

Discussion

The results reported here confirm that PS properly mixed with PXE is dispersed on a molecular scale*. The positive value of A_2 , moreover, indicates a favourable free energy of mixing. The trend in A_2 with partial bromination also accords with expectation, given that higher levels of bromination cause phase separation.

The precise interpretation of the A_2 derived from Figure 1 is hampered by the fact that the matrix compositions (i.e. the material other than the deuterio PS) differed from each other by small degrees (i.e. 0 to 9% hydrogenous PS). Finally the indication that A_2 and R_g may both increase with temperature suggests an endothermal heat of mixing, which appears inconsistent with the exothermal heat of mixing derived from the solution calorimetry study.

These studies are continuing with the goal of determin-

* Subsequent to the carrying out of the work described above, we became aware of neutron scattering work of Wignall (*Polymer* 1980, **21**, 131) on the system PS/PXE from which a value of R_g for PS consistent with that for bulk polymer has also been found

ing quantitatively the thermodynamics of mixing of PS with PXE and its brominated derivatives.

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The uptake of water vapour by an epoxide adhesive formed from the diglycidyl ether of bisphenol-A and di-(1-aminopropyl-3-ethoxy) ether

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Introduction

We have previously reported¹ the results of uptake from liquid water at temperatures between 25° and 100°C for a series of six epoxide adhesives based on the diglycidyl ether of bisphenol-A (DGEBA). One of these adhesives was selected for a more detailed study involving uptake from water vapour at 48°C, and we report the results here. We wanted to investigate more thoroughly the mechanism of water diffusion and the thermodynamics of the water-epoxide equilibrium. A parallel objective was to use the same adhesive in single lap joints with aluminium adherends and attempt to relate the loss of joint strength upon exposure to wet air to the diffusion coefficient of water in the adhesive. Results of this latter investigation are available, and will be published later.

Experimental

The adhesive consisted of 100 g 'Shell Epikote 828' and 32.5 g di-(1-aminopropyl-3-ethoxy) ether (DAPEE). The former is based on the diglycidyl ether of bisphenol-A (DGEBA). Thin films of the adhesive were prepared by casting on tin foil using a method we have previously described¹. Films were 50-170 μm thick, and pieces used were approximately 10 mm x 40 mm. Cure of the adhesive was for 3 h at 80°C. To investigate the effect of varying the amount of hardener, some hardener-rich and hardener-lean films were prepared which were respectively 10% rich or deficient in DAPEE.

Uptake from water vapour at 48° ± 0.2°C was undertaken using a C. I. Electronics Vacuum Microbalance, contained within an air thermostat. The microbalance could be evacuated via its connection to a vacuum line pumped by a mechanical pump and a mercury diffusion pump. A mercury manometer, connected to the microbalance and contained within the air thermostat, could be read using a travelling microscope external to the thermostat. A flask containing water or a water-glycerol mixture was also connected to provide water vapour at a static pressure. Prior to experimentation, liquid in the flask was degassed by freezing and thawing under vacuum.

The adhesive film was suspended from one arm of the microbalance, and if necessary a small piece of wire provided a counterweight on the other arm. A 'Zerostat Gun', sold for discharging static electricity on gramophone records, was found useful in assembling the apparatus. A chart recorder with full scale deflection set at 4 mg continuously recorded the mass of the sample.

Initially, the same piece of film was used for several sorption-desorption cycles at different activities, but the scatter in the results suggested that a permanent change in the properties of the film might be taking place, even though after desorption the film always returned to its original weight. This effect was investigated by subjecting films to several sorption-desorption cycles; values of water activity were 1.0 or 0.66 during the sorption stages. In other cases a fresh film was used for each sorption experiment.

Epoxide adhesives are widely used against suitably treated

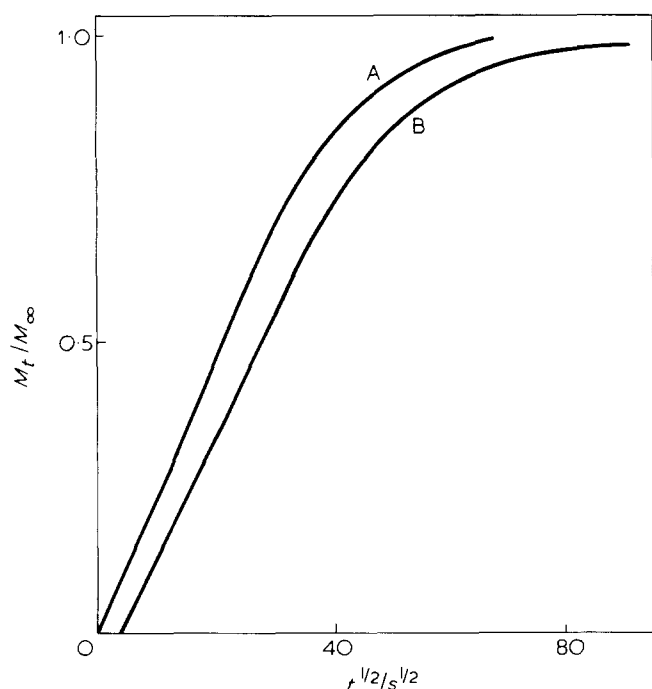


Figure 1 Sorption and desorption of water vapour by a film 104 μm thick at activity = 0.66. A, desorption; B, absorption

aluminium adherends. To see if any effects were due to the aluminium-epoxide interface, some films were cast on aluminium foil, and a strip of the foil-backed epoxide subjected to water uptake in the microbalance at water activities of 1.0 and 0.66. The aluminium foil (BDH Chemicals) was 48 μm thick. It was surface-treated by wiping with trichloroethylene and immersion in a solution of sulphuric acid (15% by volume) and chromium trioxide (50 g dm^{-3}) for 20 min. at 60–65°C. This was followed by rinsing in running tap water for 20 min. and drying for 30 min. at 60°C.

A scanning electron microscope (SEM) (AEI model Corinth 275) was used to examine surfaces and microtomed sections of some films. Microtomy was performed using a Leitz base-sledge microtome on samples embedded in Durcupan ACM (Fluka). All surfaces were vacuum-coated with gold prior to microscopy.

Results

Microbalance chart records of mass against time were sampled at appropriate intervals and plots of fractional uptake (M_t/M_∞) against the square root of time constructed. M_t is the mass uptake at time t and M_∞ is the equilibrium uptake. These plots showed an initially linear region up to at least $M_t/M_\infty = 0.6$, which then curved over to give an equilibrium plateau. The diffusion coefficient D could be obtained from the slope of linear region using the following equation²:

$$\frac{d(M_t/M_\infty)}{d(t^{1/2})} = \frac{4}{l} \left(\frac{D}{\pi} \right)^{1/2}$$

Slopes could be estimated to within $\pm 2\%$, and l varied over any sample by $\pm 5\%$, giving an uncertainty of about 14% in D . The uncertainty in equilibrium solubility M_∞ is estimated as $\pm 1\%$.

In seven cases desorption was monitored also, and D obtained from the plot of fractional desorption against $t^{1/2}$ was

in very close agreement with the sorption value. The difference between the two values of D was positive in four of the cases and negative in the other three. Figure 1 shows the sorption and desorption plots obtained in one case.

The dependence of diffusion coefficient upon water activity is shown in Figure 2, and the dependence of M_∞ is shown in Figure 3. Water activity a was taken as the ratio of measured vapour pressure to saturated vapour pressure.

Varying the amount of DAPEE hardener had an insignificant effect upon D , the measured values being within the range of scatter shown in Figure 2. However, values of M_∞ were in the order rich > standard > lean, the values being 2.8, 2.7 and 2.3 at $a = 0.66$ and 5.7, 5.1 and 4.7 at $a = 1.0$ (M_∞ values have dimensions of $\text{g } 100 \text{ g}^{-1}$ of adhesive). The aluminium-backed adhesive gave a diffusion coefficient which was within the scatter of Figure 2. However, at $a = 0.66$, the uptake curve had a sigmoidal shape. The aluminium backing decreased the value of M_∞ from 5.1 to 4.0 at $a = 1.0$ and from 2.7 to 2.4 at $a = 0.66$.

The changes in D and M_∞ through successive sorption-desorption cycles are shown at $a = 1.0$ and $a = 0.66$ in Figures 4 and 5 respectively. In all cases examined, SEM revealed featureless fields of view with no evidence of cracks or flaws.

Discussion

The uptake plots show that diffusion of water in the epoxide is Fickian. Fickian diffusion is generally associated with polymers in their leathery states but we have previously shown¹ that whether in the leathery or glassy state, water diffusion in epoxides always seems to be Fickian as far as the

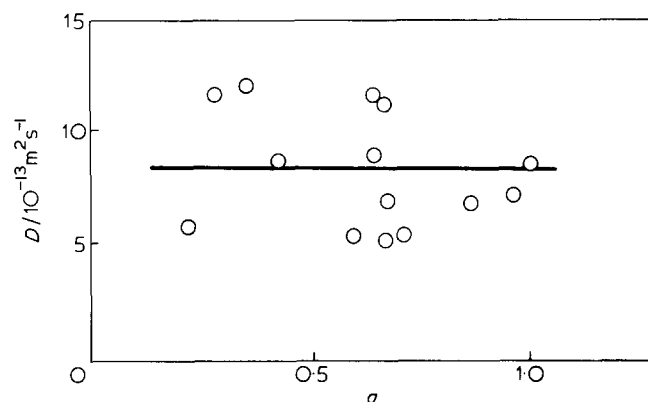


Figure 2 Dependence of diffusion coefficient upon water vapour activity

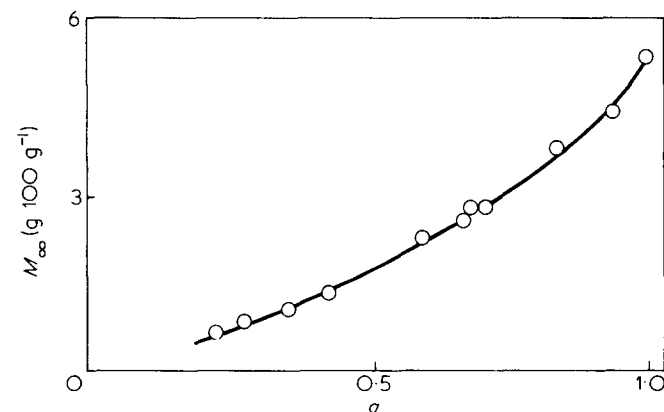


Figure 3 Dependence of solubility upon water vapour activity

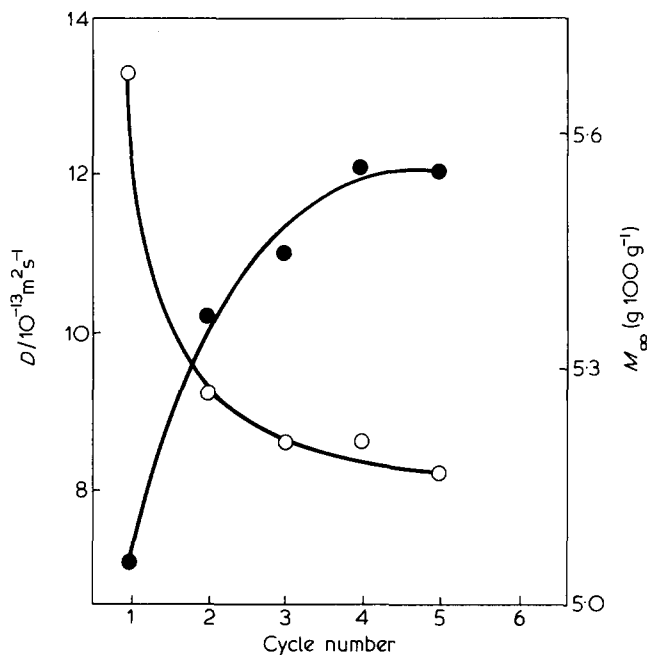


Figure 4 Changes in diffusion coefficient (○) and solubility (●) during absorption-desorption cycling at activity = 1.0

shape of uptake plots is concerned, i.e. they are linear up to $M_t/M_\infty \geq 0.6$. We have reported previously that the glass transition temperature of this adhesive is 67°C when dry, and 37°C when it has absorbed water equal in quantity to equilibration with liquid water at 25°C. At 48°C and 25°C, the amounts of water absorbed at equilibrium are very similar, 5.1 and 5.0 g 100 g⁻¹ respectively, so the films will change from the glassy to the leathery state during sorption.

Although there is a moderate amount of scatter in Figure 2, it seems to show quite clearly that D is independent of concentration. This view is reinforced by the agreement recorded between values of D for sorption and desorption experiments. The mean value of D for vapour uptake at 48°C is $9.3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, and this is in good agreement with an interpolated value for uptake from liquid water by the adhesive at 48°C of $7.9 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. The basic theory of sorptive uptake requires that these values should be the same; but large differences between them have been observed in some cases³ which would apparently contravene the zeroth law of thermodynamics. Similarly values of M_∞ for vapour and liquid should be the same; the values are 5.1 and 4.7 g 100 g⁻¹ and it is thought that some leaching during liquid sorption may lead to the difference.

The constancy of D with concentration has been observed for some other epoxide-water systems⁴, but there are reports of systems where D increases with concentration^{5,6}. The latter situation is what would be expected for a relatively hydrophilic polymer, such as an epoxide, where water sorption leads to plasticization; concentration-independent diffusion coefficients are usually found for hydrophobic polymers, such as poly(alkanes)⁷, where the actual amount of water absorbed is low. However, a constant D seems consistent with the formation of water clusters. If most of the absorbed water is in clusters, then a relatively small amount of water will remain in true solution within the epoxide, and the concentration of molecularly dispersed water will be constant over most of the range of activity, that is except at very low activities. The situation might be compared with micelle formation in soap solutions, where once the initial

micelle concentration has been exceeded the concentration of molecularly dispersed soap molecules remains constant. Only the dispersed water molecules would be mobile and so contribute to the diffusion process.

The large amount of scatter in Figure 2 can only be partly accounted for by the estimated accuracy in D of $\pm 14\%$. The rest is probably due to a dependence of D upon film thickness. Some uptake data for films of three different thicknesses are shown in the form of a plot of fractional uptake against $t^{1/2}l^{-1}$ in Figure 6. It is a condition of Fickian diffusion that these plots should coincide. Their failure to do so is one sign that diffusion is non-Fickian. The characteristics of Fickian diffusion have been summarized by Fujita⁸.

The sorption isotherm is a BET type III isotherm, and isotherms of this type have been noted previously for water-epoxide systems^{9,10}. This type of isotherm may be obtained when the forces between penetrant and polymer are small and there are strong penetrant-polymer interactions, leading to clustering. We have also examined the equilibrium data in the light of the Zimm¹¹ clustering theory and the Flory-Huggins^{12,13} theory for polymer solutions.

The clustering theory was developed to determine the degree of non-random mixing in two-component systems, and it was later applied to polymer-solvent mixtures^{14,15,16}. Starting from dilute gas statistical mechanics, Zimm derived the following relationship:

$$\frac{G_{11}}{\nu_1} = \frac{kT\beta}{\nu_1} - \phi_2 \left[\frac{\partial(a_1/\phi_1)}{\partial a_1} \right]_{p,T} - 1$$

in which G_{11}/ν_1 is the clustering function of component 1, ν_1 is the partial molar volume of component 1, β is the isothermal compressibility of the system, ϕ_1 and ϕ_2 are the volume fractions of the two components and a_1 is the activity of component 1. In polymer systems, component 1 is solvent and 2 is polymer. For binary systems far from the gas-liquid critical region, the compressibility term is about

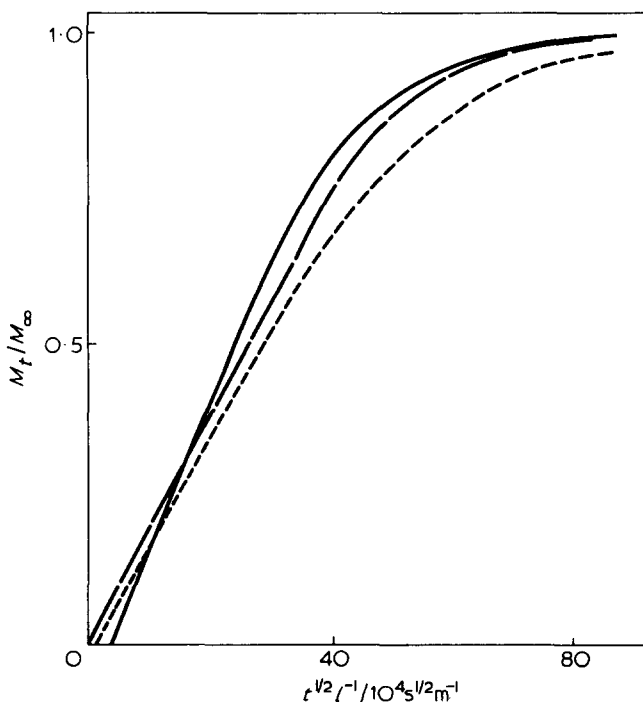


Figure 5 Changes in diffusion coefficient (○) and solubility (●) during absorption-desorption cycling at activity = 0.66

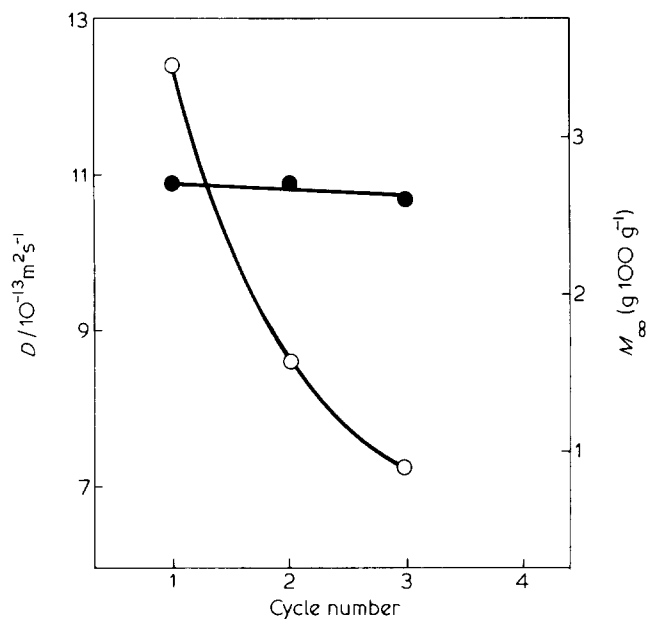


Figure 6 Reduced sorption curves for films of different thicknesses. —, 142 μm ; - - - -, 82 μm ; - · - ·, 79 μm

Table 1 Dependence of clustering function and interaction parameter on activity

a_1	G_{11}/ν_1	χ_1
0.22	17.3	2.5
0.27	17.3	2.4
0.35	17.2	2.5
0.67	16.9	2.3
0.71	16.8	2.3
0.84	16.6	2.2

0.02–0.06 and so the term involving it can be neglected.

We have used this equation to evaluate the clustering function. Values of the densities of epoxide and water at 48°C were taken as 1.18 and 0.988 g cm⁻³, and it was assumed that negligible volume change took place on mixing. A straight line plot of a_1/ϕ_1 against a_1 permitted the evaluation of the partial differential. The values obtained for the clustering function are shown in Table 1. When $G_{11}/\nu_1 = -1$, the system is ideal; and each solvent molecule excludes its own volume to other molecules, but does not otherwise affect their distribution. A value of $G_{11}/\nu_1 > -1$, as is the case here, is indicative of clustering: a value less than 1 indicates segregation of solvent molecules. It can be seen from Table 1 that G_{11}/ν_1 virtually maintains a constant value over the concentration range.

Flory and Huggins used a lattice model for polymer–solvent mixtures and their theory can be applied to vapour sorption equilibrium by using the following equation:

$$\ln a_1 = \ln \phi_1 + \phi_2 + \chi_1 \phi_2^2$$

in which χ_1 is the polymer–solvent interaction parameter. It is this latter which is the unknown in the equation, and whose constancy over the range of activity we have sought to examine. The values are collected in Table 1; χ_1 is virtually constant over the range of activity, the value (> 0.5) being indicative of poor solvation. Another system for which χ_1 is concentration-independent is that of benzene and natural

rubber¹⁷, but χ_1 generally varies with concentration. Orofino *et al.*¹⁸ studied the sorption of water in several polymers, including cellulose acetate, poly(vinylchloride) and poly(ethylmethacrylate) and found that χ_1 either increased or decreased with a_1 .

The change of M_∞ with the amount of hardener follows a trend consistent with the number of hydrophilic groups introduced by the hardener. Neither D nor M_∞ are changed much by the presence of an aluminium backing; the fact that D is not altered suggests that wicking of water along the metal–adhesive interface is insignificant. The backing foil reduces M_∞ by imposing a restriction on swelling, similar in manner to an observation for the sorption of *n*-decane by natural rubber sheets bonded to steel backing plates¹⁹.

The sorption–desorption cycling has a very slight effect on M_∞ , but, nevertheless, the trend is that M_∞ increases with cycling at unit activity (Figure 4). D decreases on cycling. These observations suggest that irreversible changes are taking place which lead to the formation of new sorption sites. Most changes occur between the first and second cycles, so the majority of change is in the first. One possible way in which new sites are formed is by microcracking of the resin. Examination of cycled films by SEM failed to show any cracks; these films did not appear in any way different from films that had not been exposed to water vapour. Other workers have observed small cracks in water-aged epoxides by both optical and electron microscopy, but for samples subjected to treatment more extreme than ours: boiling^{20,21}, freezing²² or subjection to 150°C thermal spikes²³.

Similar ageing effects have been found for the diffusion of water vapour in high-impact polystyrene and poly(ethylene terephthalate)²⁴. Samples were aged in artificial sunlight at 49°C and 50% relative humidity, and it was found that D decreased, whilst the solubility and activation energy for diffusion of water increased. It was postulated that ageing caused a modification of the site-to-site jump configuration. The effect of water on jump configuration has been examined for two epoxide systems by Kwei²⁵. Moisture was found to increase the jump frequency of polymer segments and reduce the number of polymer units in cooperative motion in a jump process. Kwei suggested that his results were consistent with the disruption of interchain hydrogen bonding by water molecules, which gave an increase in jump frequency. However, very likely, this would be reversed on removal of water; the problem is that our cycling results are irreversible. Thus neither microcracking nor changes in jump configuration seem to account for cycling results.

From the foregoing discussion it can be seen that the system studied is in some ways a model one. It agrees with the Zimm clustering theory and the Flory–Huggins theory, maintaining virtually constant values of the clustering function and the polymer–solvent interaction parameter over the range of concentration. Further, the diffusion coefficient is constant over the concentration range.

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Pressures transmitted through polymeric powders subjected to solid phase compaction

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Recent studies¹ have examined the feasibility of solid phase compaction as a production technique for polymeric powders. In order to carry out a detailed analysis of the compaction process, three materials were selected. These were poly(vinylidene chloride)(PVdC, type VR 558), poly(vinyl chloride)(PVC, type S71/102) and polypropylene. These particular materials were chosen because of their compaction characteristics. PVdC can be compacted into components with strengths up to 30 MPa without difficulty; PVC can be compacted into components but they are relatively weak; and polypropylene does not compact at all under the conditions employed so far. Detailed comparisons have been made between the powders in order to explain the differences observed in their compactability and perhaps improve the compaction characteristics of PVC and polypropylene.

As part of this comparison, tests were carried out to measure the forces transmitted through each powder when it is compacted in a metal die. The die used produced compacts with a diameter of 19 mm and heights ranging from about 1 mm to about 38 mm (h/D from 0.05 to 2). Compaction was achieved using an Amsler test machine to push a closely fitting piston down on to the powder in the die. The upper force was obtained from the read-out of the test machine and the transmitted force was obtained from a load cell in the base of the die.

The results for a compaction pressure (P_1) of 200 MPa and pressing rate of 8 MPa s⁻¹ are shown in Figure 1. At first glance, there appeared to be a trend between ease of compaction and the transmitted pressure in that the PVdC, which compacts easily, shows the greatest fall-off in transmitted pressure; whereas the polypropylene, which does not compact at all, shows very little fall-off in transmitted pressure. However, this theory was quickly discounted when it was remembered that PTFE can be compacted very easily but, as shown in Figure 1, exhibits a negligible loss in transmitted pressure. Therefore, these tests provided little insight into the compactability of different powders but it was considered that the information obtained was extremely relevant to component and die design when using polymeric powders. Many years of research, particularly with metals²⁻⁴,

ceramics⁵ and pharmaceutical materials⁶ have shown that die compaction of powdered materials is beset with problems. Most of the difficulties arise from the frictional effects within the powder mass and at the powder/metal interfaces. The resulting loss in the compacting force away from the pressing piston causes heterogeneous densification of the compact with consequent low strengths in the low density areas. It is desirable therefore to be able to predict pressure losses within a compact.

The magnitude of the loss in transmitted pressure can be estimated by considering equilibrium of forces⁷. The applied force acting downwards on the powder is balanced by the upward force F_2 plus the frictional force. For a die of diameter D , the downward force F_1 is given by $\frac{1}{4}\pi D^2 P$ where P is the pressure at that section. Similarly, F_2 will be given by $\frac{1}{4}\pi D^2 (P + dP)$. If it is assumed that the radial pressure is directly proportional to P , then the frictional force at the wall is given by $CP\pi D(dh)\mu$ where μ is the coefficient of friction, C is a constant and dh is the height of the element considered.

So

$$\frac{1}{4}\pi D^2 P = \frac{1}{4}\pi D^2 (P + dP) + CP\pi D dh \cdot \mu$$

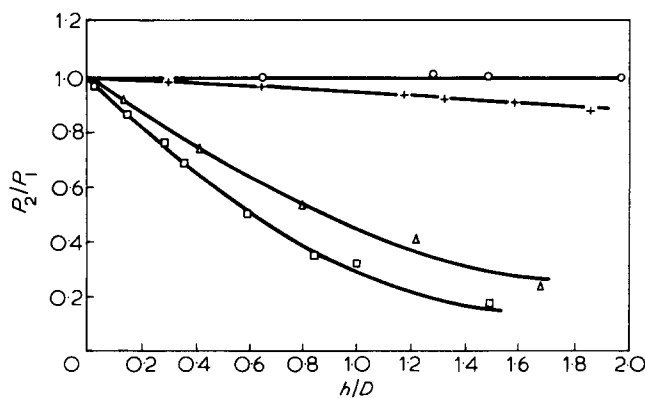


Figure 1 Transmitted pressure ratio as a function of geometry of compacts. ○, PTFE; +, polypropylene; △, PVC; □, PVdC