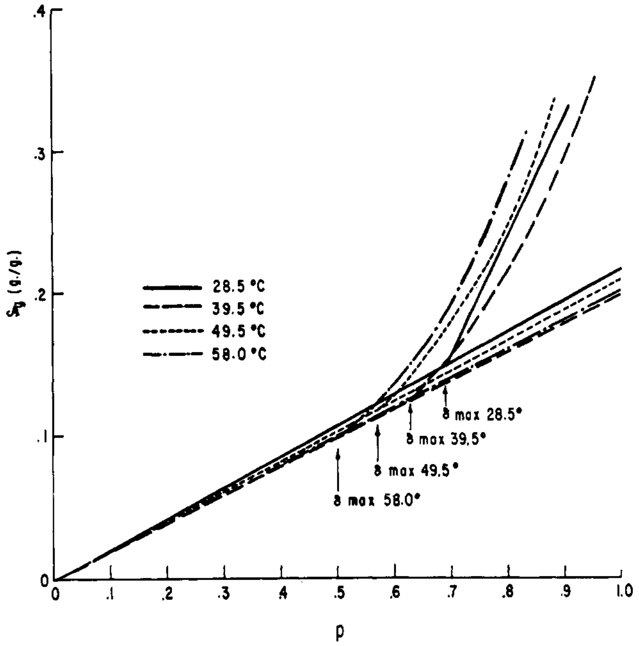


Figure 8. Degree of swelling S_v *vs.* partial pressure p of acetone in amorphous bisphenol-A polycarbonate at several temperatures (from ref 8).

We can estimate $\Delta F_{g,\mathrm{l}}$ from the difference in heat capacity, ΔC_p, of the polymer above and below the glass temperature. By standard thermodynamics, $\Delta F_{g,\mathrm{l}}$ at ambient temperature T is given by

$$\Delta F_{g,\mathrm{l}} = \Delta H_{g,\mathrm{l}} - T\Delta S_{g,\mathrm{l}} \simeq \Delta C_p(T - T_g) - \Delta C_p T_\mathrm{l} \ln T/T_g$$

If we assign to ΔC_p a typical value[8] of 0.23 J/(°K g) ($\simeq$0.29 cal/(°K cm³) for polysulfone) we obtain $\Delta F_{g,\mathrm{l}} \simeq -11 + 9 = 2$ cal/cm³ of polysulfone at 25°. Furthermore, since T_g is reduced to 25° by the absorption of about 0.25 cm³ of swelling agent per cubic centimeter of polymer, the *gradients* in excess enthalpy and free energy of the glassy polymer with swelling are $\mathrm{d}H_{g,\mathrm{l}}/\mathrm{d}S_v = -44$ cal/cm³ absorbed and $\mathrm{d}F_{g,\mathrm{l}}/\mathrm{d}S_v = -8$ cal/cm³ absorbed. The Scatchard–Hildebrand enthalpy term, $(\delta_{\text{polymer}} - \delta_{\text{solvent}})^2$, for the least soluble of

---

[8] J. M. O'Reilly, F. E. Karasz, and H. E. Bair, *J. Polym. Sci., Part C, No.* **6**, 109 (1964); F. E. Karasz and J. M. O'Reilly, *ibid., Part B,* **3**, 561 (1965).

the nonpolar agents used in the present study is 25 cal/cm^3. Without attempting quantitative summations of enthalpies and free energies, it is nevertheless clear that the excess thermodynamic quantities and the Scatchard–Hildebrand heats and free energies of mixing are of the same orders of magnitude (but of opposite sign in the case of the heats).

Swelling and solution effects arising from the excess free energy of the glassy state have been or can be identified in other systems. For example, the swelling of polycarbonate by acetone[9] at various partial pressures is endothermal by about 14 cal/cm^3 of acetone above the T_g of the swollen polymer but is zero below the T_g. That the relationship between the degree of swelling and the partial pressure of acetone in this system changes abruptly at T_g (Figure 8), whatever the ambient temperature of the swelling experiment, is a direct consequence of this fact. This change is, moreover, a direct analog of the change in slope of the swelling envelope of Figure 4 at the point that $T_g = 25°$, since the abscissas in both cases reflect the free energy of mixing.

Excess enthalpies of the glass have in some cases been measured directly by solution calorimetry.[10] Another closely related observation is that the heats of solution of permanent gases in amorphous polymers are usually more endothermal above T_g than below.[11] The usual proffered explanation for this observation has been that below T_g solution of gas in glass involves the filling of preexisting holes, whereas above T_g the gas molecule has to "make" its own hole. The close relationship between these various solubility phenomena and rationalizations is evident.

Conclusions

On the basis of these observations and ideas and our general knowledge of crazing behavior, the prognosis is not good for finding a homogeneous glassy polymer of (a) high T_g and high resistance to crazing in the dry state and (b) immunity to reductions of crazing resistance by organic agents—even by those having very dissimilar solubility parameters from that of the polymer. Resistance to dry crazing is usually high only at temperatures far below T_g where the excess free energy of the glassy state is high, and thus the general driving force for absorption of limited amounts of plasticizing agents is great.

---

(9) R. P. Kambour, F. E. Karasz, and J. H. Daane, *ibid., Part A-2*, **4**, 327 (1966).

(10) J. Stoelting and F. H. Mueller, *Kolloid Z.-Z. Polym.*, **238**, 459 (1970).

(11) P. Meares, *J. Amer. Chem. Soc.*, **76**, 3415 (1954); *Trans. Faraday Soc.*, **53**, 101 (1957).

Interpenetrating Polymer Networks of Poly(ethyl acrylate) and Poly(styrene-*co*-methyl methacrylate). I. Morphology *via* Electron Microscopy

Volker Huelck, D. A. Thomas, and L. H. Sperling*

Materials Research Center, Lehigh University, Bethlehem, Pennsylvania 18015.

Received February 2, 1972

ABSTRACT: Interpenetrating polymer networks (IPN's) have been synthesized by swelling a cross-linked rubbery polymer (I) with a second plastic monomer (II or III or II-*co*-III) plus initiator and cross-linking agent and polymerizing the second monomer *in situ*. IPN's have also been produced by inverting the order of preparation. According to the overall compositions, IPN's of elastomeric or leathery or plastic behavior have been obtained. Polymers employed were poly(ethyl acrylate) (I), polystyrene (II), and poly(methyl methacrylate) (III). Like most other types of polymer blends, IPN's exhibit a complex two-phase morphology. The electron micrographs show a characteristic cellular structure of about 1000-Å diameter simultaneously with a fine structure with phase domains of the order of 100 Å. In the midrange leathery materials the cell walls are composed of the second network polymer. The fine structure is observed most clearly within the cell walls, and probably originates through a second, later phase separation as polymerization continues beyond the initial cellular formation stage. Increasing compatibility of the two polymers is attained as methyl methacrylate mers replace styrene mers in the plastic component. This leads to the disappearance of the cellular envelopes but retention of the fine 100-Å domain structure. Inverting the sequence of preparation (swelling monomer I into network II or III) showed that the network synthesized first controls the morphology of the IPN's, comprizing the more continuous phase.

Interpenetrating polymer networks (IPN's) exhibit an intimate mixture of two polymeric networks which are superimposed within each other. IPN's are prepared by swelling a cross-linked polymer (I) with a second monomer solution (II or III or II-*co*-III) which contains an initiator and a cross-linking agent. An IPN results upon polymerizing the second monomer (or comonomer solution) *in situ*.[1-9] In the previous papers on IPN's from this laboratory, the temperature and time dependencies of viscoelastic properties were presented.[1-3] The investigations showed that an incompatible IPN pair, poly(ethyl acrylate)–polystyrene

---

(1) L. H. Sperling and D. W. Friedman, *J. Polym. Sci., Part A-2*, **7**, 425 (1969).

(2) L. H. Sperling, D. W. Taylor, M. L. Kirkpatrick, H. F. George, and R. D. Bardman, *J. Appl. Polym. Sci.*, **14**, 73 (1970).

(3) L. H. Sperling, H. F. George, V. Huelck, and D. A. Thomas, *ibid.*, **14**, 2815 (1970).

(4) L. H. Sperling, V. Huelck, and D. A. Thomas, "Polymer Networks: Structural and Mechanical Properties," S. Newman and A. J. Chompff, Ed., Plenum Press, New York, N. Y., 1971.

(5) A. J. Curtius, M. J. Covitch, D. A. Thomas, and L. H. Sperling, *Polym. Eng. Sci.*, **12**, 101 (1972).

(6) J. R. Millar, *J. Chem. Soc.*, 1311 (1960).

(7) K. Shibayama and Y. Suzuki, *Kobunshi Kogaku*, **23**, 24 (1966).

(8) K. Shibayama and M. Kodama, *ibid.*, **24**, 1 (1967).

(9) K. Shibayama and M. Kodama, *ibid.*, **24**, 104 (1967).