

Osmotic effects in water absorption by polymers[†]

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The absorption of liquids by polymers which contain liquid-soluble inclusions is described. It is shown that the equilibrium uptake of liquid can be calculated if several properties of the inclusion such as solubility as well as the modulus of the polymer are known.

INTRODUCTION

The absorption or uptake of liquids, especially water, by solid polymers such as vulcanized rubber is a problem of great practical importance. In many instances, this absorption is detrimental to the proper functioning of the polymer. For example, the absorption of water by vulcanized rubber jacketing or insulation on electrical wire and cable can reduce the insulation capacity to such an extent that electrical breakdown can occur.

Equilibrium solubility

Generally speaking, the equilibrium solubility of water in typical hydrocarbon polymers is very small. An estimate may be obtained via the limiting form of the Flory equation¹ expressed as:

$$\phi_1 = \exp - [1 + \chi_1] = \exp - \left[1.34 + \frac{v_1}{RT} (\delta_1 - \delta_2)^2 \right] \quad (1)$$

where ϕ_1 is the volume fraction of liquid absorbed at equilibrium, v_1 is the molar volume of the liquid, T is the absolute temperature, and δ_1 and δ_2 are the solubility parameters of the liquid and polymer respectively. δ_1 for water at 25°C is 23.4 (cal cm⁻³)^{1/2} and the range of δ_2 for common polymers is from a low of 7.95 (cal cm⁻³)^{1/2} for EPR to about 10.3 (cal cm⁻³)^{1/2} for a butadiene-acrylonitrile polymer². Hence when $v_1 = 18 \text{ cm}^3 \text{ mol}^{-1}$ and $T = 298^\circ \text{ K}$, equation (1) predicts a range of water solubilities of about 200 ppm for EPR to about 2000 ppm for the butadiene-acrylonitrile polymer. Direct experiments on the solubility of water in low molecular weight hydrocarbons such as the alkanes yield solubilities of the order of 50–200 ppm^{3,4} which values are in good agreement with those predicted from equation (1).

Large liquid absorption

For the commonly used polymers, the equilibrium solubility of water will range from about 0.02 to 0.2% by wt; hence the uptake of water in amounts much greater than these values must be attributed to other causes. There is

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ample evidence that has established that the absorption of substantial amounts of water occurs by means of osmosis – the polymer contains water-soluble inclusions which are not soluble in the polymer itself. The polymer surrounding these inclusions then functions as a semipermeable membrane. A similar assumption was used previously by Briggs, Edwards and Storey¹⁰.

The sequence shown in *Figure 1* will be helpful in focusing attention on the important details of the process. Consider an initial inclusion which for simplicity is assumed to be spherical in shape and of radius r_0 . Water diffuses into the elastomer at an initial rate which depends on the geometry of the test specimen and the chemical nature of the elastomer. After some time, water will come into contact with the inclusion and the inclusion will begin to dissolve. The increase in the volume of the cavity will be equal to the volume of water present in the solution. The outer boundary of the cavity is a moving boundary. The radius of the undissolved inclusion is now $r(t)$ while the radius of the cavity is $R(t)$. There is an osmotic pressure of magnitude $\pi(t)$ associated with the solution, which acts radially outwards on the cavity boundary; simultaneously, the rubber itself exerts a pressure $P(t)$ acting radially inwards on the boundary.

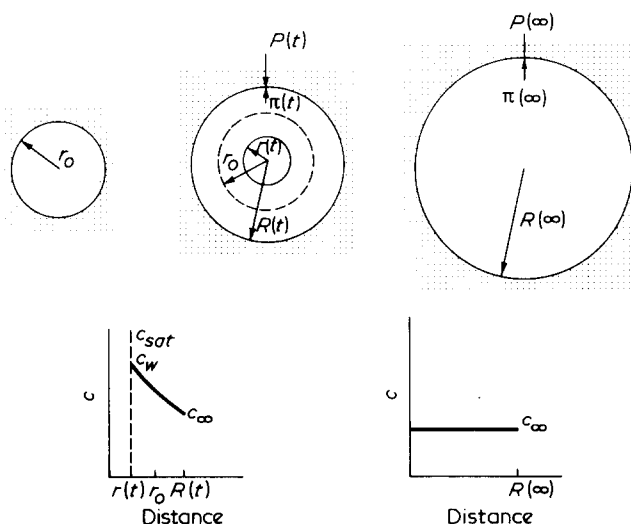


Figure 1 Schematic diagram for the growth of a cavity by diffusion of a liquid

When these two pressures are equal, the cavity will cease to grow. At this point the osmotic pressure $\pi(\infty)$ equals the retractive pressure $P(\infty)$ and the cavity reaches an equilibrium radius $R(\infty)$.

It is also of interest to examine the dependence of the concentration of solution on the cavity size. This aspect of the problem is also indicated in *Figure 1*: c_{sat} is the weight fraction of solute in a saturated solution, c_w is the weight fraction of solute at the liquid-particle interface and c_∞ is the concentration of solute far away from the interface. Of these three concentrations, c_{sat} is by definition a constant; and c_w will be almost independent of the size of the cavity i.e. independent of the quantity of solvent present in the cavity. Hence, c_∞ (the concentration of solute far distant from the liquid-particle interface) will be the major variable connected with the cavity size.

The diffusion rate of liquid depends on the cavity size. When the inclusion first begins to dissolve, the solution is relatively concentrated and hence the osmotic pressure is high. This situation constitutes a diffusional bias which produces a marked increase in the diffusion rate of the liquid. This enhancement in rate will decrease as the cavity containing the solute and solution increases in size, because the activity of the solvent interior to the rubber depends on the concentration of the solute and this will be in general a monotonically-decreasing function of time.

The rate at which the particle in *Figure 1* dissolves may be limited either by (i) the rate of diffusion of water into the cavity or (ii) the rate of dissolution of the particle itself. Which of these two factors predominates depends on the chemical nature of the elastomer and the solute. However, as a general rule, if the rate of diffusion of water is the limiting factor, the growth of the cavity will be independent of the particle size of the inclusion. If on the other hand, the limiting factor is dissolution of the particle, then the rate of growth of the cavity will be a strong function of the particle size. The growth stage of the cavity occurs when $\pi > P$ and the equilibrium cavity size is obtained when $\pi = P$. For $\pi < P$, the osmotic pressure is insufficient to maintain a given cavity size and the cavity will shrink.

CALCULATION OF EQUILIBRIUM WATER ABSORPTION

Osmotic pressure

The osmotic pressure, π , of a dilute solution⁵ in equilibrium with pure solvent can be expressed by:

$$\pi = \frac{nRT\Phi}{v_2} \left(\frac{S_2}{1 - S_2} \right) \quad (2)$$

n is the moles of particles formed upon solution of one mole of solute (for a non dissociating solute, $n = 1$); Φ is an osmotic coefficient which represents a correction term for non-ideality. For aqueous solutions of common salts, tables are available which provide values for Φ as a function of concentration^{6,7}. For electrolytes, Φ is unity for an infinitely dilute solution and decreases as concentration increases, whereupon a further increase in concentration results in an increase in Φ ^{6,7}. For non-electrolytes, Φ increases monotonically as the concentration of solution is increased. When the Φ value is not available, Φ may be set equal to unity and this is a better approximation the more dilute the solution.

v_2 is the molar volume of the solute and S_2 is the volume fraction of solute in solution and is defined as:

$$S_2 = \frac{V_2}{V_1 + V_2} \quad (3)$$

where V_1 and V_2 are the volumes of solvent and solute in the solution respectively. For future reference, we define S_2^* as the volume fraction of solute in a saturated solution; thus the total range of S is given by $0 < S_2 \leq S_2^*$.

Inflation pressure of a spherical cavity

The pressure, P , required to enlarge an isolated cavity in a large block of rubber from an initial radius r_0 to another radius r is given by⁸:

$$P = \frac{G}{2} \left[5 - \frac{4}{\lambda} - \frac{1}{\lambda^4} \right] \quad (4)$$

where G is the shear modulus and $\lambda = r/r_0$. The elastomer is assumed to be neo-Hookian. The response predicted by equation (4) is such that P increases monotonically to a limit of $5G/2$ as λ increases. It may be noted that the relationship does not depend on the initial hole size provided that the cavity is large enough to prevent the contribution of surface energy effects. In situations where this is not true, Kaelble has derived the appropriate relationships⁹.

Equation (4) is strictly valid for an isolated cavity in an infinite block of rubber. Kaelble⁹ has shown that this restriction will be valid provided that the distance, D , between the centres of two cavities of radii r_1 and r_2 , respectively, obeys the relationship:

$$D \geq 4(r_1 + r_2) \quad (5)$$

This will be true when the volume fraction of inclusion is less than about 1% or so.

Since $\lambda = r/r_0$ then $\lambda = (V/V_0)^{1/3}$ also where V is the volume of the cavity when the pressure is P and V_0 is the initial cavity volume. The volume fraction of solute in the cavity, ϕ_2 , is defined as:

$$\phi_2 = \frac{V_{2,t}}{V_1 + V_{2,t}} \quad (6)$$

where $V_{2,t}$ is the volume of solute and V_1 is the volume of solvent in the cavity. The total range of ϕ_2 is $0 < \phi_2 \leq 1$. Using equation (6), then $\lambda = \phi_2^{-1/3}$ and equation (4) becomes:

$$P = \frac{G}{2} [5 - 4\phi_2^{1/3} - \phi_2^{4/3}] \quad (7)$$

Furthermore, it is easy to show that S_2 is related to ϕ_2 via:

$$\frac{S_2(1 - \phi_2)}{(1 - S_2)\phi_2} = \frac{V_2}{V_2^*} \quad (8)$$

Since at equilibrium $\pi = P$, we have from equations (2) and (7):

$$\frac{nRT}{v_2} \left(\frac{S_2}{1 - S_2} \right) = \frac{G}{2} \left(5 - 4\phi_2^{1/3} - \phi_2^{4/3} \right) \quad (9)$$

which constitutes the basic equation relating equilibrium water absorption and solute concentration. In order to use

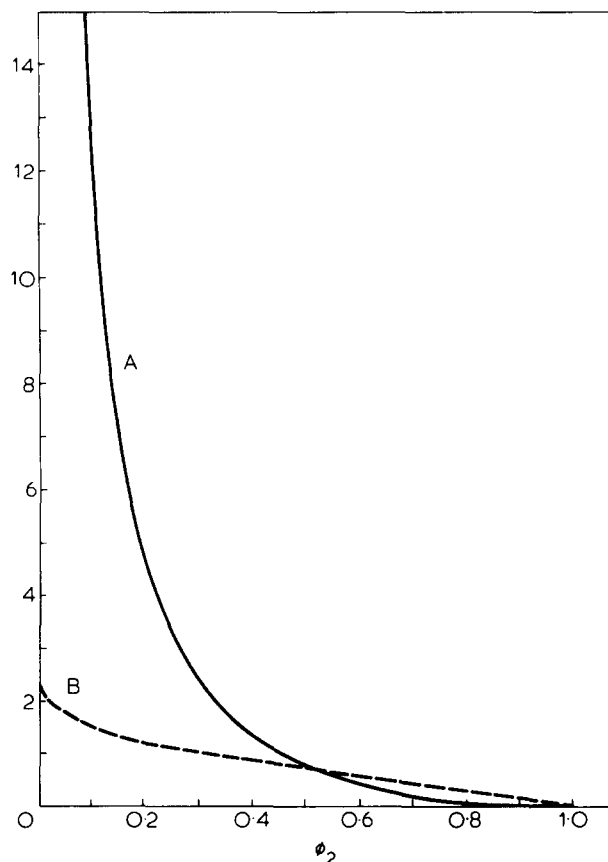


Figure 2 Dependence of the reduced variable on ϕ_2 . A —, $nRT\Phi/v_2G$; B - - - - , $nRT\Phi S_2^*/v_2G(1 - S_2^*)$

equation (8) we must distinguish between two cases: (a) at equilibrium, all the solute present is dissolved; and (b) at equilibrium, only a portion of the solute dissolves.

Solute miscible

In the first case $V_2 = V_2^*$, $S_2 = \phi_2 \leq S_2^*$ and equation (9) becomes:

$$\frac{nRT\Phi}{v_2G} = \frac{1}{2} \left(5 - 4\phi_2^{1/3} - \phi_2^{4/3} \right) \left(\frac{1 - \phi_2}{\phi_2} \right) ; \phi_2 \leq S_2^* \quad (10)$$

This is the basic equation which describes the equilibrium properties of the cavity. Fortunately, the known quantities are grouped into a reduced variable which is a function ϕ_2 alone. Unfortunately, the equation cannot be solved explicitly, so recourse is taken to graphical methods. Because of the range in ϕ_2 , it is convenient to use separate graphs.

Figure 2 shows a plot (A) of the quantity $nRT\Phi/v_2G$ as a function of ϕ_2 for the range $\phi_2 > 0.1$. Figure 3 shows the corresponding plot (in log-log coordinates) for the range $\phi_2 < 0.1$, but plotted as $(1/\phi_2) - 1$ rather than as ϕ_2 itself. Most cases of interest fall in the range $\phi_2 < 0.1$. Using these two figures, one calculates the value of the quantity $nRT\Phi/v_2G$, since all values are presumably known for a given system and the corresponding value of ϕ_2 is read off from the appropriate plot. From the definition of ϕ_2 , it is easy to show that:

$$w_1 = \rho_1 \frac{w_2}{\rho_2} \left(\frac{1}{\phi_2} - 1 \right) ; \phi_2 \leq S_2^* \quad (11)$$

where w_1 and w_2 are the weights of liquid and solute in the cavity at equilibrium and ρ_1 and ρ_2 are the corresponding densities. Thus, equations (10) and (11) permit the calculation of the equilibrium uptake of liquid for a given system. A particularly simple result appertains when $\phi_2 \leq S_2^* \leq 0.1$. In this region,

$$\frac{nRT\Phi}{v_2G} \approx 2 \left(\frac{1}{\phi_2} - 1 \right) ;$$

and hence, equation (11) becomes:

$$w_1 = \rho_1 \frac{w_2 nRT\Phi}{2M_2G} ; \phi_2 \leq S_2^* < 0.1 \quad (12)$$

where M_2 is the molecular weight of the solute.

As an application of equation (12) we compare the measured water absorption with values calculated via equation (12) for a polybutadiene containing varying amounts of salt and crosslinked to various extents by means of variable amounts of peroxide curing agent. These data were reported by Briggs, Edwards and Storey¹⁰ and are listed in Table 1. It

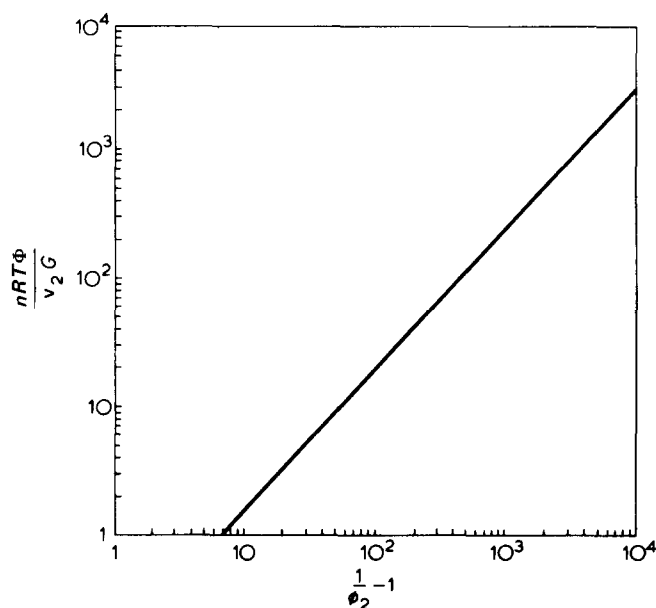


Figure 3 Dependence of the reduced variable on $(1/\phi_2) - 1$ for $\phi_2 < 0.1$

Table 1 Effect of salt on water absorption in *cis*-polybutadiene vulcanizates¹⁰

Salt	w_2 (%)	G	w_1 (% expt.)	w_1 (% calc.)
NaCl	0.2	55	27	22
	0.2	66	20	19
	0.2	89	14	14
	0.5	50	46	62
	0.5	68	47	45
	0.5	76	31	40
	1.0	50	137	123
	1.0	70	74	88
	1.0	83	47	74
Na ₂ SO ₄	2.0	47	264	262
	2.0	67	135	184
	2.0	86	78	143
	0.5	49	39	39
	0.5	63	24	30
	0.5	77	16	25

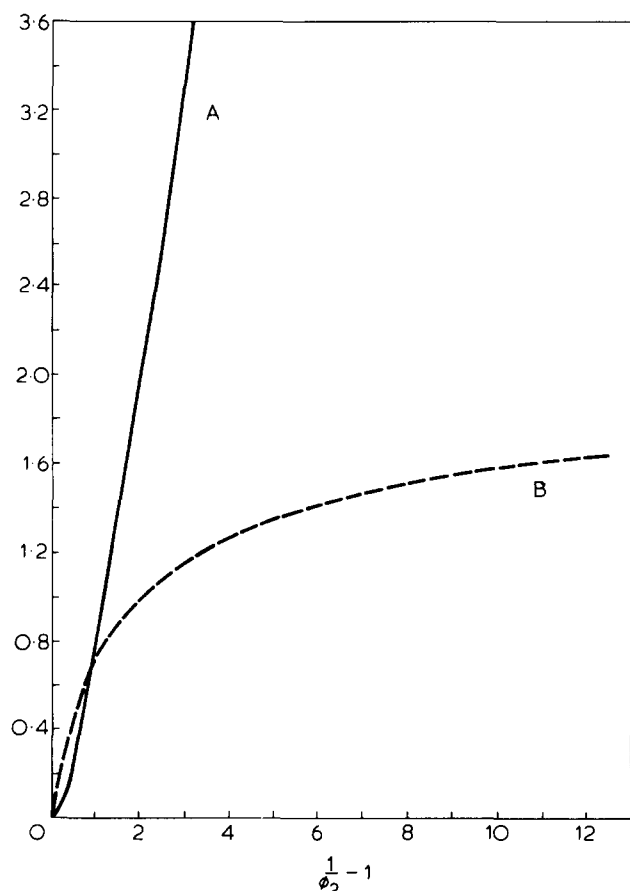


Figure 4 Dependence of the reduced variable on the function $1/\phi_2 - 1$. A —, $nRT\Phi/\nu_2 G$; B - - - - , $nRT\Phi S_2^*/\nu_2 G(1 - S_2^*)$

may be seen that the measured values of w_1 for both NaCl and Na_2SO_4 corresponds very well with the calculated values. In using equation (12), n for NaCl was taken as 2 and Φ was set equal to unity. For Na_2SO_3 , n was taken as 3 and Φ again was set equal to unity. It may be noted that equation (12) contains no adjustable parameters since in principle all values for the variable are determinable.

It is of interest to consider that, for an elastomer, if G is taken equal to $\nu_e RT$ where ν_e is the concentration of effective network chains, then equation (12) shows that w_1 , the weight of water absorbed, is temperature independent (apart from the very small temperature dependence of ρ_1 which may be neglected). Hence, it is therefore feasible to accelerate water absorption tests by performing the experiments at elevated temperatures. Provided no chemical degradation of the elastomer occurs, essentially the same absorption of water will be observed at all temperatures. This is not true for plastics or for polymers when the temperature of testing is below T_g , since for glasses the shear modulus decreases with temperature. In fact, if one takes G for a glass as inversely proportional to T , then according to equation (12), w_1 will vary as T^2 and the water absorption value will show a very strong temperature dependence.

Solute incompletely miscible

It has been tacitly assumed that all the solute present will have dissolved when the cavity reaches its equilibrium size. However, this state of affairs may not always be true. For limited solubility, the highest osmotic pressure will be reached when the solution in the cavity is saturated with respect to the solute. For this case, setting $\pi = P$, and $S_2 = S_2^*$ and $\phi_2 > S_2^*$:

$$\frac{nRT\Phi S_2^*}{\nu_2 G(1 - S_2^*)} = \frac{1}{2} [5 - 4\phi_2^{1/3} - \phi_2^{4/3}] ; \phi_2 > S_2^* \quad (13)$$

which is the analogue of equation (10). In this expression, it is also possible to express the reduced variable on the right hand side of the equation as a function of ϕ_2 alone. Unfortunately, it is not possible to solve equation (13) analytically; therefore, it is depicted graphically in Figures 2 and 4 (B). In practice, one computes the value of the reduced variable and uses the plot to estimate ϕ_2 . If $\phi_2 > S_2^*$, equation (13) applies; this value of ϕ_2 is used with equation (11) and w_1 is thereby obtained. If $\phi_2 \leq S_2^*$, equation (13) is not appropriate; equation (10) is used to estimate a correct value of ϕ_2 .

This procedure is illustrated using data from Briggs, Edwards and Storey¹⁰ on *cis*-polybutadiene containing the sparingly soluble salt PbCl_2 (Table 2). Two test temperatures, 75°C and 160°C, were employed¹⁰. Values of ϕ_2 are calculated, assuming total solubility (equation 10), and partial solubility (equation 11). From the conditions that, when $\phi_2 \leq S_2^*$, equation (10) is valid; and then $\phi_2 > S_2^*$, equation (13) is valid, the values of w_1 were computed and are shown in the last column. With the exception of the two highest modulus samples tested at 160°C, agreement is excellent.

Estimation of solute concentration from water absorption data

The discussion has assumed that the nature and content of the solute are known. In most applications of practical interest, this is not so. Referring to the general forms of the basic equations (10) and (13), it is evident that estimates of ϕ_2 can only be obtained if all the quantities present in the reduced variable are known or can be estimated. In order to do this, the nature of the solute must be known.

In the absence of any such information it is possible to use equation (12) to estimate an effective concentration of the solute. Upon rearrangement of equation (12), one obtains:

$$\frac{2w_1 G}{\rho_1 RT} = \frac{nw_2 \Phi}{M_2} = nm_2 \Phi ; \phi_2 \leq S_2^* < 0.1 \quad (14)$$

Table 2 Effect of sparingly soluble salts on water absorption¹⁰. PbCl_2 in *cis*-polybutadiene

Temperature 75°C, $S_2^* = 0.00414$					
w_2 (%)	G	ϕ_2 (equation 10)	ϕ_2 (equation 13)	w_1 (% expt.)	w_1 (% calc.)
5	29	0.0024	—	64†	355
5	60	0.0048	0.035	13†	24
5	82	0.0067	0.170	4.0	4.2
5	102	0.0080	0.295	2.5	2.1
5	114	0.0090	0.355	1.5	1.8
Temperature 160°C, $S_2^* = 0.0105$					
5	38	0.0025	—	280†	341
5	78	0.0051	—	112†	166
5	108	0.0069	—	20†	123
5	134	0.0086	—	8	98
5	148	0.0094	0.0094	4.2	90

† Equilibrium weight gain not achieved within time scale of the experiment; 500 h at 75°C and 100 h at 160°C

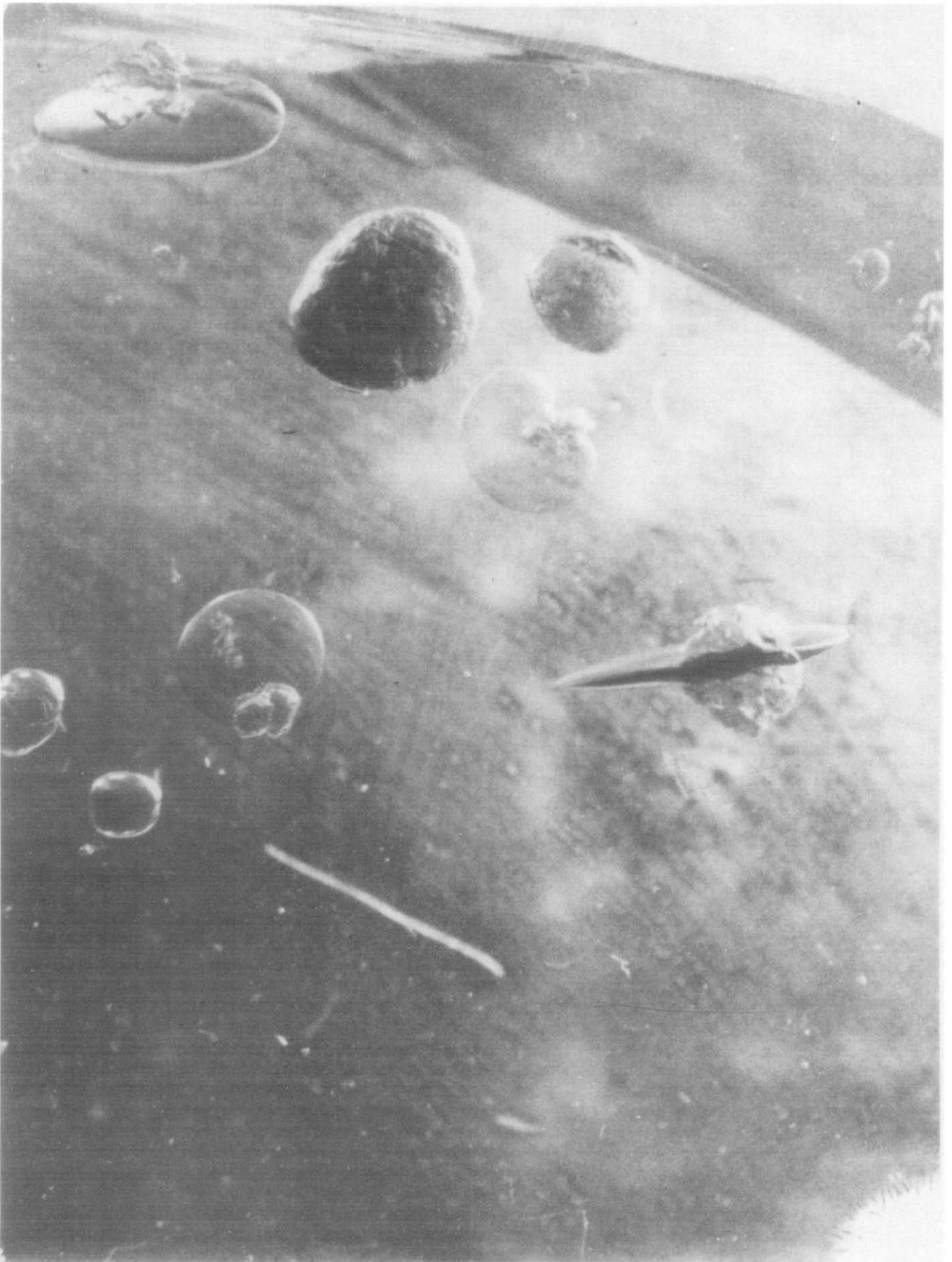


Figure 5 Development of disc-shaped cracks in rubber containing irregularly shaped solute particles

Table 3 Water absorption of various elastomers¹⁰

Material	G_{160° (psi)	w_1 (%)	Gw_1 (psi)	nm_2 (mol 100g ⁻¹ rubber $\times 10^3$)
Pale crepe	59	30	1770	7.0
Pale crepe	99	19	1880	
Polysar Krylene	164	33	5410	20
Polysar Krylene	190	26	4940	
Polysar Krynac 800	109	6.5	710	2.9
Polysar Krynac 800	164	4.9	803	
cis-polybutadiene	191	1.0	191	0.76
cis-polybutadiene	259	0.8	207	
Ethylene-propylene	113	1.1	124	0.48

where m_2 is the concentration of solute (mol). With $\Phi = 1$, one can estimate nm_2 since the values for the quantities on the right hand side of the equation are presumably available. Fortunately, there is a simple method to test the applicability of equation (14). It requires that w_1 be measured at several values of G ; when the relationship applies, the product w_1G will be constant. Thus, we have an equation which will permit one to estimate the concentration of solution as well as a method of determining its applicability.

To demonstrate the use of equation (14), we have used data published by Briggs, Edwards and Storey¹⁰ (listed in Table 3). Briefly, these workers studied the absorption of water for several types of elastomers containing only added peroxide curing agent. For most of the elastomers, the water absorption was determined at two values of G . Also listed is the product Gw_1 and as may be seen, the product is constant for each elastomer. The last column lists the effective concentration of solute in mol 100 g⁻¹ rubber. Of the elastomers listed, Krylene has the highest content of solute (20×10^{-3} mol) while ethylene-propylene has the lowest (0.5×10^{-3}); a 40-fold difference.

A similar treatment has been carried out previously by Briggs, Edwards and Storey. In their work, the quantity of liquid absorbed as a function of salt content (for the case of complete solubility only) was expressed implicitly in the form of an infinite series. The present results (one for complete solubility, equation (10) and one for partial solubility, equation (13) which are restricted to vulcanizate containing about 1–2% by volume or less of liquid soluble solute), are presented in closed form expressions which are considerably more convenient to employ.

Both the Briggs, Edwards and Storey¹⁰ approach and that used here express the stored-energy function of the rubber in terms of the simple kinetic theory function (containing the single strain invariant I_1). Although the kinetic theory function is known not to apply to rubber at large strains, it was shown by Gent and Lindley⁸ that the use of a more complex stored-energy function (containing the two strain invariants I_1 and I_2) gave results which were identical essentially to that provided by equation (4) for extension ratios less than 4 (the region of most interest here).

Solute particle shape

It has been assumed that the solute particles were spherical in shape. If they are not, the same relationships developed above should still be applicable. However, it has been observed that when irregularly shaped particles imbedded in

rubber dissolve, very high local stresses may be produced which lead to the formation of disc-shaped cracks¹¹ which of course lead to permanent damage. An example of this is shown in Figure 5. Small crystals of CoCl₂ were incorporated into a transparent silicone rubber which was then totally immersed in water. The growth of the solute cavity was observed microscopically. Many of the cavities developed large disc-shaped cracks extending several times the length of the initial crystal size.

Rate effects

The question of rate of absorption is a very difficult question and no effort will be made here to treat the problem. However, it is possible to estimate approximately how long it should take for a given system containing a spherically shaped solute to reach equilibrium absorption, t_∞ . This is done using a result published by Rosner¹² which is given by:

$$t_\infty = \frac{1}{2} \frac{\rho_2}{\rho_1} \frac{r_0^2}{D \ln(1+B)} \quad (15)$$

where

$$B = \frac{c_{sat} - c_\infty}{1 - c_{sat}}$$

and D is the diffusion coefficient of the solute in the solvent. For irregularly shaped particles, r_0^2 may be replaced by $(V/s)^2$ where V is the volume and s is the surface area of the particle.

As an illustration, if one assumes $c_\infty = 0$, then for AgBr one has $B = 8.4 \times 10^{-8}$, while for sucrose one has $B = 2.04$. Hence, assuming r_0 and D are equal for these two solutes, it will take about 10^8 times longer for a rubber containing AgBr as a solute to reach equilibrium swelling than it would for rubber containing sucrose. The effect of temperature on increasing the rate of diffusion is due primarily to increases in both the diffusion coefficient as well as to increase in B which come about because c_{sat} normally increases with temperature.

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