

## Cracking in a glassy epoxy resin induced by water absorption

R. F. Fedors

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Ca. 91103, USA

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### Introduction

In an earlier publication<sup>1</sup> some effects of water absorption in an elastomer containing water soluble inclusions were reported. It was observed that the inclusions dissolved (partially or completely) in water that diffused to the vicinity of the inclusion. This process led to the formation of a cavity containing a near saturated solution of the inclusion in water plus any remaining undissolved inclusion. Some of these growing cavities developed disc-shaped cracks which grew in size until their lengths were 5–10 times larger than the size of the initial inclusion. Such cracking constitutes a new mechanism of failure for elastomeric materials. The present report notes the observation of the formation of similar cracks, also produced by water absorption, in a rigid glassy epoxy. This finding demonstrates that this type of failure occurs in high modulus glassy polymers, as well as low modulus elastomers, and thus seems to be a general phenomenon.

### Experimental

The samples were prepared by a two stage process, as before<sup>1</sup>. 100 parts of epoxy resin, Der 332, and 10 parts of catalyst No 9, Emmerson and Cuming, was mixed at room temperature. Sufficient mixture to form a layer about 0.25 in thick was introduced into a 3 in diameter aluminium weighing dish, which was then covered to keep out dust and subsequently allowed to cure at room temperature. Water soluble materials in the form of small particles or crystals were placed on the surface of the cured epoxy and a second layer of mixed resin, also about 0.25 in thick, was placed over the first layer, thereby encapsulating the water soluble material. The samples were allowed to cure for an additional 24 h, after which time they were removed from the aluminium weighing dish. The size of the samples was thus 3 in in diameter and 0.5 in in thickness. This epoxy system is transparent with an amber cast so that the imbedded inclusion could be easily observed. Several substances were used as inclusions, including: sucrose, potassium acetate, cobaltous chloride and calcium nitrate.

### Results and discussion

The inclusion begins to dissolve when the diffused water reaches the surface of the inclusion to form a cavity containing, initially, a near saturated solution of the inclusion in water and any remaining undissolved inclusion. The rate at which the inclusion dissolves is a very strong function of both the particle size and the solubility of the inclusion in water<sup>2</sup>. Generally, the smaller the particle, the faster it dissolves; also, the more soluble the inclusion, the faster it dissolves. Large ranges in the time required for a cavity to form can be easily obtained by simply varying either particle size or solubility or both.

It should be noted that the effects reported here are not restricted to the uptake of water. Similar behaviour will also be observed with other solvents and inclusions. The primary requirement is that the inclusion be insoluble in the polymer matrix but soluble in the solvent.

The difference in the chemical potential of the water in the pure state and in solution, which manifests itself as an osmotic pressure, tends to make the initially concentrated solution in the cavity more dilute. This effect is the driving force for the growth of the cavity.

Opposing this growth is the hydrostatic pressure exerted by the polymer on the boundary of the cavity. At equilibrium, the osmotic pressure tending to make the solution more dilute, and thereby to increase the volume of the cavity, equals the hydrostatic pressure exerted by the polymer on the boundary of the cavity which tends to decrease the size of the cavity. A more complete discussion of these phenomena as well as derivation of equations which can be used to estimate the cavity size and extent of water absorption, has been presented previously<sup>2</sup>.

A simple example that indicates the extent of water absorption and the magnitudes of the pressures involved may be of interest. It can be shown that the relationship between the volume fraction of water,  $\phi_1$ , present in the cavity within a polymer containing a water soluble inclusion whose volume fraction, also in the cavity,  $\phi_2$ , is given by:

$$\frac{nRT\Phi}{\bar{V}_2G} = \frac{1.365\phi_1^2}{1-\phi_1}, \quad \phi_1 < 0.6 \text{ (equilibrium, complete (1) solubility)}$$

where  $n$  is the number of ions or particles each molecule of inclusion produces on solution,  $R$  is the gas constant,  $T$  is the temperature in degrees Kelvin,  $\Phi$  is the osmotic coefficient which is a correction factor for non-ideality of the solution,  $\bar{V}_2$  is the partial molar volume of the inclusion and  $G$  is the shear modulus of the matrix.

This expression is an approximate form of a more general expression<sup>2</sup>. For the indicated limitation, i.e.  $\phi_1 < 0.6$ , equation (1) provides values which do not differ by more than 2% from those calculated using the full expression. Equation (1) assumes that at equilibrium, when the cavity growth has ceased, the inclusion is completely dissolved. In cases where this is not the case, another equation can be derived<sup>2</sup>:

$$\frac{nRT\Phi}{V_2G} = 1.365 \phi_1 \left( \frac{1 - S_2^*}{S_2^*} \right), \phi_1 < 0.6 \text{ (equilibrium, (2) partial solubility)}$$

where  $S_2^*$  is the volume fraction of solute in solution at saturation.

Again, equation (2) yields values that are within 2% of those calculated by the complete expression<sup>2</sup>. As pointed out elsewhere<sup>2</sup>, the two cases of total and partial solubility at equilibrium lead to different results and must be carefully distinguished.

For a given polymer-inclusion system, it cannot be determined *a priori* which case, i.e. whether complete or partial solubility, is applicable. However, it has been shown that the applicable equation is that which provides the smaller value of  $\phi_1$ , or equivalently the lower water uptake.

For purposes of illustration, it is assumed that the inclusion is potassium acetate and the matrix is a rigid epoxy. Therefore,  $n = 2$ ,  $T = 293^\circ\text{K}$ ,  $\Phi \approx 1$ ,  $\bar{V}_2 \approx 55 \text{ cc/mole}$ ,  $S_2^* \approx 0.59$  and  $G = 10^5 \text{ psi}$ . Thus equation (1) becomes:

$$\phi_1 = \frac{98}{G^{1/2}}, \quad \phi_1 < 0.6 \text{ (complete solubility equilibrium)} \quad (1a)$$

or:

$$\frac{V_{\text{H}_2\text{O}}}{V_{\text{salt}}} = \frac{98}{G^{1/2} - 98} \quad (1b)$$

where  $V_{\text{H}_2\text{O}}$  is the volume of water absorbed at equilibrium and  $V_{\text{salt}}$  is the volume of salt present.

Equation (2), which is valid for partial solubility, becomes:

$$\phi_1 = \frac{13\,800}{G}, \quad \phi_1 < 0.6 \text{ (partial solubility, equilibrium)} \quad (2a)$$

or:

$$\frac{V_{\text{H}_2\text{O}}}{V_{\text{salt}}} = \frac{13\,800}{G - 13\,800} \quad (2b)$$

It is interesting to note that the variation of  $\phi_1$  depends inversely on shear modulus in the case of partial solubility and inversely on the square root of the shear modulus for the case of complete solubility.

Using the fact that  $G = 10^5 \text{ psi}$ , equation (1b) predicts a value of  $V_{\text{H}_2\text{O}}/V_{\text{salt}}$  of 0.45, while equation (2b) predicts a value of 0.16 for this ratio. Hence, in this example, the equation is chosen that provides the smaller value and hence gives a system of partial solubility.

For a given inclusion, the shear modulus of the matrix determines which of two cases is applicable. There is a unique value of  $G$ , say  $G^*$ , that corresponds to a change over from one condition, of partial solubility, to the other, of complete solubility. This value of  $G^*$  can be obtained by setting equations (1) and (2) equal, and yields:

$$G^* = \frac{nRT\Phi S_2^{*2}}{1.365 \bar{V}_2 (1 - S_2^*)^2} \quad (3)$$

Using the appropriate values for the parameters,  $G^* = 20\,000 \text{ psi}$ . Thus, using this result, the range of applicability can be written as:

equation (1), (1a) or (1b) for  $G \leq G^*$

equation (2), (2a) or (2b) for  $G \geq G^*$

It is of some interest to note that of the quantities which appear in equation (3) and which determine the value of  $G^*$ ,  $S_2^*$  is the most prominent.

It is possible to estimate the magnitude of the pressure acting radially on the surface of the cavity. It can be shown that this pressure  $P_1$  is given by<sup>2</sup>:

$$P = \frac{G}{2} [5 - 4(1 - \phi_1)^{1/3} - (1 - \phi_1)^{4/3}] \quad (4)$$

For the example of potassium acetate,  $\phi_1$  calculated from equation (2b) and substituted into equation (4) yields a

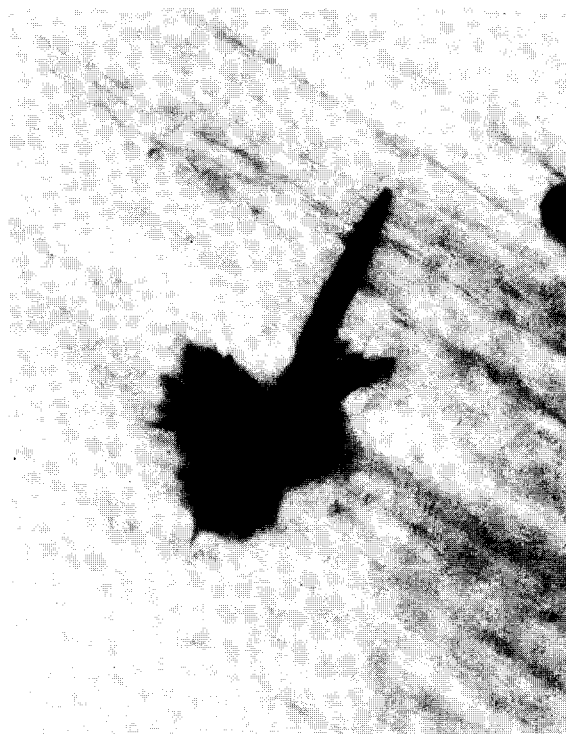


Figure 1 Cracks induced around a potassium acetate inclusion present in rigid epoxy by water absorption



Figure 2 Cracks induced around a cobaltous chloride inclusion present in a rigid epoxy by water absorption

pressure or triaxial load on the surface of the cavity of about 19 000 psi — a considerable loading. It is now apparent that sufficient pressures are developed to cause cracks to be initiated and to grow.

An example of such a process is shown in *Figure 1*. The inclusion is potassium acetate and the cracks were observed after about 1 800 days' immersion time in distilled water.

The original inclusion was cubical in shape. The fine lines which radiate from the particle constitute a system of hundreds of small cracks. The main crack is located on the upper right hand side of the photograph. *Figure 2* shows a crack produced by a cobaltous chloride inclusion. The other features represent air bubbles and smaller crystals of the inclusion that have not yet led to cracks. The potassium acetate system is interesting in that numerous smaller radially disposed cracks also form. Normally, only one crack forms and grows and this is typified by *Figure 2*.

The gradual formation, growth and sometimes cracking of these cavities has been followed microscopically and measured as a function of time. In addition, by using solutes which form coloured solutions, such as cobaltous chloride, it is possible to measure the optical density and thereby calculate the osmotic pressure. This technique seems to be a convenient tool for determining the strength of a transparent material under pure hydrostatic triaxial tension.

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## A corresponding states interpretation of the temperature dependence of the intrinsic viscosity of polystyrene in isopropyl acetate

Randal W. Richards

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK  
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### INTRODUCTION

Dilute solution properties of polymers are generally described via the excluded volume parameter<sup>1</sup>. In its turn, the excluded volume parameter has, in the main, been expressed by the original equation given by Flory<sup>2</sup>, since this contains the temperature dependence directly as  $(1 - \theta/T)$  where  $\theta$  is the theta temperature of the polymer-solvent system. The limitations of such an expression to the neighbourhood of the theta temperature have been recognized for some years<sup>3</sup>.

Additionally, the original Flory theory cannot predict the presence of a lower critical solution temperature, a general phenomena of all polymer solutions. In recent years, the thermodynamics of polymer solutions have been re-described by equation of state<sup>4a, b, c</sup> and corresponding states theories<sup>5a, b</sup>, either of which predict the presence of a lower critical solution temperature. Thus far, to our knowledge, no attempt has been made to incorporate such theories into the excluded volume parameter expression and compare the predictions with experiment. This paper presents such an