Diffusion kinetics of a dialkyne in silicone rubber by density profiling

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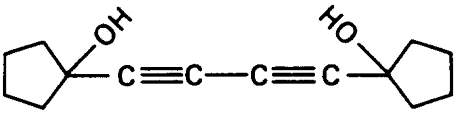
The technique of density profiling was used to monitor the diffusion of bishydroxycyclopentylbutadiyne (HCPB) through a silicone rubber. Reaction of HCPB with excess hydrosilane sites, unreacted during the polymer cure process, immobilized part of the diffusant and led to the development of a concentration front, or plateau, in the diffusion profiles. Kinetic modelling was used to reproduce the salient features of the profiles and to provide a means of obtaining a diffusion coefficient. The diffusion coefficient was found to be a decreasing function of concentration, in contrast to the behaviour observed in most systems.

(Keywords: diffusion kinetics; density profiling; silicone; bishydroxycyclopentylbutadiyne; density gradient; plateau)

INTRODUCTION

In this study, we wished to monitor the diffusion of a hydrogen getter, bishydroxycyclopentylbutadiyne (HCPB), structure I, through a silicone rubber encapsulant.



(I)

A number of techniques developed to monitor the diffusion of relatively small molecules through polymeric matrices were considered. These include i.r. absorption[1], fluorescence[2], u.v. absorption[3] and radioactive labelling[4]. Each of these methods has its own advantages and disadvantages, but in general the spectroscopic techniques require that the diffusant produce a signal which can be distinguished from the polymer background. While this is generally not a concern with radioactive labelling, questions of safety and materials availability become important. The data for the current study were acquired using the technique of density profiling, originally developed to study the depth dependence of polymer ageing[5]. The only conditions necessary for application of the technique are a change in polymer density with addition of diffusant and a known relationship between density change and diffusant concentration. As will be shown below, non-Fickian diffusion profiles were obtained for this system owing to reaction of diffusant with hydrosilane sites in the polymer.

EXPERIMENTAL

The silicone used in this study was Sylgard 184 (Dow Corning). The material consists of a vinyl end-capped poly(dimethylsiloxane) with a degree of polymerization of approximately 400. This prepolymer is cured by a vinyl addition with the silane groups on a short siloxane chain, with a degree of polymerization of 10. Unless otherwise noted, each sample was formulated as a 10:1 ratio of prepolymer to curing agent. This composition, which is the manufacturer's recommendation, represents an excess of curing agent such that one-half the silane groups remain unreacted after cure.

Silicone cylinders were prepared in glass vials, allowed to cure partially overnight, and then final cured at 71°C for 3 h. In order to form a planar interface between an HCPB layer and the cylinder, HCPB powder was mixed with uncured silicone and added to the vials. The HCPB settled to the bottom of the uncured region, forming a sharp, void-free interface with the precured cylinder. The top layer was then allowed to cure at room temperature for ~72 h before the vials were placed in an oven to accelerate diffusion. As the HCPB diffused into the silicone, the density of the silicone was observed to increase. This meant that density profiling techniques could be used to follow quantitatively the diffusion process. This technique, which has recently been reviewed[6], involves the use of a density gradient column to monitor the density of a series of successively cut slices proceeding from the surface of a sample into its interior. A 100 cm long density gradient column with a density range of approximately 1.03 to 1.07 g cm^{-3} was prepared from calcium nitrate–water solutions using forced mixing techniques controlled by liquid pumps. The column is of double-wall construction, which allows temperature control at 23 ± 1°C using a circulating water bath. The column was calibrated using glass calibration balls of known density (measured at 23°C), available from Techne Inc.

Samples for the density measurements were obtained from the approximately 36 mm long silicone cylinders after removal from the ageing ovens. A rectangular core of approximate dimensions 2 mm × 2 mm × 36 mm was removed from the inside of the cylinder, and thin slices parallel to the original HCPB–silicone interface obtained from this core sample. Before introduction into the column, each slice was wetted with a water solution and carefully examined under a microscope to make sure air bubbles were not attached to the sample. Once in the column, samples required ~0.5–2 h to reach equilibrium, dependent primarily on sample size. Density results were

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obtained for a sufficient number of slices from each core to characterize the density increase that occurs as the interface is approached. Constant-density results, characteristic of the pure silicone, were eventually reached at points beyond the extent of the HCPB diffusion. This baseline density was subtracted from the density results closer to the interface to obtain the changes in density reported in this paper. By carrying out experiments on various sizes of samples (different surface-to-volume ratios), no evidence could be found for possible measurement artifacts caused either by selective sorption of the column liquid or by air bubbles too minute to be readily observed. From repeated measurements performed on identical samples, our estimated experimental scatter is less than $1 \times 10^{-4}\,g\,cm^{-3}$.

A separate experiment was performed to correlate density changes to absolute diffusant concentrations. Two limiting cases are possible. If HCPB diffuses into free volume in the silicone matrix, with no concomitant swelling, the change in silicone density would be equal to the weight of added HCPB per unit volume. Alternatively, if diffusion of HCPB into the polymer caused the matrix to swell by an amount equal to the original HCPB volume (ideal mixing), the final density would be a weighted average of the silicone ($1.0404\,g\,cm^{-3}$) and HCPB ($1.1645\,g\,cm^{-3}$) densities. A preweighed slice of cured silicone of about 1.5 mm thickness was sandwiched between two other silicone slices which were in turn surrounded by layers of HCPB. The assembly was then aged at 120°C for seven days to diffuse HCPB into the inner slice. Its change in weight could then be correlated with its change in density. The outer silicone slices were used to prevent direct contact between the weighed slice and the HCPB layers, which would lead to the adherence of small HCPB crystals to the surface of the weighed slice.

The results of this experiment showed that $>90\%$ of the density change could be accounted for by ideal mixing, in agreement with the theory of Cohen and Turnbull[7], which predicts that there is far less free volume of sufficient size than is necessary to accommodate the observed concentration of HCPB. This allowed us to calculate HCPB concentrations from the measured changes in density. It was found that for each $0.01\,g\,cm^{-3}$ change in density, $0.3\,mol\,l^{-1}$ of HCPB is absorbed.

RESULTS AND DISCUSSION

Diffusion profiles for a series of samples aged at 80°C for times ranging from 9 to 120 days are shown in *Figure 1.* The horizontal bars for each data point show the thickness of the slice and its location relative to the HCPB–silicone interface. With the exception of the profile taken at the very earliest time, each curve is clearly non-Fickian, characterized by a sharp concentration gradient near the interface and a concentration front or plateau region deeper in the sample. This can be explained in terms of reaction of HCPB with residual hydrosilane sites in the silicone. The silicone cure process consists of hydrosilation of vinyl end-caps. Since half the hydrosilane groups are unreacted after cure, they are available for reaction with the diffusant. The two possible reactive sites on the HCPB are the hydroxy group and the carbon–carbon triple bonds. In either case, reaction with the silicone immobilizes it, giving rise to plateau formation. Evidence for the presence of immobilized getter molecules is provided by extraction data. Slices of silicone taken from different sample depths were extracted with acetone, a good solvent for HCPB, and the solvent then driven off. Sample weight loss for the slice taken in the plateau region (where presumably most HCPB molecules would be immobilized and unextractable) was nearly identical to the weight loss of a slice with no HCPB. However, slices taken closer to the interface showed progressively larger weight losses.

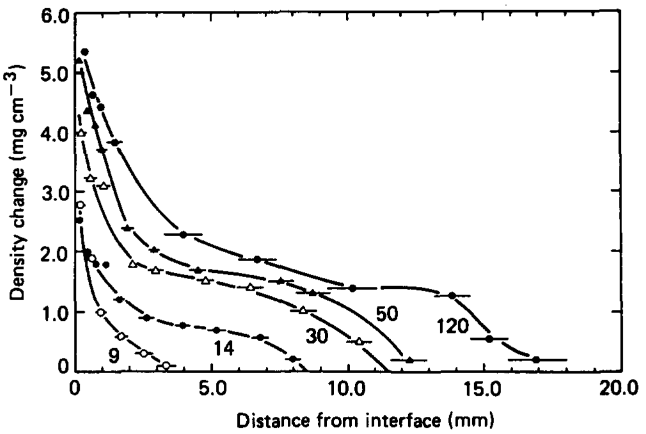

Figure 1 Diffusion profiles for samples aged at 80°C for times ranging from 9 to 120 days. Silicone was a 10:1 formulation

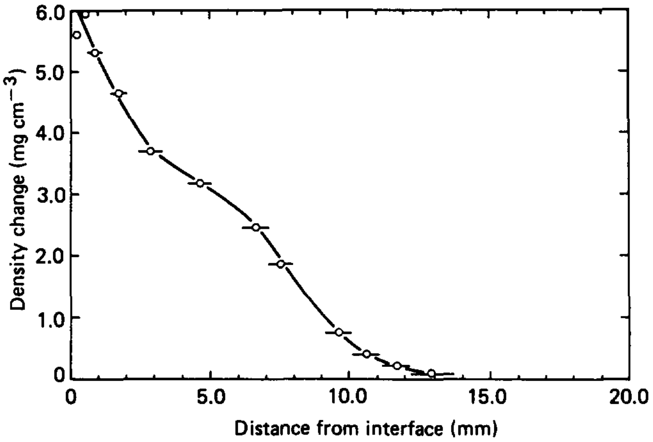

Figure 2 Diffusion profile for 6.6:1 formulated sample aged 64 days at 80°C

One would expect that if residual hydrosilane sites are reacting with HCPB, the height of the plateau would increase if the silicone formulation were changed to give a greater excess of curing agent. This is shown to be the case in *Figure 2,* for a silicone sample with a 6.6:1 ratio of prepolymer to curing agent. This formulation will give a residual concentration of hydrosilane groups after cure that, to a first approximation, is twice that of the corresponding concentration in the 10:1 formulation. The diffusion profile in *Figure 2* was from a sample aged 64 days at 80°C. Although changing the silicone composition leads to complex changes in profile shape, the plateau height is increased by about a factor of 2, as expected.

The salient features of these diffusion profiles were verified by kinetic modelling using a diffusion–reaction equation[8]. If C_R, C_M and C_B are the concentrations of accessible reactive sites, mobile HCPB molecules and bound HCPB molecules, respectively, and the zero superscripts on these quantities are the maximum values of these concentrations, then $C = C_M + C_B$ is the total concentration and

$$C^0 = C^0_M + C^0_R = C^0_M + C_R + C_B \tag{1}$$

Since the increase in the total concentration of HCPB in a volume element with time is due solely to the diffusion of the mobile species, the diffusion equation is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C_M}{\partial x}\right) \tag{2}$$

where the diffusion coefficient $D = D_0 f(C/C^0)$ is taken to be a function of concentration alone. Assuming a second-order reaction between the mobile HCPB molecules and the accessible reactive sites in the silicone matrix,

$$M + R \xrightarrow{k} B \tag{3}$$

yields the rate equation

$$\frac{-\mathrm{d}C_R}{\mathrm{d}t} = \frac{\mathrm{d}C_B}{\mathrm{d}t} = kC_M C_R \tag{4}$$

which is to be solved simultaneously with the diffusion equation. Rewriting equations (2) and (4) with the reduced variables

$$T = D_0(C^0_M/C^0)t \tag{5}$$

$$K = kC^0/D_0 \tag{6}$$

$$c = C/C^0, \quad \text{etc.} \tag{7}$$

gives

$$\frac{\partial c}{\partial T} = \frac{\partial}{\partial x}\left(f(c)\frac{\partial c_M}{\partial x}\right) \tag{8}$$

and

$$\frac{\mathrm{d}c_R}{\mathrm{d}T} = -Kc_M c_R \tag{9}$$

These equations were solved using an explicit finite-difference method[9], with initial and boundary conditions appropriate to semi-infinite media:

$$\begin{aligned} c_M = c_B = c &= 0, & x > 0, t = 0 \\ c_R &= 1, & x \geqslant 0, t = 0 \\ c_M &= 1, & x = 0, t \geqslant 0 \end{aligned} \tag{10}$$

A typical solution to the above equations is shown in *Figure 3* where the time development of a concentration profile is displayed. If the rate constant for the reaction is large compared to the diffusion coefficient, a plateau or concentration front moves into the sample as $T^{1/2}$. The sharpness of the concentration front is determined by K or the ratio of the rate constant to the diffusion coefficient. The sharpness increases with K, and a value of $K = 2500$ was used for the model profiles in *Figure 3*. Defining

$$M = C^0_M/(C^0_M + C^0_R) \tag{11}$$

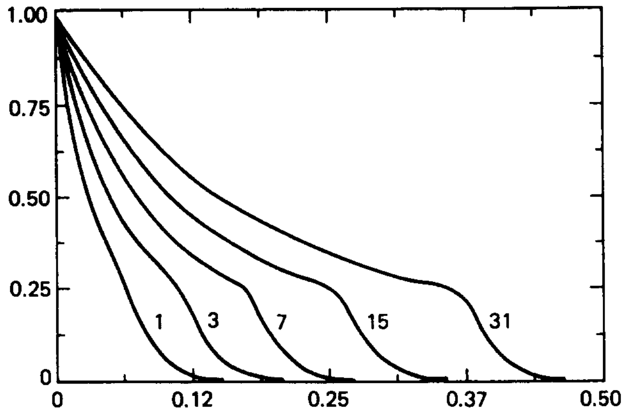

Figure 3 Model-generated diffusion profiles using $K = 2500$, $z = 99$ and $M = 0.762$

gives the height of the plateau as $1 - M$. The profiles in *Figure 3* used $M = 0.762$ which reproduced the experimental plateau heights of *Figure 1*. In the actual samples, residual hydrosilane sites probably exhibit a range of accessibilities or tendencies to react with diffusant. As a consequence, some minimum amount of HCPB would have to diffuse through each volume element to ensure reaction of diffusant with the less reactive hydrosilane sites. In effect, M would be time-dependent. This would explain the lower plateau height for the 14 day curve in *Figure 1*, while samples aged for longer times approached the limiting value of the plateau height. The average accessibility of the hydrosilane sites increases with temperature, resulting in the higher plateau height for the profile produced with 110°C ageing. In fact, 120°C data indicate that at that temperature the plateau approaches the maximum height limited by the total concentration of residual sites, i.e. all sites become accessible.

The concave nature of the concentration profiles near the HCPB–silicone interface can be explained, in part, by a diffusion coefficient that decreases with concentration, which is unusual, but not unprecedented. For example, such a relationship was recently reported for the diffusion of an acid dye through chitosan[10]. The shape of the profile observed here is not very sensitive to the functional form of the concentration dependence and the form

$$D = D_0/(1 + zc) \tag{12}$$

was used with $z = 99$ in *Figure 3*. One possible explanation as to why the value of D decreases with diffusant concentration involves the reaction of some of the HCPB molecules with more than one site. This would increase the crosslink density of the silicone, making it more rigid and providing a greater impediment to the free motion of unbound molecules. This hypothesis was tested by comparing the swelling of HCPB-free and HCPB-loaded silicone samples in ethylene dichloride. As no difference in the solvent uptake was observed, sorption of HCPB appears not to increase the crosslink density significantly. The possibility of consecutive reactions (with or without effecting additional crosslinking) was also incorporated into the kinetic model and qualitative agreement between the model and experimental profiles was somewhat improved. However, while consecutive reactions may play a role in explaining the details of the concentration profiles, the data do not warrant inclusion of the extra parameters that would be required for a more quantitative treatment.

Another explanation for the decrease in D with concentration is that the introduction of rod-like HCPB molecules into the highly flexible polymeric matrix decreases that flexibility and slows the further absorption of HCPB. This is in agreement with the proposal that the anomalously high diffusion coefficients found in silicones are the result of its high internal chain mobility[11]. While the data regarding a decrease in chain flexibility are not conclusive, an observed increase in silicone modulus with HCPB loading is consistent with that mechanism.

An estimate of the concentration-averaged diffusion coefficient can be obtained from the rate at which HCPB is absorbed. For the strong concentration dependences observed here, the total amount of HCPB absorbed as of time t, m_t, is simply given by

$$m_t = \frac{2}{\sqrt{\pi}}\left(\frac{\bar{D}T}{D_0}\right)^{1/2} = \frac{2}{\sqrt{\pi}}(\bar{D}Mt)^{1/2} \qquad (13)$$

where $\bar{D}$ is an averaged diffusion coefficient that can be approximated for D decreasing with concentration by[12]

$$\bar{D} = 1.85\int_0^1 c^{0.85} D\, \mathrm{d}c \qquad (14)$$

The above relationships were verified with the kinetic model using equation (12), with $D_0 = 1$ and $z = 99$. Equations (13) and (14) predict that the slope of m_t vs. $T^{1/2}$, in this case, should be 0.162 and independent of M. The model result of 0.166(2) is in very good agreement and represents the average over five values of M ranging from 0.6 to 1.0.

A plot of the areas under the three curves in *Figure 1*, where the plateau had reached its limiting value, *versus* $t^{1/2}$ showed excellent linearity (correlation coefficient = 0.9997) and gave $D = 2.8 \times 10^{-8}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$. $\bar{D}$ for the 6.6:1 formulation was found to be $5.5 \times 10^{-8}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$. That $\bar{D}$ should be somewhat higher in this case is reasonable, given the higher final concentration of lower molecular weight curing agent. A single profile of the 10:1 formulation aged for 31 days at 110°C is shown in *Figure 4*. $\bar{D}$ was calculated to be $1.2 \times 10^{-7}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ giving an activation energy of $13\ \mathrm{kcal\ mol}^{-1}$. A similar activation energy is obtained when data from samples aged at 120°C are included.

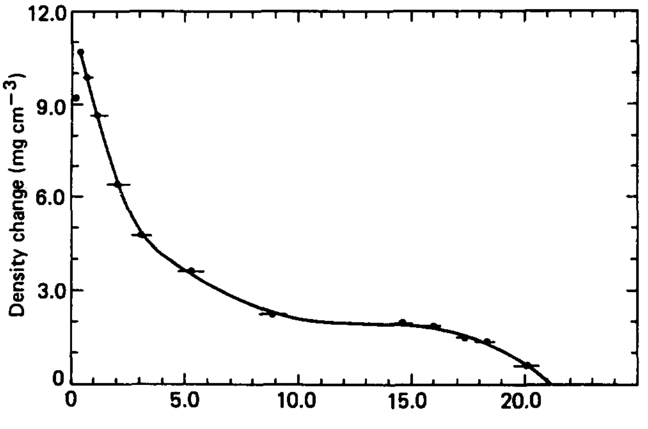

Figure 4 Diffusion profile for 10:1 formulated sample aged at 110°C for 31 days

CONCLUSIONS

The technique of density profiling is described as a new method for studying the diffusion of small molecules into polymers. The technique was successfully applied to the diffusion of a dialkyne into silicone rubber. The diffusion profiles obtained were characterized by the development of a concentration front, or plateau, due to the reaction of diffusant with residual hydrosilane sites in the matrix. Kinetic modelling reproduced the general shapes of the profiles and provided a means to determine an average diffusion coefficient, $\bar{D}$, since the diffusion coefficient appears to be a decreasing function of diffusant concentration. The total amount of diffusant absorbed (as monitored by the areas under the experimental diffusion profiles) was linear with $t^{1/2}$, as predicted.

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