

Acknowledgment

We are grateful to Dr N. Yamazaki, Dr S. Nakahama and Mr T. Saito of Tokyo Institute of Technology for carrying out elemental analyses of the crosslinked polymers.

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Water-treeing as an osmotic phenomenon

R. F. Fedors

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

(Received 16 April 1980)

Introduction

In a recent paper, Meyer and Filippini¹ discussed the propagation mechanism of water-treeing, which is described as a fracture phenomenon caused by mechanical stresses of electrical origin, observed in the electrical insulation of power cables in contact with humidity. Particularly comprehensive reviews of treeing phenomena are recently given by Eichhorn² and Ieda³.

According to Meyer and Filippini¹, water-treeing is generally thought to occur in three sequential steps: (1) absorption of water to form a water-filled pocket; (2) initiation of a channel from this pocket; and (3) propagation and growth of channel. It is generally observed that high a.c. or d.c. voltages favour the formation of water-trees².

We propose that the osmotic pressure resulting from the absorption of water by water-soluble inclusions present in the insulation can at least be a contributing factor in the type of water treeing discussed by Meyer and Filippini¹. The osmotic pressures which develop can be substantial and can lead to the formation of numerous cracks surrounding the inclusion, which are remarkably similar in appearance to water-treeing formed in the presence of electric fields. Although osmotic pressure alone is sufficient to produce the effect, it is believed that the presence of an electric field increases the rate and possibly the size of the water trees which ultimately form.

Formation and growth of water trees

In a previous paper⁴, it was shown that inclusions of water soluble substances imbedded in a rubber (silicone) led to the formation of cracks within the rubber when moisture is present. Briefly, the process is as follows: water diffuses into the polymer and comes into contact with the inclusion. The inclusion begins to dissolve and form a near-saturated solution. During this process a cavity forms around the inclusion which acquires a spherical or near spherical shape as more water diffuses into the cavity. The driving force for this process is the difference in chemical potential of the water in the bulk phase outside and the water as solvent for the inclusion inside the polymer. Since the chemical potential of water inside is less than that outside, water moves into the cavity. This movement of water gives rise to a pressure termed the osmotic pressure and this pressure is exerted by the solution on the boundary of the cavity. The polymer behaves as a semipermeable membrane which prevents the dissolved inclusion from leaving the cavity. At equilibrium, the osmotic pressure equals the hydrostatic pressure exerted by the polymer on the surface of the cavity. These osmotic pressures are substantial and can reach values of a few thousand atmospheres.

A subsequent paper⁵ showed how the equilibrium water uptake by this osmosis mechanism can be estimated and it was pointed out that the important variables to consider are the shear modulus of polymer and the solubility of the inclusion material in water.

In the initial study⁴, it was observed that the cavities often ruptured to form disc-shaped cracks. Apparently this process occurred because the initial dry inclusions

* This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100 sponsored by the National Aeronautics and Space Administration.

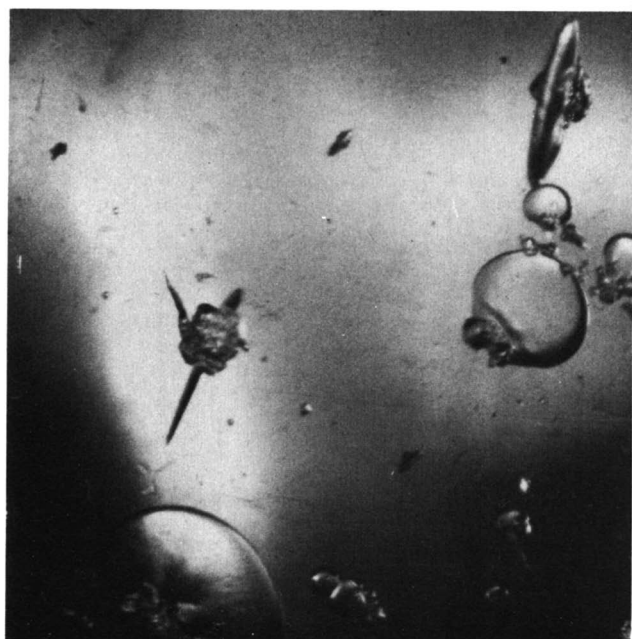


Figure 1 Cracking in a silicone elastomer containing cobaltous chloride crystals as an inclusion. Magnification 20x

were irregular and non-spherical in shape and hence, the polymer surface in contact with the inclusion was also irregular in shape. When water is absorbed, the initial irregular shape is transformed into a spherical shaped cavity. However, since the initial shape was irregular, there will be surface regions of higher stress concentration and it is believed that these regions are responsible for the initiation of the crack and subsequent growth driven by osmotic pressure. This is supported by the observation that cracking is not observed when the initial inclusion is spherical in shape. Once the crack begins to grow, there is an immediate decrease in osmotic pressure. Since the crack now in effect increases the volume of the cavity there will be a drop in the concentration of inclusion in water and hence also a decrease in the osmotic pressure. As the osmotic pressure is decreased, the driving force for propagation of the crack also decreases and we have a situation where the driving force for propagation decreases as the crack grows in size. Experimentally, it has been observed that the propagation rate of water-tree channels decreases as the channel length increases¹ and this behaviour is simply explained on the basis of osmotic effects as described above. Were the electric field the primary force in the propagation of the channels or cracks, one would expect an increase in propagation rate with increase in crack length contrary to what is observed experimentally².

We have observed that in elastomeric systems⁴, the cracks which form are disc-shaped and become arrested when the crack length is roughly 5–10 times larger than the size of the initial inclusion. Figure 1 shows typical cracks which formed in a transparent silicone elastomer containing inclusions composed of small cobaltous chloride crystals.

For the work carried out using silicone rubber, cracking was first noticed about 1 week after the samples were immersed in water. The time span needed for cracks to form depends on the size of the inclusion, the solubility of inclusion in water as well as on the diffusion coefficient of water in the polymer.

We have also carried out these kinds of experiments using a rigid glassy matrix, specifically an epoxy resin⁶. It was found that the same general phenomena observed with the elastomeric system were also observed with the epoxy system except that the time scale for the first appearance of a crack was lengthened by a factor of about 250 using samples of the same geometric shape and size as previously. Whereas cracking was observed in the elastomer in about 1 week cracking in the epoxy took 5 years to occur. This difference in the time scales is primarily a reflection of the differences in diffusion rate of water in polymers above and below T_g , i.e. glassy polymers have much reduced coefficients of diffusion than do polymers in the rubbery state.

Figures 2 and 3 show the two types of cracking failures observed in the epoxy system which contained small crystals of potassium acetate as inclusions. Figure 2 shows cracks which are qualitatively similar to those observed in the elastomeric system. Figure 3 shows inclusions which, instead of a single large crack, have numerous cracks to produce a feather-like effect. We believe this difference is due to differences in the extent of surface irregularity of the initial inclusion — the greater the degree of irregularity of shape of the inclusion, the greater the tendency to produce feather-like cracks. The phenomenon shown in Figure 3 and produced entirely by mechanical forces, i.e. osmosis, is similar to that observed in electrical water trees. (Compare Figure 3 of this paper with Figure 1 of Meyer and Filippini¹.)

To provide an indication of the magnitude of the osmotic pressures involved, we can estimate, according to the procedures given in ref. 6, that the equilibrium osmotic

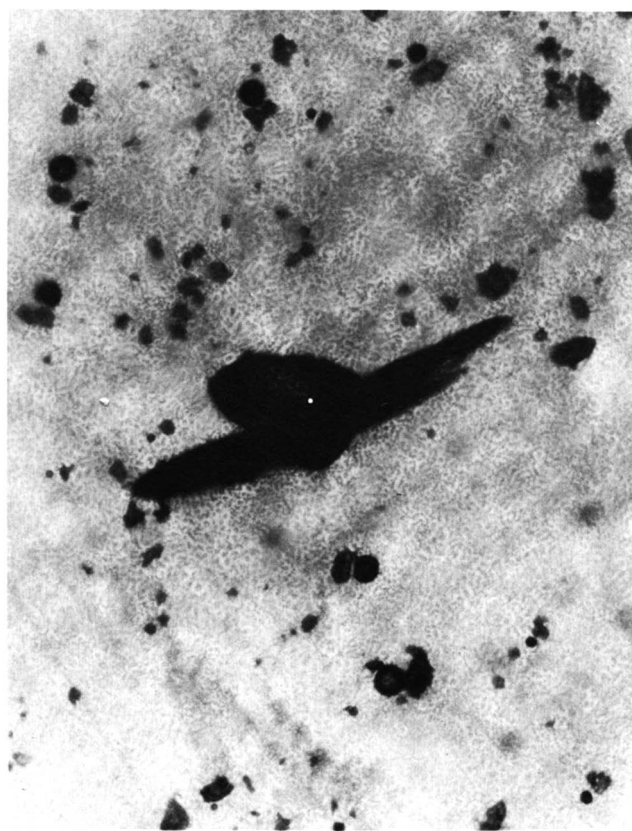


Figure 2 Cracking in a rigid epoxy containing potassium acetate crystals as an inclusion. Magnification x20



Figure 3 Formation of numerous feather-like cracks around a potassium acetate inclusion in a rigid epoxy. Magnification x20

pressure for the epoxy-potassium acetate system is about 19 000 p.s.i. — a considerable pressure.

The question of the rate of absorption of water and hence the rate of crack growth is a difficult one. Fortunately, it is possible to obtain relative and qualitative estimates of the time required for an inclusion to dissolve. Rosner⁷ showed that the lifetime, t_{∞} , of an isolated particle immersed in a solvent which dissolves the

particle is given by:

$$t_{\infty} = \frac{1}{2} \frac{\rho_2}{\rho_1} \left(\frac{V}{S} \right)^2 \frac{1}{D \ln(1+B)}$$

where ρ_1 and ρ_2 are the densities of the particle and solvent, respectively; V and S are the volume and surface area of the particle, respectively; D is the diffusion coefficient of the solute in the solvent; and B is a parameter which is given in approximate form by:

$$B = \frac{C_{\text{sat}}}{1 - C_{\text{sat}}}$$

where C_{sat} is the concentration, expressed as weight fractions, at saturation of the inclusion in water. Although as stated previously, these expressions apply specifically to the dissolution of an isolated particle, it can be used in the present context to obtain relative time scales. To show the enormous effect of solubility on the time scale, we compare an inclusion of silver bromide for which $B = 8 \times 10^{-8}$ with sucrose for which $B = 2$. Assuming the same size and shape for each inclusion and assuming equal values of D for both, then Rosner's equation predicts it will take about 10^8 times longer for the silver bromide inclusion to dissolve than it would for a sucrose inclusion.

It thus appears that osmotic forces alone can result in water-trees which are qualitatively the same as those produced in the presence of electric stresses. Hence, it appears that mechanical stresses of electric origin are not necessarily the sole contribution to water-treeing. It is believed that electric field effects shorten the time required for treeing to occur by primarily producing an increase in water absorption rate by a mechanism such as electrophoresis and by modifying or augmenting some of the primary steps, such as crack initiation.

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