Absorption of liquids by rubber vulcanizates

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The effect of liquid absorption by rubber vulcanizates (swelling) can lead to very large reductions in both the rupture stress and the rupture strain. These reductions occur because the solvent reduces the glass transition temperature of the elastomer. The extent to which a solvent lowers T_g depends, among other things, on the quantity of solvent imbibed. In this paper it is shown that under some restrictions, it is possible to estimate the quilibrium absorption of liquids from a knowledge of the chemical structure of the polymer and the solvent.

INTRODUCTION

The behaviour of an elastomer when exposed to fluids is important in many and diverse applications. If an elastomer absorbs fluid to an appreciable extent, several changes in the physical properties can be expected to occur, e.g. the dimensional change – the elastomer undergoes an increase in size and a good estimate of this increase can be obtained from a knowledge of the weight increase due to fluid pick-up by assuming additivity of volumes. An increase in size of the elastomer may mean that it can no longer effectively perform its intended function. In one reported incident, it was proposed in 1964 that all DC-8 aircraft be grounded because the phosphate ester brake fluid was causing swelling of landing gear seals thereby tending to jam them. This problem was solved by replacing the elastomer used for these seals by another which was more resistant to swelling[1].

Not so clear are the more subtle effects such as the effect of the absorbed fluid on the time-scale (or the effective temperature) of the elastomer. It is well-known that the addition of low molecular weight liquids tends to reduce the glass transition temperature, T_g, of an elastomer. An analysis of this effect by Kelley and Bueche[2] showed that the reduction in T_g depended upon specific bulk properties of both polymer and diluent, e.g. poly(methyl methacrylate) containing 20 vol % diethyl phthalate had a T_g about 50°C lower than that of the pure polymer. The T_g value of a material can be taken as a reference state and many aspects of mechanical and rheological behaviour can be normalized by taking T_g as the reference temperature[3]. It has been found that the ultimate tensile strength decreases monotonically as the difference between the test temperature and T_g is increased[4]. The behaviour of the ultimate strain is more complex, since it first increases then passes through a maximum and finally decreases monotonically with increase in temperature, i.e. the response is bell-shaped. For gum elastomers, the maximum occurs roughly at temperatures 50°–60°C greater than T_g. Hence, as a rough rule of thumb, for elastomers with T_g values of about $-40°C$ or less, the ultimate strain response at room temperature and above will correspond to the right hand portion of the bell where the ultimate strain is monotonically a decreasing function of test temperature[5]. The same kinds of behaviour are observed with elastomers containing reinforcing filler except that for a given T_g value the temperature of the maximum increases with increase in filler content.

The dependence of both the stress-at-break, and the strain-at-break on the normalized temperature $T - T_g$ is shown schematically in *Figure 1*. In part A the monotonic decrease of the breaking stress with increase in $T - T_g$ is evident and part B shows the bell-shaped dependence of the breaking strain on $T - T_g$. The apparent difference in responses is an artifact of this method of plotting for plots of the breaking stress normalized to unit network chain against time to failure, since all elastomers studied including SBR, viton, fluorosilicone, polyurethane, etc., have a common shape and can be superposed to a single curve by a single translation along the time scale. This is also true for the time dependence of the strain-at-break but for this case only data to the right of the maximum can be so superposed[6]. Hence, if the T_g of an elastomer is decreased by whatever means, but particularly when swelled by a fluid, then the test temperature has been increased by the same amount and since both the ultimate stress and strain are decreasing functions we can confidently predict that values of both parameters will decrease; in some cases this decrease can be substantial. We also suspect that properties such as abrasion resistance, fatigue life, cut growth resistance, tear resistance, etc. will also decrease.

As an unusual example, consider the gradual deterioration of silicone heart valve prostheses. A majority of the prosthetic heart valves currently used consist of a silicone poppet contained within a metallic cage. The poppet moves within the

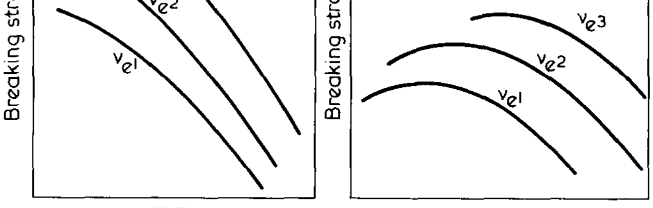

Figure 1 Schematic for the dependence of both the stress-at-break and the strain-at-break on reduced temperature, $T - T_g$ for elastomers having 3 different degrees of crosslinging

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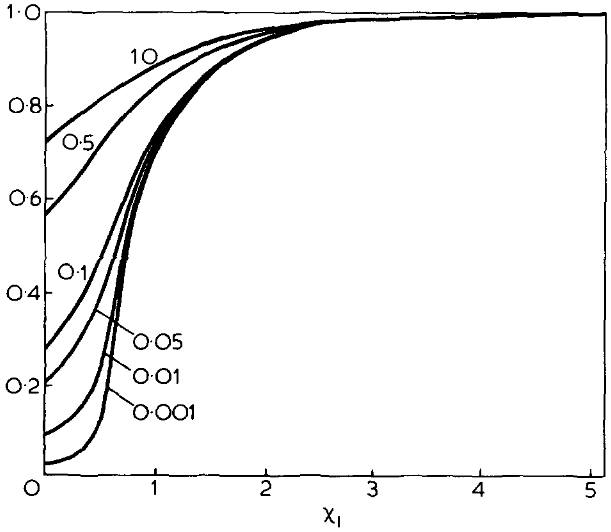

Figure 2 Dependence of V_2 on χ_1 for various values of the volume ratio

cage in such a manner that one-way blood flow is maintained. It has been found that about 2–3% of the poppets fail and have to be replaced. Failure is characterized by discolouration, wear and splitting and although the exact cause has not been firmly established, it is generally believed that the absorption of blood lipid or lipid-type material (*ca* 15% by weight) by the poppet is the underlying cause of the observed changes[7,8,9]. Hence, not only should consideration be given to changes in the physical dimension of an elastomer which interacts with a fluid, but also to the effect of such interaction on the mechanical properties, that is especially true when the elastomer is subjected to dynamic loading.

In such applications, it would be highly desirable to have methods for estimating the probable extent of interaction between a given elastomer and fluid. Several such systems have been developed which use the solubility parameter, δ, defined as

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} \tag{1}$$

where ΔE is the molar energy of vapourization and V is the molar volume. The general idea is that the closer the value of δ for both the elastomer and the fluid, the greater the volume swell of the elastomer[1]. However, many exceptions to this rule were noted[1]. More recent developments have lead to the 'three-dimensional' solubility parameters wherein the total parameter is separated into three contributions: (a) nonpolar or dispersive contribution, δ_D, (b) a polar contribution, δ_p and (c) hydrogen bonding parameter, δ_H so that the total solubility parameter is now expressed as[10].

$$\delta = (\delta_D^2 + \delta_H^2 + \delta_P^2)^{1/2} \tag{2}$$

To use this approach, it is necessary first to carry out experiments in which the solubility of a given polymer is studied using a wide range of solvents which vary widely in their δ_D, δ_H and δ_P contributions. Values for δ_D, δ_H and δ_P for various low molecular solvents have been published[11]. However, no corresponding set of contribution for polymers appears to have been compiled.

We now describe an alternative method for estimating the interaction between elastomers and solvents which although more limited in scope, does not require as input any experimental data.

DISCUSSION

Flory and Rehner[12] showed that for crosslinked elastomers the relationship between concentration of effective network chains, ν_e, and volume fraction of rubber in the swollen gel at equilibrium, v_2, is given by,

$$V_0\nu_e = -\frac{\ln(1-v_2) + v_2 + \chi_1 v_2^2}{v_2^{1/3} - v_2^2} \tag{3}$$

where V_0 is the molar volume of the solvent and χ_1 is the polymer solvent interaction coefficient. Considering the assumptions implied in deriving equation (3), it is generally considered to be more valid at high v_2, i.e., at small extents of swelling. The product $V_0\nu_e$ is really the ratio of the molar volume of the solvent to the molar volume of the effective network chains; and will be referred to as the molar volume ratio.

Figure 2 shows a plot of v_2 versus χ_1 for several values of the molar volume ratio in the range 0.001 to 10. For typical vulcanizates, ν_e is usually less than about 200×10^{-6} moles per cm^3, while the molar volumes of the solvent will be generally less than about 500 cm^3/mole. Of the extensive compilation of δ values for low molecular weight liquids in reference 13, the largest molar value reported is 418.5. Thus, in general $V_0\nu_e$ for most elastomer–solvent systems will be 0.05 or less, and for most practical systems, the molar volume ratio will be even less than this value. However, this point is not critical to our arguments, but does lead to a simplification. Considering *Figure 2* we may distinguish two broad regions: (a) for large χ_1 values, roughly $\chi_1 > 1$, the curves are relatively flat and large changes in χ_1 result in only small changes in v_2, and (b) for small χ_1 values roughly $\chi_1 > 1$, relatively small changes in χ_1 produce very large changes in v_2; this especially so for $V_0\nu_e$ values of 0.05 or less, the curves converge at large v_2 such that for χ_1 values greater than 1, the response becomes independent of the value of $\nu_e V_0$ and hence, the precise values of ν_e or V_0 do not have any influence on the swelling behaviour. That is, swelling is independent of the degree of crosslinking provided $\nu_e V_0$ is 0.05 or less. For this range also, swelling is even independent of the presence or absence of crosslinks. Hence, equation (1) can be simplified to

$$\ln(1-v_2) + v_2\left(1 - \frac{v_2}{v_1}\right) + v_2^2\chi_1 = 0 \qquad \chi_1 > 1 \text{ and } V_0\nu_e \ll 1 \tag{4}$$

For low molecular weight substances, this equation gives semiquantitative agreement when the molar volume of the solute is much greater than that of the solvent. For example, the solubility of water in the higher hydrocarbon can be calculated to within a few percent using equation (4); on the other hand, the solubility of hydrocarbons in water may not. A satisfactory method of using equation (4) more conveniently is to prepare a plot of v_2, or some other function of swelling, against χ_1. Then when the appropriate χ_1 value is available for a particle polymer-solvent system, the value of v_2 can be obtained directly from the plot.

Another limiting form appropriate to very large values of

Table 1 Swelling of silicone rubber in various solvents[21]

Solvent	δ_{calc}	V_{calc}	δ_{expt}	V_{expt}	$S_{calc,\%}$	$S_{expt,\%}$
Methanol	13.8	43.5	14.5	40.4	1.7	3.2
Ethanol	12.6	59.6	12.7	58.4	2.0	10.3
Acetonitrile	11.2	57.5	11.9	52.4	11.0	3.3
Propanol	11.8	75.7	11.9	74.7	3.0	31.2
Butanol	11.3	91.8	11.4	91.5	3.6	26.3
sec-Butanol	11.1	92.1	10.8	91.8	13	51.7
o-dichlorobenzene	10.8	108.4	10.0	112.7	4.5	38.4
Cyclohexane	9.8	107.3	9.9	104.2	52.0	38.4
Dioxane	8.65	88	9.9	85.7	340	37.9
Ethylene dichloride	9.91	80.2	9.8	78.7	30	45
MEK	8.99	93.9	9.3	89.5	116	89.9
Butyl cellulose	10.8	128	8.9	131	3.0	15.4
Cellusolve acetate	8.91	137	8.7	126	68	19.4

the molar volume ratio can be obtained from equation (3). When $V_0\nu_e$ is large, v_2 will be close to unity and hence, we have,

$$\ln(1 - v_2) = 1 + \frac{1}{2}V_0\nu_e + \chi_1 \tag{5}$$

in which case both ν_e and V_0 contribute to the swelling of the system.

It has been shown that χ_1 can be written as

$$\chi_1 \doteq 0.34 + \frac{V_0}{RT}(\delta_1 - \delta_2)^2 \tag{6}$$

where R is the gas constant, T the absolute temperature and δ_1 and δ_2 are the solubility parameters for the polymer and solvent, respectively. The value of the constant has been taken equal to 0.34[13] although values in the range 0.3 to 0.5 have been reported[14]. This equation reduces the problem of employing equations (4) and (5) to the problem of estimating V_0 and the solubility parameters of both the solvent and polymer. Several tabulations of these quantities have been prepared[13,15–18]. However, in the absence of such data, recourse may be had to additive atom and group increments which can be used to estimate both δ_1 and δ_2 from a knowledge of the chemical structure alone[19]. In a more recent paper, very extensive additive atomic and group contributions for V_0 as well as δ_1 and δ_2 have been reported[20].

We have taken the swelling data for a peroxide-cured silica-filled polymethylsiloxane elastomer in various solvents reported by Yerrick and Beck[21]. *Table 1* shows the measured swell values and those calculated from equations (4) and (6), using the group increment for V_0, δ_1 and δ_2 from reference 20. Only the data for swelling ratios less than about 100% have been used (this corresponds to $\chi_1 > 0.8$ which is close to values of χ_1 for which the swelling response becomes independent of ν_e). The calculated volume of liquid absorbed per unit volume of vulcanizate compares very favourably with the experimentally measured values. The only serious disagreement is with the solvent dioxane. The predicted volume swell is 340, while the measured values are 37.9 (about ten times less). This discrepancy is due to the estimated value of δ for dioxane (δ = 8.64) being too low. If the measured value of δ = 9.9 is used instead, the calculated swell is 27% which is much closer to the experimental value of 37.9%. This type of problem can be eliminated if one arbitrarily requires that estimates of swell will only be made when the calculated χ_1 value is equal to or greater than 0.8. Since this automatically ensures that the $v_2 - \chi_1$ response is independent of both ν_e and V_0. If the value calculated for χ_1 for a given polymer–solvent system is less than 0.80 then it is assumed that the proposed method is not applicable. Thus the requirement that $\chi_1 \geqslant 0.80$ would have eliminated the problem noted above with regard to swelling in dioxane.

The results in *Table 1*, for solvents which swell the polymer less than 100% by volume, and for $\chi_1 < 0.8$, show the estimated swellings are in reasonable agreement with the experimental data. The particular vulcanizate used by Yerrick and Beck contained a silica filler and was cured with peroxide. It is possible that some of the discrepancies between the calculated and observed swelling data may be due to preferential absorption of the swelling liquid by the filler or by additives or impurities that are soluble in the liquid.

RATE EFFECTS

So far, only the value of v_2 at equilibrium swelling has been discussed. These values are usually obtained by letting a strip of rubber soak in a suitable solvent and periodically measuring the weight or volume gains as a function of time until a steady value is obtained. For some liquids, this may mean a swelling time of a few days, while for other liquids, several months may be required to reach equilibrium swelling. These vastly different behaviours depend on the rate of diffusion of the liquid into the rubber. A schematic swelling curve (*Figure 3*) shows the dependence of S, the ratio of volume of liquid absorbed to the volume of rubber, on the square root of time. The equilibrium value of S is calculated from the equilibrium uptake of liquid and is shown as the dotted line. For the initial stages of diffusion into a plain sheet (roughly for liquid uptakes up to 50% of the equilibrium uptake), the dependence of S on time is given by[23]

$$S(t) = 2S(\infty)\left(\frac{A}{V}\right)\left(\frac{Dt}{\pi}\right)^{1/2} \tag{7}$$

where $S(\infty)$ is the volume of liquid absorbed at equilibrium per unit volume of dry rubber, A and V are the surface area and volume of the sheet, respectively, D is the diffusion coefficient and t is the swelling time. This expression predicts that $S(t)$ will be linear in $t^{1/2}$. An estimate of the minimum time required to establish equilibrium can be made by assuming that equation 7 is valid over the whole range and hence

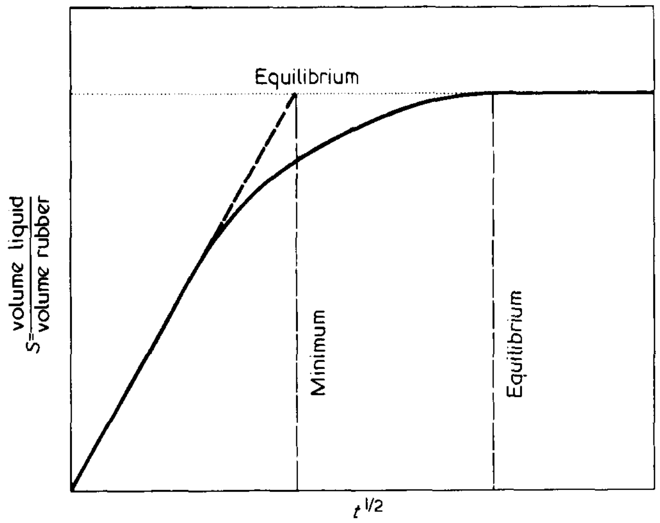

Figure 3 Schematic representation of the ratio of volume of liquid/volume of rubber on square root of time

the minimum time is the abscissa value at which equation 7 intersects the horizontal line representing $S(\infty)$, i.e., the minimum time is given by

$$t_{min} = \frac{\pi}{4D} \frac{V^2}{A^2}$$

For a given shaped specimen, the minimum swelling time is inversely proportional to the diffusion coefficient. Thus if for two liquids the diffusion coefficient varies by a factor of a thousand, we can expect that the times required to reach equilibrium swelling will also vary by a factor of about a thousand.

EFFECT OF COMPOUNDING INGREDIENTS

The previous discussion refers to the swelling behaviour of gum vulcanizates. However, in practice, rubber vulcanizates contain filler, plasticizers, antioxidants, etc. each of which may independently interact with a liquid. Generally, except for the plasticizer oils, most ingredients are insoluble in rubber and exist in discrete regions. Normally, the rubber comprises the continuous phase and the insoluble ingredients exists as the discrete phase. If the ingredient in question is soluble in the liquid, then the liquid diffuses into and starts to dissolve the particle. This solution initially saturated with respect to the solute absorbs more liquid and the cavity surrounding the inclusion increases in size. This acts like a sink and the rate of diffusion of the liquid is greater now than it would be in the absence of the inclusion. The amount by which the rate of diffusion is enhanced depends on both the particle size of the inclusion and its absolute solubility in the pure liquid. The smaller the particle size and the greater the solubility, the greater the enhancement of the diffusion.

Considering that the continuous rubber phase acts like a more or less semipermeable membrane with respect to the inclusion, the tendency is for the pure solvent to diffuse in and dilute the concentrated solution; as it does so, the cavity increases in size. The rubber phase exerts a hydrostatic pressure on the solution. Finally, the osmotic pressure exerted by the solvent in the solution becomes equal to the pressure exerted by the rubber and growth of the cavity by the diffusion of pure liquid ceases.

REFERENCES

1 Beerbower, A., Kaye, L. A. and Pattison, D. A. *Chem. Eng.* Dec 18, 1967, p 118
2 Kelley, F. N. and Bueche, F. *J. Polym. Sci.* 1961, **50**, 549
3 Ferry, J. D. *Viscoelastic Properties of Polymers,* John Wiley & Sons, New York (1961)
4 Borders, A. M. and Juve, R. D. *Ind. Eng. Chem.* 1946, **38**, 1066
5 Landel, R. F. and Fedors, R. F. in *Fracture Processes in Polymer Solids,* Ed. B. Rosen, Interscience Publishers, New York, (1964) Ch. IIIB
6 Fedors, R. F. in *The Stereo Rubbers,* Ed. W. M. Saltman, John Wiley and Sons, Inc., New York (1977), Ch. 8
7 Raible, D. A., Keller, D. P., Pierie, W. R. and Koorajian, S. *Rubber Chem. Techno.,* 1966, **39**, 1276
8 Carmen, R. and Kahn, P. *Biomed. Mater. Res.* 1968, **2**, 457
9 Chin, H. P., Harrison, E. C., Blankenhorn, D. H. and Moacanin, J., *Circulation,* Supp. I, 1971, 1–51
10 Hansen, C. M. *Ind. Eng. Chem. Prod. Res. Dev.* 1969, **8**, 2
11 Hansen, C. M. and Beerbower, A. in *Encyclopedia of Chemical Technology,* Supplement Volume, John Wiley and Sons, New York (1971), p 889
12 Flory, P. J. and Rehner, Jr., J. *J. Chem. Phys.* 1943, **11**, 521
13 Sheehan, C. J. and Bisio, A. L. *Rubber Chem. Techn.* 1966, **39**, 149
14 Bueche, A. M. *J. Polym. Sci.* 1955, **15**, 97
15 Burrell, H. and Immergut, B. in *Polymer Handbook,* Eds. J. Brandrup and E. H. Immergut, Interscience Publishers, New York (1966), IV, p 341
16 Hansen, C. M. *J. Paint Tech.* 1967, **39**, 104
17 Hoy, K. L. *J. Paint Tech.* 1970, **42**, 76
18 Gardon, J. L. in *Encyclopedia of Polymer Science and Technology,* John Wiley and Sons, Inc., New York (1965), p 853
19 Small, P. A. *J. Appl. Chem.* 1953, **3**, 71
20 Fedors, R. F. *Polym. Eng. Sci.* 1974, **14**, 147
21 Yerrick, K. B. and Beck, H. M. *Rubber Chem. Techn.* 1964, **36**, 261
22 Crank, J. *The Mathematics of Diffusion,* Oxford University Press, London (1956)
23 Southern, E. and Thomas, A. G. *Trans. Faraday Soc.* 1967, **63**, 1913