Resistance of a Polyetherimide to Environmental Stress Crazing and Cracking

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Synopsis

The environmental stress crazing and cracking (ESC) behavior of an aromatic polyetherimide (PEI) has been characterized in a wide spectrum of organic liquids and compared to the behavior of several other glassy thermoplastics. PEI's response is qualitatively similar to that of the other resins for each of which ESC resistance reaches a minimum in solvents having solubility parameters close to that of the resin. Taken as a whole, the ESC resistance of PEI is found to be quantitatively superior to that of any other glassy resin for which similar data are available for comparison.

INTRODUCTION

One of the major end-use problems faced by glassy thermoplastics is environmental stress crazing and cracking (ESC)—broadly, a reduction in the resistance to brittle failure induced by exposure to any of a large number of mostly organic liquids.

ULTEM (trademark of the General Electric Co.) polyether imide (PEI),
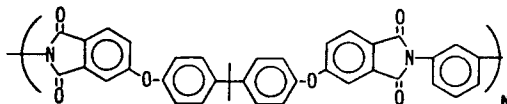
albeit a high performance resin[1] in many respects is, nevertheless, a glassy thermoplastic susceptible to swelling and/or brittle failure in some organic environments. A careful assessment of its ESC resistance and its comparison to other thermoplastics in this regard is (a) to characterize further PEI's end-use properties and (b) to provide further microstructural clues to synthetic chemists seeking in the future to make improved thermoplastics.[2]

One widely used method of assessing broadly the ESC resistance of a resin involves prestressing or prestraining specimens and exposing each to one of a wide spectrum of organic liquids until all initiation of crazes or cracks has ceased. Alternatively, the stress or strain is applied for a fixed time (e.g., 24 h). The stress or strain below which no crazes or cracks have developed is then taken as a measure of the resistance of the resin in the given environment.

This kind of testing usually produces resistance data that can be correlated in part with the solubility parameters δ_s of the liquids used. The correlation is believed to reflect the relative abilities of the liquids in the spectrum to swell the resin and lower its T_g.[2] By the simple application of classical theory the degree of swelling might be expected to be correlated by the quantity $\delta_s - \delta_p$, the difference between the solubility parameters of solvent and polymer, respectively. Since solubility parameters provide imperfect measures of heats of solution and, moreover, ignore completely the well-known molecular size ef-

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fects in the entropy of mixing, the correlation of swelling and $\delta_s - \delta_p$ is never perfect. Attempts to refine swelling theory by articulating energies of mixing in terms of dispersive, polar, and hydrogen bonding contributions have been partially successful, albeit at the expense of simplicity.[3] Departures from simple theory due to solvent molecular size effects have been corrected with substantial success.[4]

This measurement of ESC resistance also ignores the fact that specimens exposed at subcritical stresses or strains may have been weakened *vis-à-vis* strength tests conducted after the ESC environment has been removed. Nevertheless, the convenience of this kind of test for the rapid screening of a large number of liquids has resulted in the collection of a large amount of ESC data on several thermoplastics by such methods.

EXPERIMENTAL

ESC Resistance

The particular ESC test procedure for this study was identical to that used here with a number of other plastics.[5-9] PEI of $[\eta] = 0.44$ dL/g was used. Another high-T_g glassy engineering resin, ICI's VICTREX polyethersulfone, was

TABLE I
Intrinsic Viscosities in Polar Liquids

|	δ [(cal/cm^3)$^{1/2}$]	$[\eta]$ (dL/g)
Chloroform	9.3	0.481
Acetone	9.6	a
Methyl acetate	9.6	a
Methylene chloride	9.7	0.43$_6$
Dimethyl carbonate	9.9	a
Nitrobenzene	10.0	0.47$_2$
Carbon disulfide	10.0	a
Methyl formate	10.2	a
Benzonitrile	10.3	0.39$_6$
Methyl benzoate	10.5	0.49$_8$
Cyclopentanone	10.5	a
Butyronitrile	10.5	a
Acetophenone	10.6	0.43$_1$
Methyl salicylate	10.6	0.42$_1$
Pyridine	10.7	0.48$_9$
Propionitrile	10.8	a
Dimethyl acetamide	10.8	0.40$_8$
Nitroethane	11.1	a
N-methyl pyrolidone	11.3	0.49$_3$
Dipropyl sulfone	11.3	a
Sulfolane	11.3	a
Dioxolane	11.3	a
Methylene iodide	11.8	a
Acetonitrile	11.9	a
Dimethyl sulfoxide	12.0	a
Dimethyl formamide	12.1	a
γ-Butyrolactone	12.9	a
Propylene carbonate	13.3	a

a Liquid dissolves less than 1% polymer.
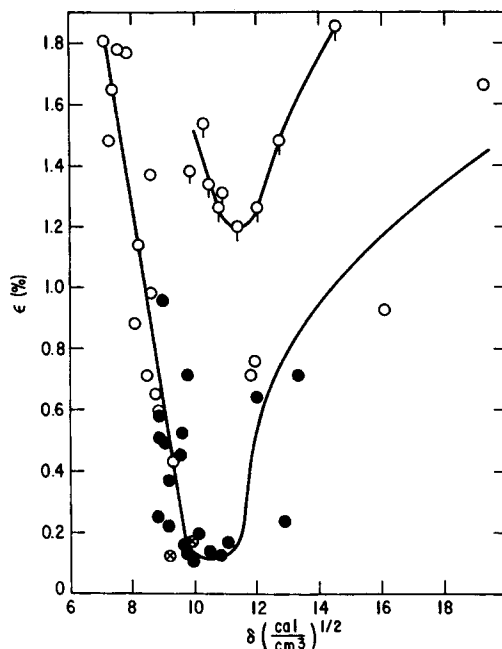
Fig. 1. Dependence of critical strain ϵ_c for crazing (O), cracking (●), and dissolution (⊗) of PEI vs. liquid solubility parameter δ. Tab-alcohol.

also characterized in this study for ESC resistance to provide a more complete comparison background for PEI. The chopped extrudates were first dried at 120°C. They were then compression molded at 300°C into plaques approximately 0.075 in. thick. Bars were cut from the plaques and the bar edges sanded smooth. The bars were washed in soap and water, rinsed, and dried. They were subsequently handled only with clean gloves.

Critical strain was measured using Bergen elliptical strain jigs, described mathematically by

$$(y/1.5)^2 + (X/5)^2 = 1$$

wherein the constants representing the semiaxes are given in inches.[10] The bars were strapped to the jigs and immersed in the test liquid. Because of the elliptical shape of the jig, the strain varies over the length of the bar. The critical strain is taken as the strain below which no craze or crack forms in 24 h. Some liquids caused preferential cracking initiating at the bar edges, which tended to result in spuriously low calculated values for ϵ_c. To circumvent this problem, a wick was placed along the center of subsequent specimens, and liquid was applied to the wick. This technique, plus the use of wide specimens, the edges of which do not come in contact with the jig surface, confined initiation to the areas under the wick.

Polymer Solubilities and Intrinsic Viscosities

One method of estimating the solubility parameter of a polymer involves measurement of its intrinsic viscosity in a range of liquids.[11] In the current study an attempt was made to make such measurements in a spectrum of aprotic polar

TABLE II
Critical Strains of Polyetherimide (PEI) and Poly(ethersulfone) (PES)

	δ (cal/cm^3)	Critical strain (%)	
		PEI[a]	PES[a]
n-Pentane	7.1	1.81 Z	
n-Hexane	7.3	1.48 Z	1.55 Z
C$_2$F$_3$Cl$_3$ (Freon 113)	7.3	>2.9 Z	2.0 Z
n-Heptane	7.4	1.65 Z	
n-Octane	7.6	1.78 Z	
Methycyclohexane	7.8	1.77 Z	
Isopropyl chloride	8.1	0.88 Z	
Cyclohexane	8.2	2.20 Z	2.36 Z
Di-n-butylamine	8.2	1.14 Z	1.09 Z
n-Butylacetate	8.5	0.71 Z	0.51 Z
Carbon tetrachloride	8.6	1.37 Z	
Isopropylbenzene	8.6	0.98 Z	
Ethylbenzene	8.8	0.65 Z	
Toluene	8.9	0.58 Ck	
Methyl n-butyrate	8.9	0.59 Z	
Dichloroethane	8.9	0.25 Ck	
o-Xylene	9.0	0.50 Ck	0.56 Z
1,2,4-Trimethylbenzene	9.0	0.96 Ck	
Methyl propionate	9.1	0.49 Ck	
Benzene	9.2	0.37 Ck	
Chloroform	9.2	0.12 Diss, Ck	
Trichloroethylene	9.2	0.22 Ck	
Ethyl formate	9.3	0.43 Z	
Methyl ethyl ketone	9.5	0.45 Ck	0.10 Ck
Methyl acetate	9.6	0.52 Ck	
Chlorobenzene	9.7	0.16 Ck	
Ethyl acetoacetate	9.8	0.71 Ck	
m-Dichlorobenzene	9.8	0.13 Ck	
3-Heptanol	9.9	1.38 Z	
Dichloroethylene	9.9	0.17 Diss, Ck	
Nitrobenzene	10.0	0.11 Ck	0.16 Diss, Ck
1,2,3-Trichloropropane	10.1	0.19 Ck	
1-Octanol	10.3	1.54 Z	
1-Heptanol	10.5	1.34 Z	1.08 Z
Cyclopentanone	10.5	0.13 Ck	
Hexanol	10.8	1.26 Z	
N,N-Dimethylacetamide	10.8	0.13 Ck	0.12 Diss, Ck
1-Pentanol	10.9	1.31 Z	
Nitroethane	11.1	0.17 Ck	0.21 Diss, Z
Butanol	11.4	1.20 Z	0.92 Z
Methylene iodide	11.8	0.72 Z	
Acetonitrile	11.9	0.77 Z	0.57 Z
Dimethylsulfoxide	12.0	0.64 Ck	0.14 Diss, Z
1-Propanol	12.0	1.26 Z	0.93 Z
Ethanol	12.7	1.48 Z	1.07 Z
γ-Butyrolactone	12.9	0.24 Ck	0.11 Diss, Z
Propylene 1,2-carbonate	13.3	0.71 Ck	0.17 Ck
Methanol	14.5	1.85 Z	
n-Methyl formamide	16.1	0.94 Z	0.59 Z
Formamide	19.2	1.69 Z	1.03 Z

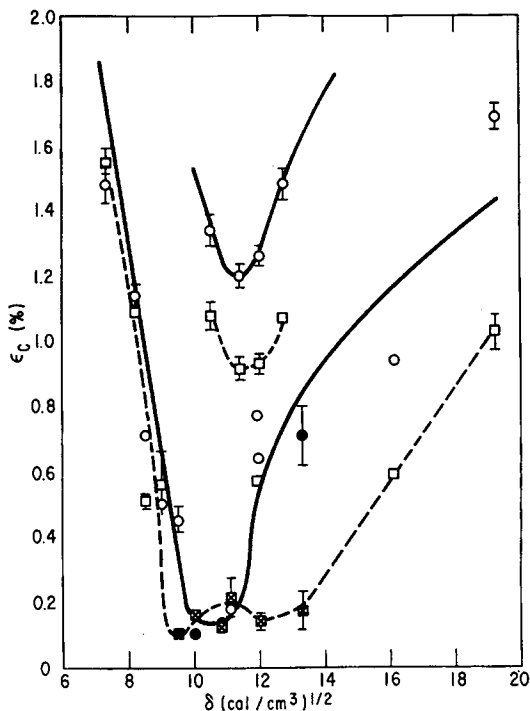[a] Z = crazing only; Ck = some or all cracks; Diss = dissolution.

Fig. 2. Critical strain ϵ_c vs. liquid solubility parameter δ for PEI (O, ●, —) and PES (□, ■, ⊠, - - - -). Dominant modes of failure observed are crazing (O, □), cracking (●, ■), and dissolution (⊠).

liquids ranging from chloroform [$\delta = 9.3$ (cal/cm³)$^{1/2}$] to propylene carbonate [$\delta = 13.3$ (cal/cm³)$^{1/2}$]. Liquids were first screened for dissolving power (>1% polymer solubility is necessary for intrinsic viscosity determination). Specific viscosities were then measured at 1%, 0.5%, and 0.33% polymer in the liquids passing the solubility screening, using Ubbelohde viscometers thermostatted at 25°C. Intrinsic viscosities were determined by standard linear regression analysis.

RESULTS

Solubilities and Intrinsic Viscosities

The aprotic liquids (plus chloroform) screened for polymer solubility are listed in Table I together with their solubility parameters. Intrinsic viscosities were measurable in 1/3 of the liquids only—that is, certain of the liquids in the range $\delta = 9.7–11.3$ (cal/m³)$^{1/2}$. However, the polymer was sufficiently soluble in about half of the liquids tested within this narrower range of δ.

With the exception of dimethyl acetamide and N-methyl pyrrolidone, the solvents are all aromatic and all of the nonsolvents in this δ range are all aliphatic. That is, there is a high correlation inside this δ range between specific details of solvent molecular structure and solvent character but little correlation with general cohesive character.
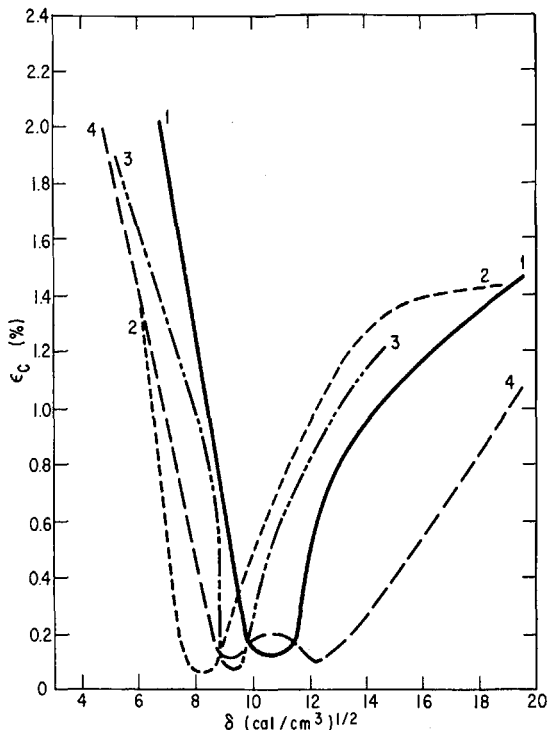
Fig. 3. Comparison of general dependence of ϵ_c in nonhydroxylic small-molecule liquids vs. δ for several glassy plastics: (1) PEI; (2) poly(2,6-dimethyl-1; 4-phenylene oxide[7]; (3) poly(vinyl chloride)[2]; (4) polysulfone.[5]

This observation is reinforced by the behavior of intrinsic viscosity: no correlation with δ is seen.

In short, this part of the study suggests—and that on the basis of the imperfect solubility window only—that the value of δ for PEI lies between 9.7 and 11.3.

ESC Behavior

The ESC results for PEI in laboratory liquids can be found in Figure 1 and Table II. As with other plastics a deep minimum in the dependence of ϵ_c on δ_s is seen, in this case centered on $\delta_s = 10$–11 $(cal/cm^3)^{1/2}$. Crazing is the predominant form of stress relaxation for liquids producing ϵ_c's above $\sim 0.7\%$. Below this level, cracking becomes predominant. Dissolution, as the predominant mode of relaxation, occurred with only two of the liquids tested both of which were chlorinated aliphatics.

Alcohols produce an $\epsilon_c - \delta_s$ relationship different from the other liquids (Fig. 1). The critical strain for each of these liquids is higher than that for a nonhydrogen bonded liquid with the same solubility parameter. This behavior again is similar to that seen with other resins. It is believed to reflect differences in degrees of swelling of plastics by hydrogen-bonded vs. "normal" liquids.

The limited results for PES are compared to those for PEI in Table II and Figure 2. The nonpolar sides of the ϵ_c correlation curves for PEI and PES are nearly the same, but in the region of the minima and for polar liquids PEI and PES behave very differently. For $\delta_p \sim \delta_s$, PES shows a small maximum in
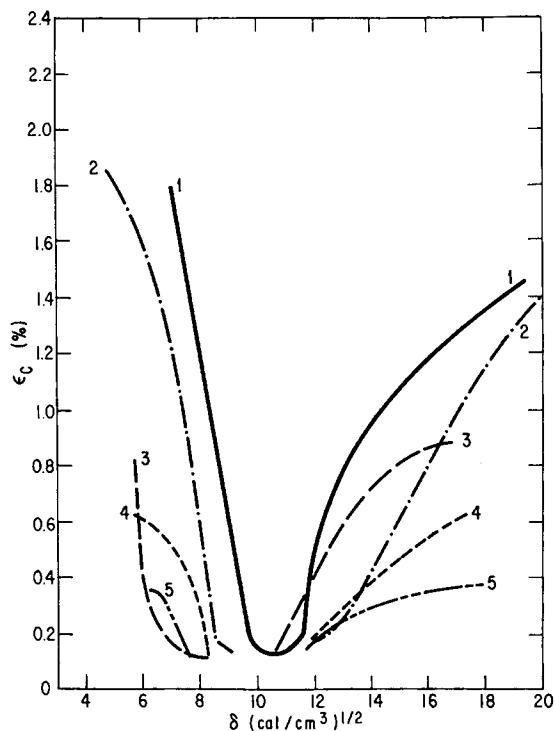
Fig. 4. Comparison of general dependence of ϵ_c on δ for nonhydroxylic small-molecule liquids for several glassy plastics: (1) PEI; (2) BPA polycarbonate[6]; (3) poly(methyl methacrylate)[12]; (4) styrene–acrylonitrile copolymer[8] and polystyrene.[9]

critical strain. This kind of behavior has been attributed to rapid swelling which acts as a competing mode of stress relaxation.[5] Thus, in this region both resins fail—PEI by rapid cracking, PES predominately by dissolution.

For the polar nonhydrogen bonded liquids tested here, PEI's ESC resistance is much greater than that of PES. Also, in alcohols, PEI's behavior is superior.

Compared to the other thermoplastics previously characterized in similar fashion[2,5–9,12] PEI is found to be superior for the most part (Figs. 3 and 4). The partial exceptions are poly(2,6-dimethyl-1,4-phenylene oxide) and poly(vinyl chloride), whose ESC resistances are greater in the more polar liquids (Fig. 3). Moreover, under critical *stress* testing (i.e., measurement of the levels of constant applied stress below which crazing or cracking did not occur), the relative superiority of PEI would likely be greater by 20–40%. This is so because the elastic modulus of PEI is 500,000 psi vs. 300,000–400,000 psi for the other resins with which PEI is compared in Figures 3 and 4.

CONCLUSIONS

PEI's profile of resistance to environmental crazing and cracking in organic liquids is qualitatively similar to the profiles of other thermoplastics. As with the other materials, PEI's profile reaches a minimum in non-H-bonded liquids

of small size in a narrow range of δ_s. Also, as with most other resins, alcohols lie on a separate correlation curve.

Taken as a whole, PEI's ESC behavior is superior to that of any other amorphous thermoplastic for which similar comprehensive data are available here for comparison. Moreover, of those thermoplastics tested, only PPO and PVC exhibited superior resistance in any portion of the solvent spectrum (the polar aprotic part). However, in a few liquids that lower the resistance of both PEI and PES markedly, PEI is seen to crack, but PES shows crazing or simply swells. In these few cases PES may possibly be considered less badly damaged than is PEI.

The solubility parameter of PEI, unfortunately, could not be fixed precisely through intrinsic viscosity measurements due to the individualism of most of the required solvents. Ironically the ϵ_c data pinpoint a δ that may be inferred as δ_p (by analogy with the ESC and swelling behavior of other thermoplastics) as well as or better than do the more fundamental $[\eta]$ measurements. Comprehensive swelling data for PEI would be necessary to verify this inference.

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