Improved Thermodynamic Approach for Predicting the ESC Behavior of Polycarbonate in Binary Liquid Mixtures

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Received 10 December 1997; accepted 17 August 1998

ABSTRACT: This article examines the environmental stress cracking (ESC) behavior of Lexan polycarbonate in a range of mixed environments. The main aim of the work was to establish whether thermodynamic correlations, which can predict ESC to some extent with single environments, hold when dealing with mixed environments. The binary solvent mixtures used were produced from combinations of water, ethanol, benzyl alcohol, trimethylhexanol, and ethylhexanol. Samples of polycarbonate were subject to three-point bend tests while immersed in environments of various composition. From these, the critical strain (ε_{crit}) required to produce crazing was determined in each case. The use of the Hildebrand solubility parameter (δ) to predict ESC behavior was examined. A simple law of mixtures would suggest that given a mixture of two environments with δ_1 and δ_2 on either side of δ for the polymer there should exist a composition at which the solubility parameter of the polymer and mixture should be equal, giving severe ESC or even solvation. Plots of $\varepsilon_{\rm crit}$ versus δ show that this is not necessarily the case. Finally, an enthalpic parameter, based on the Flory-Huggins theory and utilizing partial solubility parameters, was applied and shown to give a reasonable correlation with the critical strains obtained. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2155-2161, 1999

Key words: polymers; polycarbonate; environmental stress cracking; crazing; mixtures

INTRODUCTION

Environmental stress cracking (ESC) is a cause of major concern for designers and users of polymeric products. It accounts for a high proportion of in-service failures, occurs suddenly, often catastrophically, and has, to date, proved difficult to predict. ESC occurs when a stressed polymer comes into contact with a particular chemical or environment (most commonly, an organic solvent) and results in the sample failing at a stress significantly lower than usual.

The most widely accepted mechanism for ESC is that diffusion of the environment into the

stressed polymer causes plasticization of the surface layer, increasing the ability for chain motion. The stress causes voids to form, which, in turn, act as sites for preferential diffusion, finally leading to the coalescence of the voids to form a craze. It has generally been shown that for craze formation there must exist sufficient plasticization for a given stress/strain or vice versa.^{1,2} This yields the concept of a critical stress $\sigma_{\rm crit}$ or critical strain $\varepsilon_{\rm crit}$ for each polymer/environment combination.³

The degree of plasticization will depend on the quantity of the environment that diffuses in and also on the size of the environment molecules. Solution thermodynamics has been applied reasonably successfully to this situation. For mixing to be favorable, the Gibbs energy of mixing must be negative. The entropy change for mixing will

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Journal of Applied Polymer Science, Vol. 71, 2155-2161 (1999)

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always provide a negative contribution to this, and so to obtain mixing, the enthalpy change on mixing must be negative or positive but small.

The best treatment of polymer/liquid interaction is given by Flory–Huggins theory⁴ which deals with both the enthalpic and entropic terms of mixing. This derives expressions for the partial free energies of mixing for the solvent and polymer, ΔG_s and ΔG_p , respectively:

$$\Delta G_s = RT \left[\ln \phi_s + \left(1 - \frac{1}{m} \right) \phi_p + \chi \phi_p^2 \right] \quad (1)$$

$$\Delta G_p = RT[\ln \phi_p + (m-1)\phi_s + \chi \phi_s^2] \qquad (2)$$

where R is the universal gas constant; T, the temperature; ϕ_p and ϕ_s , the volume fractions of the polymer and solvent, respectively; m, the ratio of molar volumes of the solvent and polymer; and χ , a semiempirical interaction parameter. The interaction parameter contains both enthalpic and entropic contributions. The entropic part has been found to be close to 0.3 for a wide range of systems, and so the major factor that determines the degree of mixing is the enthalpic part of this parameter, χ_H .

This parameter can be calculated from the Hildebrand–Scatchard theory,⁵ such that

$$\chi_H = \frac{v}{RT} (\delta_p - \delta_s)^2 \tag{3}$$

where v is the solvent molar volume, and δ_p and δ_s , the solubility parameters for the polymer and solvent, respectively.

The solubility parameter is a value obtained by considering the bond energies of the components and represents the square root of the cohesive energy density. For liquids, it is obtained from the energy of vaporization, $\Delta E_{\rm vap}$:

$$\delta = \sqrt{\frac{\Delta E_{\rm vap}}{\upsilon}} \tag{4}$$

and for polymers, it is obtained by summing bond energies or by solvation studies.

For a greater degree of mixing, the term χ_H should be as small as possible, which is obtained by having $(\delta_p - \delta_s)$ as small as possible, that is, having the solubility parameters of the polymer and solvent closely matched. This has been shown to provide a useful tool in predicting the severity

of the ESC. Many studies have shown good correlations between the ESC behavior and the solubility parameter of the environment such that the most severe ESC attack is seen when the solubility parameter of the liquid closely matches that of the polymer.^{6,7}

One weakness of these simple correlations is that they take no account of the contributions to the cohesive energy of dispersive, polar, and hydrogen bonding. This can be accommodated to some extent by using Hansen partial parameters,⁸ where the total solubility parameter is made up of dispersive, δ_d , polar δ_p , and hydrogenbonding δ_b , components:

$$\delta_{\rm tot} = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \tag{5}$$

Attempts using contour plots to produce a correlation between the critical strain for crazing and the three-component solubility parameter have achieved some success,⁹ with one of the best treatments given by Mai,¹⁰ who utilized the enthalpic interaction parameter and partial solubility parameters and dealt with the effects of applied stress to produce very good correlations with several polymers in a wide range of single-component liquid environments.

Very little work has been performed to date on mixed environment systems, and yet in reality, these probably make up the bulk of environments encountered in service. A simple approach which has been used in practice is to use a law of mixtures to produce a single solubility parameter for the mixed environment. This would suggest that a mixture of two environments with solubility parameters either side of that of the polymer would, as concentration varied, yield a better solvent (and stress-cracking agent) than either of the single environments. This synergistic effect has been shown to occur only with a very limited number of environments. Solvent-solvent interactions and volumetric effects make this behavior difficult to predict using traditional solubility parameter methods. This work examines the nonlinear, nonsynergistic behavior of polycarbonate in mixed environments (predominantly of alcohols) and proposes an alternative method for predicting ESC behavior.

EXPERIMENTAL

The material used was bisphenol A polycarbonate (Lexan161), chosen as a typical amorphous ther-



Figure 1 Crazed sample showing craze width, b.

moplastic that shows clear ESC crazes. Strip samples of 13-mm width and 55-mm length were cut from a 1-mm-thick sheet. The edges of these were then ground with abrasive papers to remove excessive stress concentrations. Prior to testing, the material was annealed at 160°C for 2 h to relieve any residual stresses. The material was then stored at room temperature for approximately 4 months to ensure that differences in the physical aging between the samples was negligible. The samples were then placed in three-point bend testers of a similar design to those used by Vincent and Raha,⁹ a predetermined strain was imparted, and the sample was immediately immersed in the test liquid. The maximum strain was calculated from the applied deflection, d, the thickness, t, and span length, L, using eq. (6):

$$\varepsilon_{\rm app} = \frac{6dt}{L^2} \tag{6}$$

After a test period of 2 h, which was shown to be long enough to ensure that no further crazes would form, the samples were removed and the width of the band of crazing was measured using an optical microscope. Where no crazing was observed, a width value of zero was recorded. The craze width was determined using the criterion that if a craze extended over the middle of the sample it was used, whereas small ones originating from edge defects were not, as illustrated in Figure 1.

Several tests at different values of applied strain were performed for each mixture. The critical strain can then be determined either by calculating the strain at the edge of the band of crazes in each test or by extrapolating the craze width/applied strain curve to a zero craze width or by iteratively determining the strain required to just form crazes. The last of these methods has been shown to be the most reliable measure¹¹, and so was used throughout to determine the critical strain, although the other two methods were used to define the approximate strain required.

The environments used were all alcohols apart from water. They were water, ethanol, benzyl alcohol, ethylhexanol, and 1,3,3-trimethylhexanol (TMH). Binary mixtures of these environments were prepared to cover all possible combinations, apart from water, which was only mixed with ethanol. In all cases, the mixtures were kept covered at all times to ensure evaporation and, hence, a change in composition was minimized. Mixtures were produced to give a reasonable spread of volume percentages in each case.

The solubility parameters and molar volumes of all the environments used are listed in Table I.¹² Also included are the solubility parameters for polycarbonate, which are determined as the average values from published data, but it should be stressed that these are open to considerable

Environment	Hildebrand Solubility Parameter (MPa ^{1/2})	Hansen (Partial) (MPa ^{1/2})			Molar
		Dispersive	Polar	Hydrogen	Volume (cm ³ /mol)
Water	48.0	15.5	16	42.2	18
Ethanol	26.6	15.8	8.8	19.4	59
Benzyl alcohol	23.7	18.4	6.3	13.7	104
Ethylhexanol	20.1	16.0	3.3	10.9	157
TMH	18.5	15.4	3.0	10.0	174
Polycarbonate	22.7	18.5	8.2	10.2	—

Table I Solubility Parameters and Molar Volumes



Figure 2 Craze width versus maximum applied strain for polycarbonate in mixtures of TMH and benzyl alcohol.

debate as there is no reliable method of measuring such parameters.

RESULTS AND ANALYSIS

The values of the craze width against the applied strain are shown in Figure 2 for the benzyl alcohol/TMH system. It can be seen that for each environment the craze width decreases as the applied strain decreases, until it reaches a critical value, below which no crazes are seen. It can also be seen that this critical strain value increases as the proportion of TMH increases. Similar graphs were produced for all the combinations tested. From these, the values of the critical strain were plotted against the volume concentration. These are shown in Figures 3–9 for all the combinations tested.

From these, it can be seen that, although the general trend is between the critical strains for the two parent solvents, the behavior is decidedly nonlinear. The variations observed could be attributable to errors in measuring the critical strain, but given the large number of tests, the consistency of deviation, and a calculated error of typically 0.05% strain, this is unlikely.

With some graphs, the behavior is markedly asymmetric, especially those containing benzyl alcohol, where the addition of a small concentration of a second solvent has virtually the same effect as has pure benzyl alcohol. The curves with benzyl alcohol typically show a negative deviation from linearity, whereas the ethanol/water and



Figure 3 The critical strain for crazing versus concentration for mixtures of water and ethanol.

ethanol/TMH combinations show a positive deviation. These departures from linearity suggest that the two liquids do not act independently and that some form of synergistic or antagonistic effects are occurring.

For each of the mixtures, an "average solubility parameter" was calculated using a law of mixtures. The critical strain to crazing in each combination is plotted against this average parameter in Figure 10. As seen in previous work, if the pure liquids are considered, there is a minimum critical strain for crazing as the solubility parameter of the solvent approaches that of polycarbonate ($\sim 22 \text{ MPa}^{1/2}$). Either side of this, the critical strain increases. When considering the mixed environments, however, it is plain that this ap-



Figure 4 The critical strain for crazing versus concentration for mixtures of ethanol and benzyl alcohol.



Figure 5 The critical strain for crazing versus concentration for mixtures of ethanol and TMH.

proach is not valid. Not only is the nonlinearity discussed above apparent, but also combinations on either side of the minimum do not produce severe ESC agents. If a law of mixtures approach were to be valid, the combinations of TMH/ethanol and ethylhexanol/ethanol would be expected to produce a very low value of critical strain with intermediate compositions. This is plainly not the case.

It is clear that a more complex analysis is required that can deal with the true interaction of the two liquids with the polymer, considering synergistic/antagonistic effects as well as dealing with partial solubility parameters. A first approximation to this can be obtained by considering the enthalpic interaction parameter χ_H . This is given



Figure 6 The critical strain for crazing versus concentration for mixtures of ethanol and ethylhexanol.



Figure 7 The critical strain for crazing versus concentration for mixtures of benzyl alcohol and TMH.

by eq. (3) and can be modified to include the partial solubility parameters in combination with eq. (5):

$$\chi_{H} = \frac{\upsilon_{2}}{RT} \left[(\delta_{d1} - \delta_{d2})^{2} + (\delta_{p1} - \delta_{p2})^{2} + (\delta_{h1} - \delta_{h2})^{2} \right]$$
(7)

where the subscripts 1 and 2 refer to the polymer and liquid, respectively.

In a mixed environment, it is possible to consider the enthalpic contributions to mixing as independent and additive, proportional to the volume fraction, ϕ . This can be expressed in eq. (8),



Figure 8 The critical strain for crazing versus concentration for mixtures of benzyl alcohol and ethylhexanol.



Figure 9 The critical strain for crazing versus concentration for mixtures of TMH and ethylhexanol.

where the subscripts 1, 2, and 3 refer to the polymer and the two liquids, respectively:

$$\chi_{H} = \frac{\phi_{2}v_{2}}{RT} [(\delta_{d1} - \delta_{d2})^{2} + (\delta_{p1} - \delta_{p2})^{2} + (\delta_{h1} - \delta_{h2})^{2}] + \frac{\phi_{3}v_{3}}{RT} [(\delta_{d1} - \delta_{d3})^{2} + (\delta_{p1} - \delta_{p3})^{2} + (\delta_{h1} - \delta_{h3})^{2}]$$
(8)

The value of this enthalpic term was calculated for each of the mixtures used, and the critical strain to crazing is plotted against these values in Figure 11. It can be seen that although there are still some nonlinear effects the



Figure 10 The critical strain for crazing for all mixtures plotted against the average solubility parameter determined by the law of mixtures.



Figure 11 The critical strain for crazing for all the mixtures plotted against the enthalpic interaction parameter.

correlation is much better. Given that there are still some assumptions implicit in the model, namely, that solvent-solvent interactions have been neglected, it shows distinct promise as a tool for predicting ESC in mixed environments. One difficulty may lie in the uncertainties inherent in defining partial parameters for a polymer, but even if these were determined by fitting a reasonably small amount of experimental ESC data, the predictions obtained by this approach with a wider range of environments would then be significantly better than current methods.

CONCLUSIONS

Tests were performed on polycarbonate immersed in binary mixtures, mainly alcohols, in order to determine the critical strain for crazing in various concentrations. It was found that the critical strain correlated reasonably well with the solubility parameter for single environments, with lower critical strains seen when the environment's solubility parameter approached that of the polymer. The correlation does not hold for mixed environments as the critical strain does not vary linearly with the concentration. In addition, no significant synergistic effects were seen for environments whose solubility parameters lay on either side of that for the polymer.

A better correlation was obtained by using the enthalpic contribution to the Flory interaction parameter and using Hansen partial solubility parameters. This method is still not ideal, and further work examining the solvent-solvent interactions should lead to refinements, but it does provide a major improvement on the law of mixtures approach.

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