

# The Role of Surfactant Structure and Monoethanolamine in the Environmental Stress Cracking of Polycarbonate

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## Synopsis

The critical strains required to initiate cracking of polycarbonate exposed to a number of poly(oxyethylene)ethoxylate surfactants were determined. Solubility parameters of the surfactants were calculated from knowledge of the molecular structure. A model proposed by Jacques and Wyzgoski that uses the square of the solubility parameter difference of the surfactant and polycarbonate and the surfactant molar volume was determined to be useful for predicting critical strains for polycarbonate. A major assumption in this model is that stress cracking is related to swelling or plasticization of the polymer by the cracking agent, which ultimately leads to the polymer's failure. However, the model does not predict the observed strong stress cracking of polycarbonate by monoethanolamine. In this investigation it was determined that polycarbonate is chemically degraded by monoethanolamine. This degradation is sufficient to initiate stress cracking at lower strains than would otherwise be predicted by solubility parameter and molar volume concepts. With the knowledge obtained from this investigation, it is possible to predict which poly(oxyethylene)ethoxylate surfactants are stress cracking agents for polycarbonate.

## INTRODUCTION

The stress cracking characteristics of both a polycarbonate, and a polymer blend containing polycarbonate, exposed to windshield washer fluids were previously described.<sup>1</sup> In that study a detailed examination was conducted to determine which of the components of the fluids were responsible for the observed stress cracking behavior. Quantitatively, the criterion used to assess the stress cracking potential of a given component was to determine the minimum or critical strain required to initiate cracking of the polycarbonate when exposed to that liquid. Generally, liquids that reduce the critical strain values for the plastic to less than 0.50% are regarded as potent stress cracking agents. Two components of the windshield washer fluid, monoethanolamine and the surfactant, were determined to be strong stress cracking agents for polycarbonate.<sup>1</sup> Further results with windshield washer fluids prepared with and without surfactant and/or monoethanolamine showed that higher strains were required to crack polycarbonate upon fluid exposure once these ingredients were eliminated from the formulation. This was taken as conclusive evidence that these components are the cause of polycarbonate stress cracking in the windshield washer fluid. Both components, however, are considered essential as effective wetting and degreasing agents for the fluid.

Since the late 1960's efforts have been directed towards *a priori* predictions to ascertain whether stress cracking will occur for a given polymer-liquid pair.<sup>2-12</sup> For a wide range of organic agents in several glassy polymers

(including polycarbonate), Kambour and colleagues have shown stress cracking to be related to the equilibrium solubility of the absorbed organic agent in the polymer and the attendant reduction of the polymer's glass transition temperature.<sup>2-9</sup> They have also pointed out that obtaining such data is laborious and time-consuming; however, a general correlation of critical strain with the solubility parameter difference of the liquid and polymer was shown. Jacques and Wyzgoski further refined the solubility parameter model by taking into account the molecular size of the organic agent.<sup>12</sup>

The scope of the work presented in this paper covers a detailed investigation into the mechanisms of stress cracking of polycarbonate by surfactants and monoethanolamine. Also the utility of the solubility parameter model in predicting the stress cracking behavior for a variety of poly(oxyethylene)ethoxylate surfactants is examined.

## EXPERIMENTAL

### Materials

Lexan LS2-111 polycarbonate in pellet form, supplied by General Electric Co., was used in this investigation. Tensile specimens conforming to ASTM D638 Type I specifications were molded using a New Britain injection molding machine according to the supplier's recommendations. Prior to testing, these specimens were dried for 24 h at 100°C, and this was followed by vacuum annealing at 155°C for 6 h to relieve residual stresses. Samples were annealed between two Teflon sheets with a glass plate on top to prevent the specimens from curling or warping. They were slowly cooled to room temperature inside the oven to prevent air quenching.

Surfactants and monoethanolamine were used as received without further purification. However, extensive analyses were performed on the surfactants to determine their chemical structures.

Densities of the surfactants were determined using a Weld pycnometer at 20°C as described by Daniels et al.<sup>13</sup> These densities and other characterizations are listed in Table I. Ethylene oxide content and peak molecular weights were determined by nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC), respectively. Densities and molecular weights were used to calculate molar volumes. Also, the structures of the ethoxylates were determined using NMR. Other stress cracking agents were of reagent grade quality and were used as received.

### Critical Strain Determination

Critical strains were determined using an elliptical bending form. This device allowed the simultaneous exposure of the sample to a spectrum of strains and permitted, in principle, the determination of critical strain with a single sample. In practice, however, it was necessary to use several specimens to establish the experimental variability and define the critical strain. The detailed description of this apparatus and its use were reported by Wyzgoski and Jacques.<sup>14</sup> Measurements were performed 48 h after the samples were exposed to the stress cracking liquids. Samples were covered with a cotton

TABLE I  
Characterization of Nonionic Surfactants

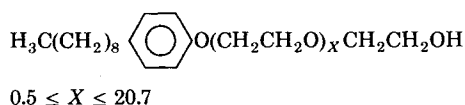
Surfactant	Base alcohol for ethoxylate	Ethylene oxide (mol)	Density at 20° C (g/cm <sup>3</sup> )	Molecular weight (g/mol)
A	Octylphenol	1.7	0.9950	400
B	Octylphenol	2.9	1.0169	450
C	Nonylphenol	1.5	0.9861	400
D	Nonylphenol	4.1	1.0221	550
E	Nonylphenol	4.0	1.0184	500
F	Nonylphenol	6.0	1.0375	600
G	Nonylphenol	7.0	1.0477	750
H	Nonylphenol	8.0	1.0545	800
I	Nonylphenol	9.4	1.0647	900
J	Nonylphenol	3.8	1.0209	500
K	Nonylphenol	21.7	1.0706	2700
L	6-Dodecanol	8.0	1.0035	900
M	<i>n</i> -Dodecanol	6.0	0.9891	900
N	2,6,8-Trimethylnonanol	3.0	0.9161	400
O	2,6,8-Trimethylnonanol	7.0	1.0019	1000

gauze saturated with the liquid to prevent evaporation of the liquid during the interim period.

## RESULTS

### The Role of the Surfactant

In order to examine systematically the effect of ethylene oxide content on the stress cracking of polycarbonate, a family of ethoxylated nonylphenol based ethylene oxide surfactants was used. The general structure of this class of surfactant is shown below:



In Figure 1, the critical strain required to initiate stress cracking of polycarbonate is plotted as a function of ethylene oxide content in the surfactant. The data show a systematic decrease in critical strain in going from 1.5 to 8.0 mol of ethylene oxide with an apparent slight increase in critical strain for 9.4 mol of ethylene oxide. An upswing in this curve is evident since the surfactant containing 21.7 mol of ethylene oxide has a critical strain greater than 2.3% (which is the upper limit of the elliptical bending form used). Unfortunately, however, there are no data between 9.4 and 21.7 mol of ethylene oxide which would more clearly define the curve. These results do show that for the nonylphenol ethoxylate based polyoxyethylene containing 6 or less mol of ethylene oxide that the critical strains for polycarbonate are greater than 0.5% and continue to increase monotonically with decreasing mol of ethylene oxide.

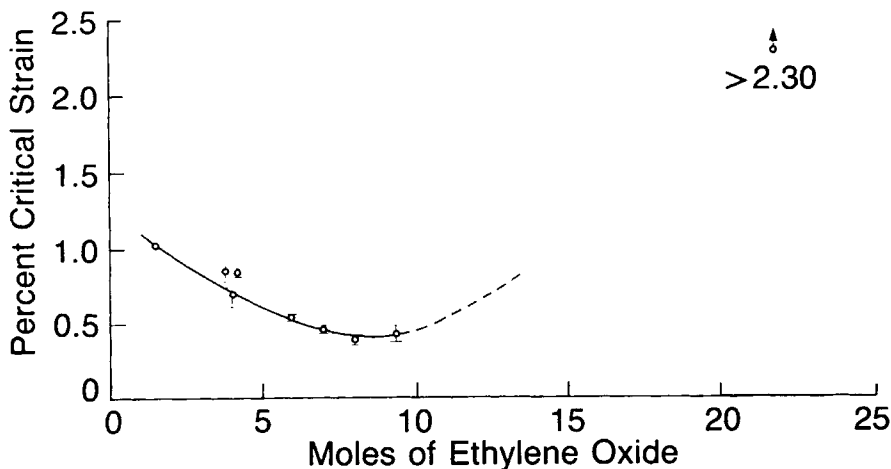


Fig. 1. The effect of ethylene oxide content contained in the structure of nonylphenol based surfactants on the critical strain for polycarbonate.

The systematic variation of critical strain with ethylene oxide content suggests that this behavior may be interpreted straightforwardly in terms of the molecular structure of the surfactant, and thus related to the solubility parameter. In general, a comparison of the solubility parameter of the polymer with that of the liquid has been useful in understanding the observed stress cracking characteristics of the system:<sup>7</sup> The smaller the solubility parameter difference, the greater the potential for stress cracking to occur. Consequently, it is desirable to apply the concept of solubility parameter differences to surfactants. Unfortunately, the solubility parameters for a wide class of surfactants have not been reported in the open literature.

From a knowledge of the surfactant structure, however, it is possible to calculate its solubility parameter. The solubility parameter of polyoxyethylene, which is a major constituent of the surfactant, has been reported<sup>15</sup> to fall between 8.9 and 12.7 (cal/cm<sup>3</sup>)<sup>1/2</sup>. For our calculations we have chosen 10.8 (cal/cm<sup>3</sup>)<sup>1/2</sup>, which is the midpoint of the reported values. Also, Hoy<sup>16</sup> has described a method, based on molecular constituents, that may be used to calculate solubility parameters. Hoy's method involves the assignment of a value for each molecular constituent which are summed and then divided by the molecular weight to obtain the solubility parameter. Using Hoy's method, one may then calculate the solubility parameter of the ethoxylate portion of the surfactant. By estimating the solubility parameter of polyoxyethylene, and calculating the solubility parameter of the ethoxylate portion, the following equation was used to determine the solubility parameter of the surfactant:

$$\delta_{\text{surfactant}} = \frac{M_E(\delta_E)}{M_S} + \frac{M_{\text{PEO}}(\delta_{\text{PEO}})}{M_S}$$

where  $M_E$  = molecular weight of ethoxylate portion of surfactant,  $M_{\text{PEO}}$  = molecular weight of polyoxyethylene portion of surfactant,  $M_S$  = molecular weight of surfactant,  $\delta_E$  = solubility parameter of ethoxylate portion of surfactant, and  $\delta_{\text{PEO}}$  = solubility parameter of polyoxyethylene portion of surfactant. Thus, the determination of the solubility parameter of the surfac-

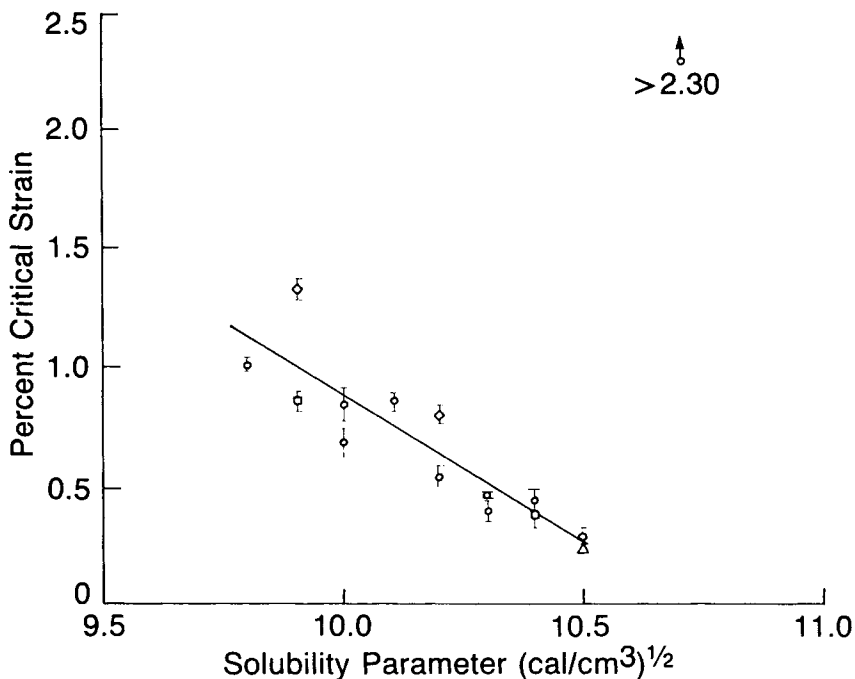


Fig. 2. The influence of surfactant solubility parameter on the critical strain for polycarbonate: (○) poly(oxyethylene)ethoxylates of nonylphenol; (□) poly(oxyethylene)ethoxylates of 2,6,8-trimethylnonanol; (◇) poly(oxyethylene)ethoxylates of octylphenol; (○) poly(oxyethylene)ethoxylate of 6-dodecanol; and (△) poly(oxyethylene)ethoxylate of n-dodecanol.

tant is based on the sum of fractional contributions of the ethoxylate and ethylene oxide portions of the molecule on a normalized molecular weight basis.

In Figure 2, the critical strain for polycarbonate is plotted against the calculated solubility parameters for the various surfactants. The majority of the surfactants used were from the nonylphenol ethoxylate series and are shown as circles; others are identified as indicated. The trend in the data is for a decrease in critical strain with increasing surfactant solubility parameter, with the exception occurring with the surfactant of highest solubility parameter, which did not initiate cracking up to an imposed strain of 2.3%.

Previously, Jacques and Wyzgoski<sup>12</sup> had incorporated a molar volume term to take into account wide distributions of molecular weight of stress cracking agents from homologous series. Following their example, one may plot the critical strain against the molar volume ( $V_0$ ) times the squared difference in the solubility parameter of the polymer and surfactant ( $\delta_p - \delta_0$ )<sup>2</sup> (Fig. 3). For this purpose, a solubility parameter of 10.4 (cal/cm<sup>3</sup>)<sup>1/2</sup> was used for polycarbonate since it gave the best overall fit for the data. Solubility parameter values for polycarbonate have been reported from 9.5 to 10.6 (cal/cm<sup>3</sup>)<sup>1/2</sup>.<sup>7</sup> The results of Figure 3 show a monotonic relationship of critical strain with  $V_0(\delta_p - \delta_0)^2$ . Furthermore, this plot shows that when  $V_0(\delta_p - \delta_0)^2$  is greater than 20 cal/mole for surfactants, the critical strain for polycarbonate is greater than 0.50%, and consequently such surfactants are not considered potent stress cracking agents for the material.

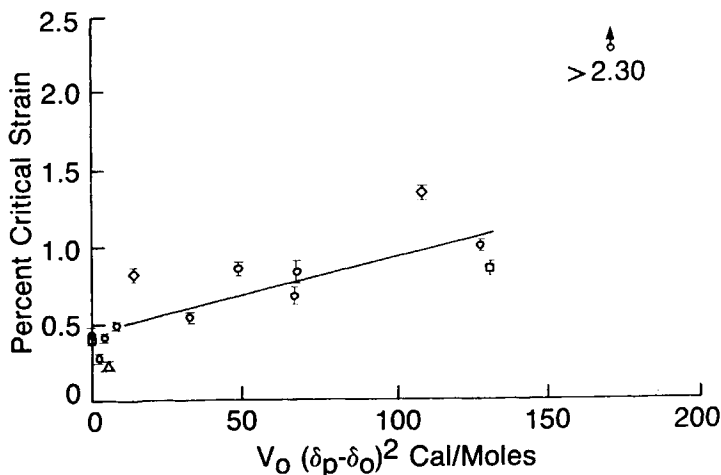
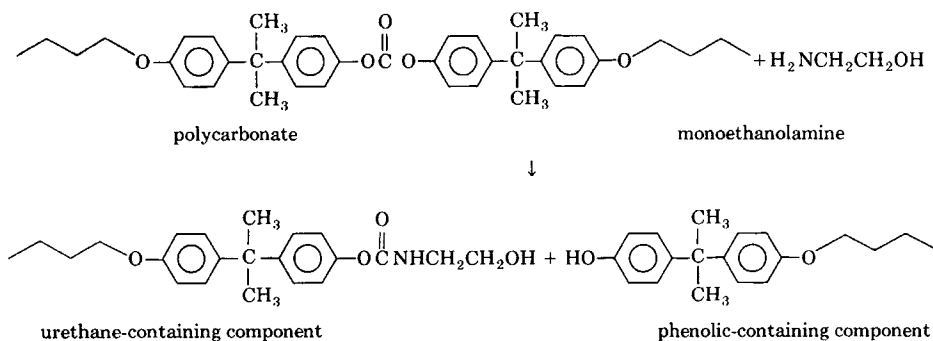


Fig. 3. Critical strain for polycarbonate exposed to poly(oxyethylene)ethoxylate surfactants as a function of surfactant molar volume times the square of the difference in solubility parameters of polymer and surfactant; (○) poly(oxyethylene)ethoxylates of nonylphenol; (□) poly(oxyethylene)ethoxylates of 2,6,8-trimethylnonanol; (◇) poly(oxyethylene)ethoxylates of octylphenol; (○) poly(oxyethylene)ethoxylate of 6-dodecanol; and (△) poly(oxyethylene)ethoxylate of *n*-dodecanol.

### The Role of Monoethanolamine

The critical strain of polycarbonate exposed to monoethanolamine was determined to be 0.19%. This is considered to be extremely low, thereby, indicating that this liquid is a severe stress cracking agent for polycarbonate. Based on the model using solubility parameters and liquid molar volume (described in the previous section),  $V_0(\delta_p - \delta_0)^2$  for monoethanolamine is 1573 cal/mol. This is much greater than any of the surfactants, and, therefore, monoethanolamine would not be expected to stress crack polycarbonate based upon solubility alone.

However, polycarbonate is known to undergo aminolysis reactions in the presence of monoethanolamine. According to Caldwell and Jackson,<sup>17</sup> this reaction results in cleavage of the aromatic carbonate linkage, as shown below, to yield a urethane group and a phenolic compound.



To confirm this reaction, 5.2 g of polycarbonate was placed in a vial containing 12 mL of monoethanolamine and allowed to stand overnight at room

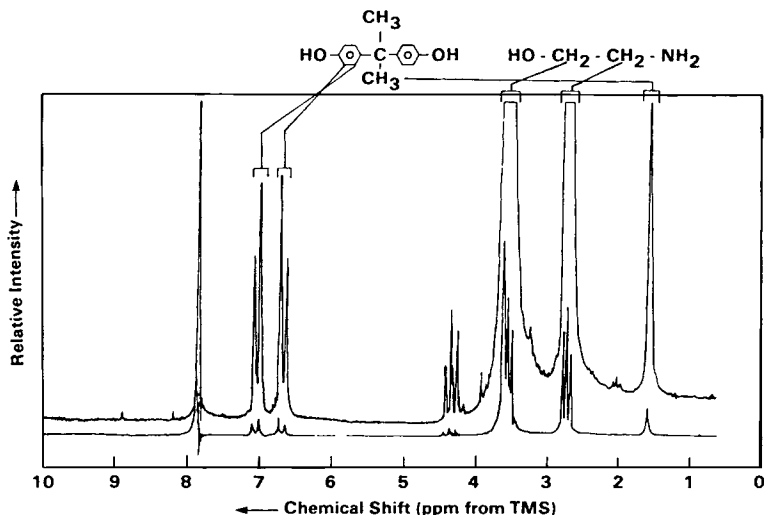


Fig. 4. NMR spectrum and peak assignments of the supernatant liquid of a polycarbonate and monoethanolamine mixture.

temperature. It was observed that the clear monoethanolamine became dark amber. However, there was no apparent dissolution or swelling of the polycarbonate. The lack of swelling of the polymer is consistent with the large difference in solubility parameters— $10.4 \text{ (cal/cm}^3)^{1/2}$  for polycarbonate compared to  $15.52 \text{ (cal/cm}^3)^{1/2}$  for monoethanolamine.<sup>16</sup> The monoethanolamine was decanted and analyzed for degradation products using NMR spectroscopy. The NMR spectrum of this supernatant liquid is shown in Figure 4. The expected monoethanolamine peaks are very prominent (as labeled). The peaks around 6.6 and 7.0 ppm are consistent with those assigned to bisphenol A, one of the predicted degradation products. There was no evidence, how-

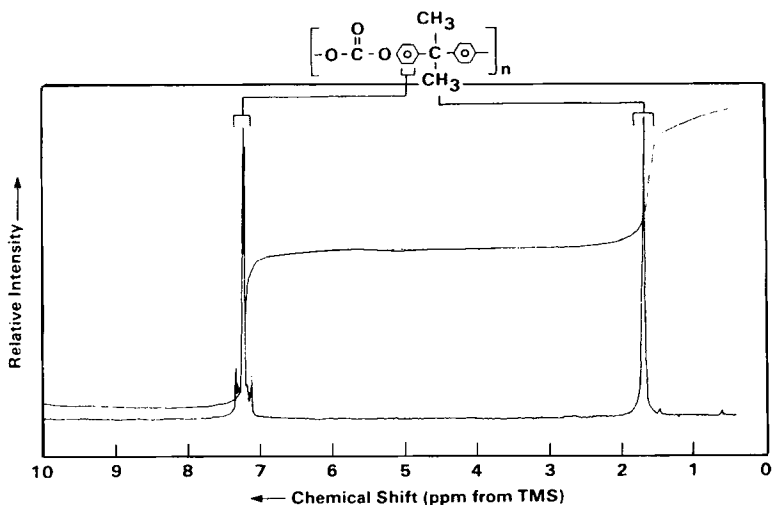
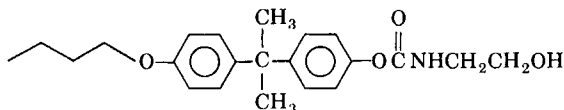


Fig. 5. NMR spectrum and peak assignments for polycarbonate dissolved in deuterated chloroform.

ever, of the other expected degradation product:



The apparent absence of this product in the supernatant liquid is believed to be due to its low solubility in monoethanolamine.

A reference spectrum of undegraded polycarbonate dissolved in deuterated chloroform is shown in Figure 5. There is no evidence of the degradation product observed in Figure 4.

The presence of the expected degradation product, bisphenol A, in the decanted monoethanolamine confirms the previous experiments of Caldwell and Jackson,<sup>17</sup> indicating that monoethanolamine chemically degrades polycarbonate. Presumably, this degradation leads to the initiation of stress cracking in polycarbonate.

## DISCUSSION

Based on the results presented in Figure 3, the stress cracking behavior of polycarbonate exposed to poly(oxyethylene)ethoxylate surfactants may be described by concepts involving the solubility parameter differences of the surfactant and polymer, and surfactant molar volume. This treatment is consistent with the mechanism most often advanced to explain the role of organic agents in environmental stress cracking. This mechanism requires the stress cracking agent to locally plasticize the polymer, thereby reducing the glass transition temperature of the affected region and facilitating the polymer's deformation in the form of crazing.<sup>5</sup> This treatment allows the prediction of which surfactants in this class will be relatively strong stress cracking agents for polycarbonate, and, as such, these surfactants should not be used in fluids that may contact polycarbonate parts.

The other stress cracking agent for polycarbonate used in the windshield washer fluid, monoethanolamine, cannot be treated in the previously described manner. In the case of monoethanolamine, which is strongly alkaline with a pH value of 14, stress cracking is due to an aminolysis reaction with polycarbonate at the aromatic ester linkage. This reaction severs the polymer chain and leads to a reduction of the polymer's molecular weight. Polycarbonate is known to stress crack in some other specific alkaline environments. For example, an equivolume mixture of a 6.25*N* NaOH solution with ethanol will produce a potent stress cracking agent for polycarbonate, whereas either one alone is comparatively inert to the material.<sup>18</sup>

## CONCLUDING REMARKS

The stress cracking mechanisms of polycarbonate exposed to monoethanolamine and surfactant are quite different. In the former case, stress cracking is due to a chemical reaction resulting in molecular degradation. The latter case involves a physical process which leads to localized weakening of the structure through plasticization. It was determined in this investigation



that for polycarbonate exposed to surfactants of poly(oxyethylene)ethoxylates, the stress cracking potential is predictable based on knowledge of the surfactant structure and molar volume.

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