

Prediction of Environmental Stress Cracking of Polycarbonate from Solubility Considerations

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Synopsis

Simple thermodynamic relationships as well as semiempirical solubility parameter plotting techniques were examined as methods for predicting critical crazing strains of polycarbonate exposed to linear and branched alkanes. In general, measured critical strains correlated with predicted solubilities based on the Flory-Huggins equation. Solubility parameters could also be used to predict critical strains if molecular size differences between specific alkanes were taken into account. These techniques were then extended to polar and hydrogen bonding liquids using two-dimensional solubility parameter plotting representations. A comprehensive listing of critical strains for polycarbonate exposed to over 80 liquids and liquid mixtures is included.

INTRODUCTION

The tendency of glassy plastics to craze or crack when exposed to liquid environments at stresses well below their yield stress in air has been extensively studied.^{1,2} Although the exact mechanism of environmental stress crazing is not known, it is generally accepted that absorption of the liquid and concomitant T_g reduction are intimately related to stress cracking behavior. Several authors³⁻⁸ have shown correlations between the critical crazing stress (or strain) of a polymer exposed to a stress cracking agent and the equilibrium solubility of the liquid in the polymer.

Since equilibrium solubility data are not readily available and require long measurement times, rational attempts have also been made at predicting solubility, and thus stress cracking behavior, directly from molecular and physical properties of the liquid environments. Kambour and co-workers have shown that a general correlation exists between critical strain and the liquid solubility parameter δ for poly(phenylene oxide),³ polysulfone,⁴ polystyrene,⁵ and polycarbonate⁶ exposed to a wide variety of liquid environments. Vincent and Raha⁹ have extended this concept to include a hydrogen bonding parameter to aid in predicting stress cracking characteristics of poly(methyl methacrylate), poly(vinyl chloride), and polysulfone. Henry¹⁰ has used the three-dimensional solubility parameter approach of Hansen^{11,12} to evaluate critical strains of polycarbonate and polysulfone. Other authors^{13,14} have suggested that surface energy and molecular size may be correlated with critical strain or stress. Barton¹⁵ has presented a comprehensive review of the various solubility parameters and methods used to characterize polymer solubility.

Recently, the stress cracking characteristics of polycarbonate exposed to a wide variety of aliphatic hydrocarbons were analyzed in our laboratories.¹⁶ It was found that none of the solubility parameter methods normally used for predicting stress cracking behavior gave an adequate correlation with critical strain for this

class of liquids. In addition, initial sorption studies indicated that many of these liquids have extremely low equilibrium solubilities which would be attained only after extended time periods. This led us to evaluate methods for predicting solubility and to examine the assumptions inherent in the use of solubility parameters. Simple thermodynamic relationships as well as solubility parameter plotting techniques were examined. The purpose of this report is to present methods that may be used to obtain an a priori estimate of the stress cracking susceptibility of polycarbonate exposed to aliphatic hydrocarbons as well as other polar and nonpolar liquids.

Prediction of Solubility from Solution Theory

To a first approximation, solution theory developed by Huggins¹⁷ and Flory¹⁸⁻²⁰ may be used to predict the solubility of a penetrant in a polymer. Although the assumptions inherent in this treatment are seldom met,²¹ the Flory-Huggins equations provide a useful framework for estimating solubility. At constant temperature and pressure, the partial molal free energy of mixing for the penetrant and the polymer may be given by the well known equations

$$\Delta\bar{F}_0 = RT [\ln \phi_0 + (1 - 1/m)\phi_p + \chi\phi_p^2] \quad (1)$$

$$\Delta\bar{F}_p = RT [\ln \phi_p - (m - 1)\phi_0 + m\chi\phi_0^2] \quad (2)$$

where the subscripts 0 and *p* refer to the penetrant and polymer, respectively; $\Delta\bar{F}$ is the partial molal free energy of mixing; *R* is the gas constant; *T* is temperature; ϕ is volume fraction; *m* is the number of elements per polymer molecule; and χ is the semiempirical interaction parameter between polymer and penetrant. The term χ is usually treated as an adjustable parameter which is used to fit experimental data to solution theory. However, with few assumptions,^{21,22} χ for nonpolar systems may be related to the well-known Hildebrand solubility parameter by the relation

$$\chi = \chi_s + \frac{V_0(\delta_p - \delta_0)^2}{RT} \quad (3)$$

where χ_s is the entropy contribution to χ ; *V*₀ is the molar volume of the penetrant; and δ_0 and δ_p are the solubility parameters of the penetrant and polymer, respectively. Experimentally, χ_s is found to be between 0.3 and 0.4 for many systems. At equilibrium, the partial molal free energies of mixing are equal to zero, and the expression defining the equilibrium between swollen polymer and solvent is given by Hildebrand and Scott²¹ as

$$0 = \Delta\bar{F}_0 = RT \left[\ln(1 - \phi_p) + (1 - 1/m)\phi_p + \chi_s\phi_p^2 + \frac{V_0(\delta_p - \delta_0)^2\phi_p^2}{RT} \right] \quad (4)$$

This equation may be further divided into enthalpy and entropy contributions:

$$\Delta\bar{F}_0 = -T \Delta\bar{S}_0 + \Delta\bar{H}_0 \quad (5)$$

where

$$\Delta\bar{H}_0 = V_0(\delta_p - \delta_0)^2\phi_p^2 \quad (6)$$

and

$$\Delta\bar{S}_0 = -R [\ln(1 - \phi_p) + (1 - 1/m)\phi_p + \chi_s\phi_p^2] \quad (7)$$

Solving eq. (4) for ϕ_p yields the equilibrium volume fraction of penetrant in the polymer.

Solubility theory has also been extended by Blanks and Prausnitz²³ to include polar contributions. For a polar-polar system, the heat of mixing may be given by

$$\Delta\bar{H}_0 = V_0[(\lambda_p - \lambda_0)^2 + (\tau_p - \tau_0)^2]\phi_p^2 \quad (8)$$

where λ and τ are defined respectively as the nonpolar and polar solubility parameters. For nonpolar-polar systems, induction contributions must be considered.

Solubility Parameters

In many instances solubility parameters may be used directly to predict solubility without an involved thermodynamic calculation. The normal procedure in one component solubility parameter treatments is to assume that solubility is controlled by the heat of mixing component, $\Delta\bar{H}_0$. Solubility is then inversely proportional to the difference $\delta_p - \delta_0$. Thus, for good solvents, where the heat of mixing is small, $\delta_p \approx \delta_0$. As the difference between the solubility parameter of the solvent and polymer becomes greater, the heat of mixing increases and solubility decreases. When the solubility is plotted against δ_0 , a maximum usually occurs at $\delta_p = \delta_0$.

One serious limitation of the solubility parameter approach is that it does not account for polar and hydrogen bonding forces. What is often done in practice to overcome this deficiency is to develop solubility maps which plot δ against semiempirical values of dipole interactions, hydrogen bonding, or other collective parameters that give a good correlation with solubility.²⁴⁻²⁸ Hansen^{11,12} has extended this concept and divided the solubility parameter into three components:

$$\delta_i^2 = \delta_d^2 + \delta_e^2 + \delta_h^2 \quad (9)$$

where δ_d , δ_e , and δ_h refer to the dispersion, polar, and hydrogen bonding contributions to the total solubility parameter δ_i . The individual solubility parameters are evaluated from experimental solubility observations. Hansen's solubility parameters δ_e and δ_h may be collectively defined as

$$\delta_a = (\delta_e^2 + \delta_h^2)^{1/2} \quad (10)$$

Thus, δ_a becomes an effective polar solubility parameter and is qualitatively equivalent to τ in eq. (8). When values of δ_e and δ_h are not known, δ_a may be estimated by the difference between δ_0 for a polar liquid and for its homomorph.^{15,23} As Barton¹⁵ has pointed out, the total solubility parameter δ_i evaluated from empirical values of individual solubility parameters should not be expected to be identical with the Scatchard-Hildebrand solubility parameter δ_0 .

When using solubility parameters, it must be remembered that solubility is determined by both enthalpic and entropic factors. The use of either one-, two-, or three-dimensional solubility parameter maps largely ignores entropic factors and therefore results in only an approximation of the true solubility of a series of liquids in a given polymer. In summary, for polymer-liquid systems whose equilibrium solubilities have not been measured, one can attempt to correlate

critical strain values with predicted equilibrium solubilities using eq. (4) or, more simply, establish an empirical correlation with solubility parameters.

EXPERIMENTAL

Critical strain is the minimum static strain at which crazes or cracks will form when a polymer is exposed to a liquid or vapor environment. Critical strains for polycarbonate exposed to aliphatic hydrocarbons were measured on an elliptical bending form as described in a previous paper.¹⁶ Lexan LS2-111 polycarbonate was injection molded into tensile specimens conforming to ASTM D638 Type I according to the manufacturer's recommendations. Critical strains reported in this study represent an average of five measurements for each test liquid.

RESULTS AND DISCUSSION

Aliphatic Hydrocarbons

Critical Strain Measurements. The measured critical strains of polycarbonate exposed to 16 linear and branched alkanes are presented in Table I along with appropriate physical constants of the liquids. The critical strain data are plotted as a function of the number of carbon atoms in the chain in Figure 1. In general, the normal alkanes show an increase in critical strain with increasing chain length, while the 2-methyl alkanes show a slight decrease in critical strain with chain length. However, the most significant structural variable is branching. This is most evident in Figure 2, where critical strains for the isomeric hexanes are plotted as a function of hexane boiling point, which is a relative measure of branching.²⁹ For these isomers critical strains increase from 0.85% to 1.68% as branching increases. A similar trend is observed for the octane isomers examined, i.e., *n*-octane, 2-methylheptane, and isooctane (see Table I).

Predicted Solubilities. The equilibrium solubilities for aliphatic hydrocarbons in polycarbonate were estimated from solution theory using eq. (4). A computer-assisted trial and error procedure was used for these calculations. It was assumed that $m = 500$ and $\delta_p = 10$. Calculated solubilities for both $\chi_s = 0$ and $\chi_s = 0.3$ are shown in Table I. The most critical variable in these calculations is the choice of δ_p . The solubility parameter for polycarbonate by Small's method³⁰ is 9.8 to 10 and ranges from 9.5 to 10.5 from swelling measurements in nonpolar solvents.¹⁵ Also shown in Table I are the solubilities measured by Kambour et al.⁶ The agreement between predicted and measured solubilities is reasonably good for the lower molecular weight alkanes, but some inconsistencies appear as the molecular weight is increased. These differences may be due to deficiencies in eq. (4) in predicting solubilities or may be caused by the difficulties in measuring equilibrium solubilities of the higher molecular weight alkanes.

Measured critical strains for polycarbonate exposed to alkanes are plotted as a function of predicted solubility in Figure 3. As expected, critical strain decreases as solubility increases. Undoubtedly, a better correlation between critical strain and predicted solubility could be obtained by using some of the refinements which have been developed in solution theory.²¹ However, even without modification, the Flory-Huggins equations provides a surprisingly good estimate

TABLE I
Physical Constants and Solubilities for Normal and Branched Alkanes and Critical Strains of Polycarbonate Exposed to These Liquids

Liquid	Molecular weight	Boiling point, °C	Molar volume V_0	Solubility parameter δ (ref. 32)	Solubility ϕ_0		Critical strain, %		
					Ref. 6	Equation (5)	Ref. 6	This work	
<i>n</i> -Pentane	72.15	36	116	7.02	0.100	0.068	0.96	0.71	0.83
<i>n</i> -Hexane	86.17	69	132	7.27	0.112	0.075	1.02	0.71	0.85
<i>n</i> -Heptane	100.2	98	147	7.50	0.131	0.086	0.98	0.87	0.89
<i>n</i> -Octane	114.2	126	164	7.54	0.110	0.074	0.93		0.92
<i>n</i> -Decane	142.3	174	195	7.74	0.109	0.073	1.05		1.01
<i>n</i> -Tetradecane	198	252	259	7.0[6]	0.003	0.053	1.18		
<i>n</i> -Hexadecane	226	280	292	8.0[22]	0.011	0.051	1.27		
2-Methylbutane	72.15	28	116	6.75		0.065			1.07
2-Methylpentane	86.17	60	132	7.03		0.075			1.02
2-Methylhexane	100.2	90	148	7.29		0.088			1.01
2-Methylheptane	114.2	114	165	7.34		0.074			0.99
3-Methylpentane	86.17	63	127	7.13		0.097			1.05
2,3-Dimethylbutane	86.17	58	129	6.97		0.071			1.36
2,2-Dimethylbutane	86.17	50	133	6.71		0.041			1.68
2,3-Dimethylpentane	100.2		(144) est.	7.3[6]		0.096	1.04		
2,2,4-Trimethylpentane (isooctane)	114.2	99	165	6.86		0.029			1.66

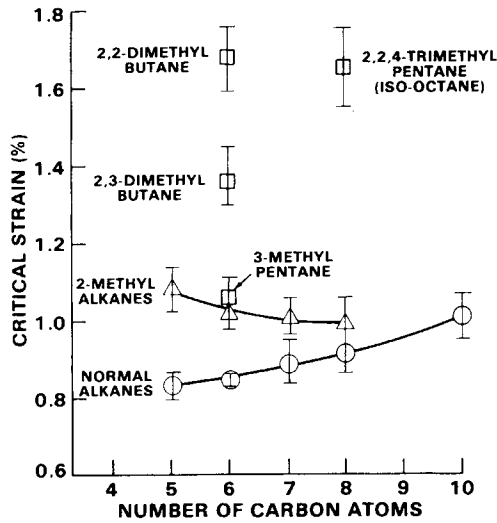


Fig. 1. Critical strains of polycarbonate exposed to aliphatic hydrocarbons.

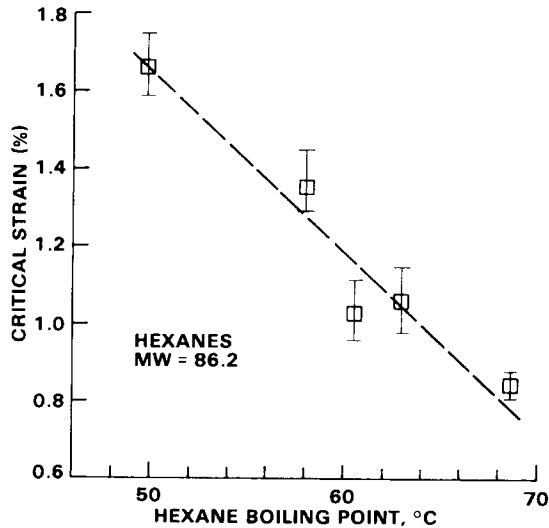


Fig. 2. Critical strains of polycarbonate exposed to hexane isomers as a function of the hexane boiling point.

of solubility and, despite quantitative inaccuracies, does give a method for predicting the relative critical strains of polycarbonate exposed to a wide variety of linear and branched alkanes.

It is also interesting to consider the extreme case where critical strain equals zero in Figure 3. The straight line intercepts the predicted solubility axis above 0.18. This volume fraction is similar to the measured liquid solubility of 0.20 which Kambour reports will reduce the glass transition temperature of polycarbonate to room temperature.⁶ The critical strain for polycarbonate exposed to such a liquid would be expected to be zero, or very small, since the surface of the material would be rubbery. This comparison reinforces the usefulness and general validity of the correlation shown in Figure 3 although, strictly speaking, the relation between critical strain and solubility may be nonlinear, particularly for relatively good solvents.

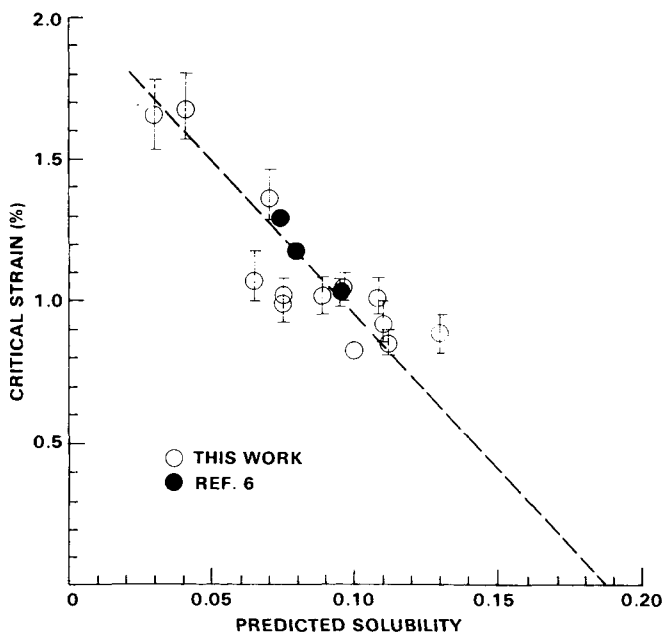


Fig. 3. Critical strains vs predicted solubility for polycarbonate exposed to aliphatic hydrocarbons: (O) This work; (●) reference 6. (Data from reference 6 are critical strains, not measured solubilities.)

Solubility Parameters. Since the alkanes are nonpolar and are not capable of hydrogen bonding, the Scatchard-Hildebrand solubility parameter would be expected to correlate with critical strain. As seen in Figure 4(a), this is not the case. The failure of the solubility parameter alone to predict critical strain is primarily due to the fact that critical strains in linear aliphatic hydrocarbons increase with chain length in spite of increasing favorable solubility parameters, as noted by Kambour.² Since solubility is dependent on molecular volume as well as specific intramolecular forces, both of these factors were incorporated into a single predictive term. The best correlation with critical strain was obtained when the term $V_0(\delta_p - \delta_0)^2$ was used. This term comes directly from the Hildebrand-Scott heat of mixing term, eq. (6), and is directly related to the Flory-Huggins interaction term χ . As shown in Figure 4(b), there is good correlation between critical strain and the term $V_0(\delta_p - \delta_0)^2$.

The effects of chain length and branching shown in Figures 1 and 2 may therefore be explained in terms of the relative contributions of V_0 and $(\delta_p - \delta_0)^2$ to the partial heat of mixing. Solubility is maximized as the heat of mixing is minimized. For branched isomers, the molar volume is approximately constant, but branching reduces the surface area of the molecule and thus decreases the intermolecular forces. The net result is a decrease in solubility parameter and an increase in critical strain with branching. Increasing chain length increases the molar volume V_0 but reduces the square of the difference between solubility parameters, $(\delta_p - \delta_0)^2$. The relative magnitude of these changes determines whether critical strain increases with increasing chain length, as in the case of the normal alkanes, or decreases with chain length, as in the case of the 2-methyl alkanes. Presumably, for a sufficiently broad range of molecular weights, both series of alkanes should exhibit a minimum in critical strain with chain length.

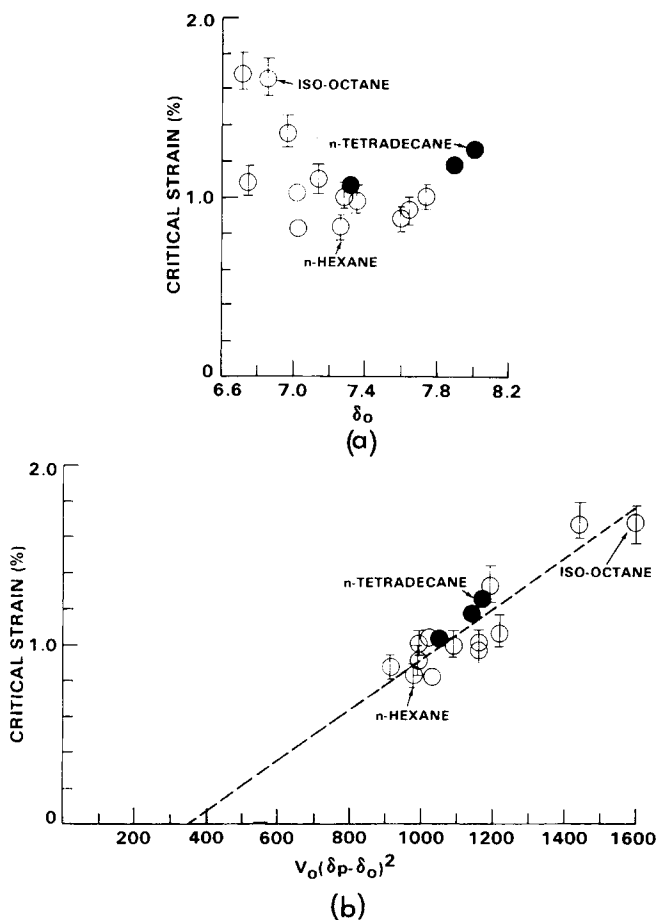


Fig. 4. Measured critical strains of polycarbonate exposed to aliphatic hydrocarbons vs (a) solubility parameter of liquid, and (b) molar volume times the square of the difference in solubility parameters of liquid and polymer: (O) this work; (●) reference 6.

For the relation shown in Figure 4(b), it is interesting to consider the case when critical strain equals zero. At this point the corresponding term $V_0(\delta_p - \delta_0)^2$ is equal to 350. It might be expected that this term should also equal zero, representing the case when $\delta_p = \delta_0$, i.e., a perfect solvent. However, for liquids having molar volumes of 100–150, a difference in solubility parameter of only 1.5–2.0 would give the limiting value of $V_0(\delta_p - \delta_0)^2 = 350$. To answer the question why such liquids might have corresponding critical strains of zero, one can again refer to Kambour's results (Fig. 1).⁶

Liquids having solubility parameters within 2.0 of polycarbonate are observed to cause high swelling of polycarbonate and reduce the glass transition below room temperature. As previously mentioned, the critical strain of polycarbonate exposed to such high-swelling liquids would be expected to be near zero. Thus, the extrapolation of the correlation presented in Figure 4(b) to zero critical strain does not lead to an inexplicable result but rather to one readily interpreted in terms of available solubility and solubility parameter data. It is especially noteworthy that the prediction of zero critical strain for relatively good solvents is obtained using data from liquids which themselves are relatively poor solvents for polycarbonate.

Nonpolar, Polar, and Hydrogen Bonding Liquids

Critical Strain Measurements. The critical strains for polycarbonate exposed to nonpolar, polar, and hydrogen bonding liquids have been reported by Kambour et al.⁶ and Henry.¹⁰ Including our data on hydrocarbons and some hydrocarbon mixtures, over 80 liquids and mixtures have been examined for this polymer. These data are summarized in Table II.

Solubility Parameters. The major difficulty in predicting stress cracking behavior of a wide variety of liquids is in determining the polar and hydrogen bonding contributions to the total solubility parameter. For this reason solution theory methods are often inaccurate. Although Blanks and Prausnitz²³ have extended solution theory to include polar components as shown in eq. (8), this approach involves empirical terms to account for inductive effects and is not applicable to solutions that exhibit specific interactions, such as hydrogen bonding. Thus, solubility parameter correlations are, at the present time, the only methods for rapidly assessing the solubility and stress cracking characteristics of polymers exposed to a broad class of polar, nonpolar, and hydrogen bonding liquids.

Kambour et al.⁶ have shown that the Scatchard-Hildebrand solubility parameter alone is only marginal in predicting critical strains for polycarbonate exposed to polar and nonpolar liquids. Henry¹⁰ has examined correlations of critical strain with Hansen's solubility parameters δ_{0d} , δ_{0e} , and δ_{0h} . In general, only the δ_{0h} plots showed any meaningful variation with critical strain. We have examined several of the two-dimensional^{9,23,24,31} and three-dimensional^{11,12,25,26} solubility parameter mapping techniques discussed in the literature using the data in Tables I and II. For critical strain prediction, the two-dimensional techniques appear to be as accurate as the three-dimensional methods examined and are preferred because of their simplicity.

One example of a two-dimensional critical strain map is shown in Figure 5 for the data in Tables I and II, which are plotted as a function of δ_{0d} , Hansen's nonpolar solubility parameter, and δ_{0a} , the collective polar solubility parameter described by eq. (9). Values of δ_{0d} and δ_{0a} presented in Table II were determined from the comprehensive listing of Hansen's solubility parameters compiled by Barton.¹⁵ For binary mixtures, values of δ_0 were calculated as the sum of the individual liquid δ_0 values in proportion to the volume fraction of each liquid present in the mixture. Each of the critical strains shown in Figure 5 is the average of all reported values rounded to the nearest 0.1%. Liquids with molar volumes greater than 150 are shaded in this figure. Solvents are designated by the letter S. Considering the inherent scatter in critical strain measurements, fairly well-defined contours may be drawn that separate liquids which cause crazing at relatively low, moderate, or high strains.

Most of the liquids shown in Figure 5 have molar volumes near 100. Liquids with molar volumes greater than 150, such as the higher molecular weight alcohols and hydrocarbons, show higher critical strains than lower molecular weight components with approximately the same polar and nonpolar solubility parameters. This is evident in Figure 5. The data were therefore replotted with the coordinates $V_0(\delta_{pd} - \delta_{0d})^2$ versus $V_0(\delta_{pa} - \delta_{0a})^2$ in Figure 6. The polar solubility parameter for polycarbonate, δ_{pd} , and the nonpolar solubility parameter, δ_{pa} , are defined by the relationship

$$\delta_p = 10 = (\delta_{pd}^2 + \delta_{pa}^2)^{1/2} \quad (11)$$

TABLE II
 Critical Strains of Polycarbonate and Physical Constants of Liquid Crazing Agents^a

Liquid crazing agent	Molar volume V_0	Total solubility parameter δ_{0t}	Nonpolar solubility parameter δ_{0d}	Polar solubility parameter δ_{0a}	Critical strain, %		
					This work	Ref. 6	Ref. 10
Hydrocarbons (in addition to TABLE I)							
Benzene	89.4	9.1	9.0	1.0	<0.3		0.2
Toluene	106.8	8.9	8.8	1.2	0.3		
Xylene	121.2	8.8	8.7	1.6	<0.3		0.37
Ethylbenzene	123.1	8.8	8.8	0.3	<0.3		
<i>n</i> -Butylbenzene	155.8	8.6			<0.3		
1,2,4-Trimethylbenzene	137.0	9.0			<0.3		
Carbon tetrachloride	97.1	8.7	8.7	0.3		0.46	
Cyclohexane	108.7	8.2	8.2	0.1		0.84, 0.88	0.86
Methylcyclohexane	128.3	7.8	7.8	0.5			
Ethers							
Diethyl ether	104.8	7.7	7.1	2.9			0.13
Ketones							
Acetone	74.0	9.8	7.6	6.1		0.44, 0.57	
Methyl ethyl ketone	90.1	9.3	7.8	5.1		0.14, 0.50	
Methyl <i>n</i> -propyl ketone		8.7[6]				0.53	
Cyclohexanone	104.0	9.6	8.7	4.0			0.15
Esters							
Methyl acetate	79.7	9.2	7.6	5.1		0.39, 0.78	
Ethylene carbonate	66.0	14.5	9.5	10.8		0.52	
Isoamyl butyrate		8.4[6]				0.18	
<i>n</i> -Butyl acetate	132.5	8.5	7.7	3.6		0.36, 0.38	0.31
Methyl <i>n</i> -butyrate		8.0[6]				0.50	
Propylene 1,2-carbonate	85.0	13.3	9.8	9.0		0.28	
Dibutyl phthalate	266	9.9	8.7	4.6			0.41
Dimethyl phthalate	163	10.8	9.1	5.8			0.31
α -Butyrolactone	76.8	12.9	9.3	8.9			0.30
β -Propiolactone		13.3[6]				0.60	
Nitrogen Compounds							
Nitromethane	54.3	12.3	7.7	9.5	0.69		
Nitroethane	71.3	11.1	7.8	7.9		0.72	
Nitrobenzene	102.7	10.9	9.8	4.6		0.51, 0.51	
Acetonitrile	52.6	12.0	7.5	9.3		0.32, 0.82	
Formamide	39.8	17.9	8.4	15.9		1.3, 1.79	
<i>N</i> -Methylformamide		16.1				0.26, 0.39	0.31
<i>N,N</i> -Dimethylformamide	77.0	12.1	8.5	8.7		1.57	1.5 to 2
Monohydric Alcohols							
Methanol	40.7	14.5	7.4	12.7	1.19	0.98, 1.37	1.22
Ethanol	58.5	13.0	7.7	10.4	1.16	0.84, 1.02	0.97
1-Propanol	75.2	12.0	7.8	9.1		0.76, 1.05	
2-Propanol	76.8	11.5	7.7	8.5		1.01, 1.02	
1-Butanol	91.5	11.3	7.8	8.2		0.94	0.71
1-Pentanol	109	10.6	7.8	7.1		0.91, 0.94, 0.91	
<i>n</i> -Hexanol							0.71
Heptanol		10.5[6]				0.72	
1-Octanol	158	10.2[33]	8.3[33]	6.0[33]		0.93	
1-Nonanol		10.3[6]				1.15	

1-Decanol	190.6	10.0[33]	8.6[33]	5.1[33]	0.97	
Undecanol		9.9[6]			1.02	
1-Dodecanol	233	9.8[33]	8.5[33]	5[33]	1.17	
Tridecanol		9.6[6]			1.04	
Benzyl alcohol	103.6	11.6	9.0	7.4	0.17, 0.35	
Cyclohexanol	106	11.0	8.5	6.9	0.98	1.48
2-Ethylhexanol		9.5[10]				0.87
Allyl alcohol	68.4	12.6	7.9	9.7		0.56
Polyhydric Alcohols						
Ethylene glycol	55.8	16.1	8.3	13.8	1.9	
Glycerol	73.3	17.1	8.5	15.4	>1.9	0.77
Propylene glycol	73.6	14.8	8.2	17.2	1.41, 1.51	
Triethylene glycol	111	13.5	7.8	10.8	0.94, 1.02	
Others						
Carbon disulfide	60.0	10.0	10.0	0.3	.41	—
Dimethyl sulfoxide	71.3	13.0	9.0	9.4	0.25, 0.40	0.31
Dodecamethylpenta- siloxane		5.35[6]			1.19, 1.78	
Perfluoromethyl- cyclohexane		5.85[6]			1.59	
Hexamethyl-di- siloxane		6.0[6]			1.48, 1.66	
Glacial acetic acid		10[10]				0.15
Methyl Cellosolve		10.8[10]				0.15
Freon 113		7.2	7.2	0.8	0.95, 1.26	
Water	18	23.4	7.6	21.9	1.9	
Hydrocarbon Mixtures						
75% Pentane/25% isooctane	128	6.98	6.98	0	1.05	
50% Pentane/50% isooctane	141	6.94	6.94	0	1.25	
25% Pentane/75% isooctane	153	6.90	6.90	0	1.4	
75% Toluene/25% isooctane	121	8.39	8.35		0.32	
50% Toluene/50% isooctane	136	7.93	7.90	0.5	0.40	
25% Toluene/75% isooctane	150	7.37	7.35	0.3	0.60	
25% Benzene/75% isooctane	146	7.42	7.40	0.25	0.74	
25% <i>n</i> -Butylbenzene/ 75% isooctane	163	7.30	7.30		0.75	

^a Physical constants of liquid crazing agents are proportional averages.

Choosing $\delta_{pd} = 9.5$ and $\delta_{pa} = 3$ gave the best fit to the data. This method of plotting the data gives a reasonably good correlation between critical strain and the molar volume solubility term for both small and large molecules. Liquids with solubility parameters near δ_{pd} or δ_{pa} tend to be good solvents and have low values of critical strain. As the difference between the solubility parameters of the liquid and polymer increase, critical strains increase. Critical strains of high molecular weight alcohols and hydrocarbons are much better defined by including the molar volume terms as in Figure 6 than by using polar and nonpolar solubility parameters alone as in Figure 5. For other liquids with relatively large molar volumes, such as commercial plasticizers, solubility parameter mapping should also include a molar volume term.

Of the 80 plus liquids represented in Figure 6, only two fall outside the general

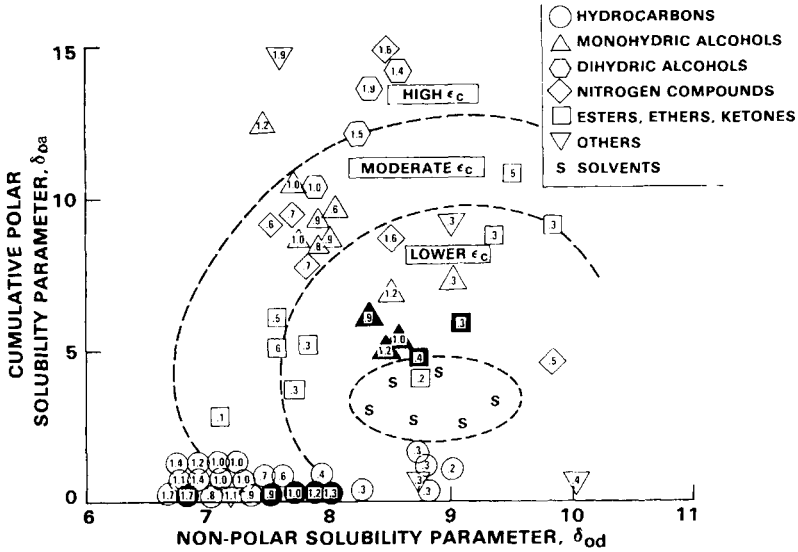


Fig. 5. Solubility parameter map of polycarbonate critical strain (ϵ_c). Numbers included in symbols are values of critical strain. Liquids having molar volumes greater than 150 are represented by filled symbols. O, hydrocarbons; Δ , monohydric alcohols; \circ , dihydric alcohols; \diamond , nitrogen compounds; \square , esters, ethers, ketones; ∇ , others; S, Solvents.

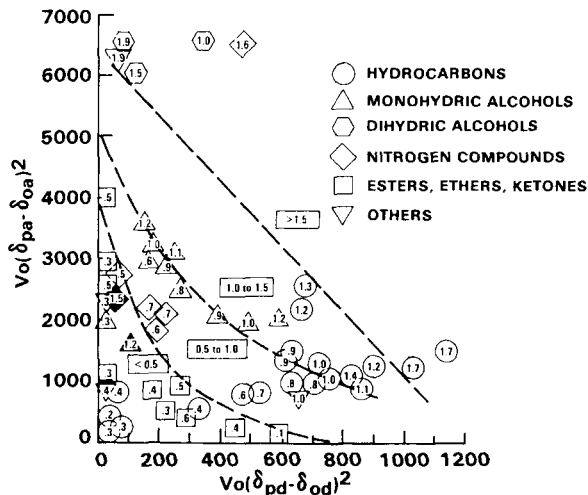


Fig. 6. Solubility parameter map of polycarbonate critical strain with a molar volume term. Numbers included in symbols are values of critical strain. Liquids falling outside the general critical strain contours are represented by filled symbols. O, hydrocarbons; Δ , monohydric alcohols; \circ , dihydric alcohols; \diamond , nitrogen compounds; \square , esters, ethers, ketones; ∇ , others.

critical strain contours. These are dimethylformamide (DMF) and cyclohexanol, which are shown shaded in the figure. Cyclohexanol is a poorer solvent than predicted by its solubility parameters and thus exhibits a higher critical strain than expected. DMF exhibits a high value of critical strain even though this liquid is adsorbed to relatively high equilibrium concentrations. The behavior is believed to be related to rapid stress relaxation which occurs before crazes can propagate and grow and results in anomalously high apparent values of critical strain. Methylene chloride, a good solvent for polycarbonate, exhibits similar

behavior and only causes crazing at very high values of strain. From a practical point of view, such good solvents would naturally be avoided in usage of polycarbonate parts, and their lack of fit in Figure 6 is not considered a serious drawback to the solubility parameter mapping approach.

CONCLUSIONS

The most accurate measure of the ability of a liquid to reduce the critical strain for brittle fracture of a glassy polymer is the equilibrium solubility of the liquid in the polymer. Because of the difficulties of measurement, however, equilibrium solubilities of most potential stress cracking agents are not available in the literature. In these cases, an a priori estimate of solubility, and thus stress cracking susceptibility, may be obtained using either polymer solution theory or semi-empirical solubility parameters.

For nonpolar liquids, such as the aliphatic hydrocarbons, the Flory-Huggins equation with a heat of mixing term using Hildebrand solubility parameters gives a reasonable estimate of equilibrium solubility. Solubility parameters alone may also be used to predict the relative stress cracking behavior of linear and branched hydrocarbons if the influence of molecular size as well as differences in solubility parameters for polymer-liquid pairs are taken into account.

For a broad range of liquids that exhibit polar, hydrogen bonding, and van der Waals interactions, the Flory-Huggins equations cannot be used to unambiguously determine solubilities or critical strains. However, a two-dimensional solubility parameter representation employing a molar volume term provides critical strain contours for polycarbonate that can be used to predict the stress cracking behavior in pure liquids and mixtures of hydrocarbons. The applicability of this approach to other liquid mixtures and other polymer systems is presently being determined.

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References

1. S. Rabonowitz and P. Beardmore, *CRC Rev. Macromol. Sci.*, **1**, 1 (1972).
2. R. P. Kambour, *Macromol. Rev.*, **7**, 1 (1973).
3. G. A. Bernier and R. P. Kambour, *Macromolecules*, **1**, 393 (1968).
4. R. P. Kambour, E. E. Romagosa, C. L. Gruner, *Macromolecules*, **5**, 335 (1972).
5. R. P. Kambour, C. L. Gruner, E. E. Romagosa, *J. Polym. Sci., Polym. Phys.*, **11**, 1879 (1973).
6. R. P. Kambour, C. L. Gruner, E. E. Romagosa, *Macromolecules*, **7**, 249 (1974).
7. Y. Imai and N. Brown, *J. Mater. Sci.*, **11**, 417 (1976).
8. J. C. Devins and C. W. Reed, in *Ann. Conf. on Electr. Insul. and Diel. Phenom., Natl. Acad. Sci.*, 1971, p. 86.
9. P. I. Vincent and S. Raha, *Polymer*, **13**, 283 (1972).
10. L. F. Henry, *Polym. Eng. Sci.*, **14**, 167 (1974).
11. C. M. Hansen, *J. Paint Technol.*, **39**, 104 (1967).
12. C. M. Hansen, *J. Paint Technol.*, **39**, 511 (1967).
13. B. L. Earl, R. L. Loneragan, J. H. T. Johns, M. Crook, *Polym. Eng. Sci.*, **13**, 390 (1973).
14. R. L. Bergen, Jr., *SPE J.*, **24**, 77 (1968).
15. A. F. M. Barton, *Chem. Rev.*, **75**, 731 (1975).

16. M. G. Wyzgoski and C. H. M. Jacques, *Polym. Eng. Sci.*, **17**, 854 (1977).
17. M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941).
18. P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941).
19. P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).
20. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.
21. J. H. Hildebrand and R. L. Scott, *Solubility of Nonelectrolytes*, Dover, New York, 1964.
22. J. H. Hildebrand, J. M. Prausnitz, R. L. Scott, *Regular and Related Solutions*, Von Nostrand-Reinhold, New York, 1970.
23. R. F. Blanks and J. M. Prausnitz, *Ind. Eng. Chem. Fundam.*, **3**, 5 (1964).
24. *Technical Bulletin PA12-770*, E. I. du Pont de Nemours & Co., Electrochemical Dept., Wilmington, Delaware.
25. J. D. Crowley, G. S. Teague, Jr., and J. W. Lowe, Jr., *J. Paint Technol.*, **38**, 496 (1966).
26. R. C. Nelson, R. W. Hemwall, and G. D. Edwards, *J. Paint Technol.*, **42**, 637 (1970).
27. H. Burrell, *Interchem. Rev.*, **14**, 3 (1955).
28. J. L. Gardon, *J. Paint Technol.*, **38**, 149 (1966).
29. R. T. Morrison and R. N. Boyd, *Inorganic Chemistry*, Allyn and Bacon, Boston, 1968.
30. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
31. E. D. Lieberman, *Off. Dig. Fed. Soc. Paint Technol.*, **29**, 1069 (1957).
32. K. L. Hoy, *J. Paint Technol.*, **42**, 76 (1970).
33. K. D. Nisbet, *Polym. Prepr.*, **17**, 385 (1976).

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