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Moisture absorption characteristics of rubber particulate filled epoxy adhesives

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Results are reported for the moisture absorption characteristics of bisphenol epoxy adhesives containing between 8 and 12% rubber particles by weight. The maximum moisture content and the initial rate of absorption were determined for specimens maintained at temperatures of 23 and 60° C in atmospheres with relative humidities of 12, 76 and 100%. The swelling of samples immersed in water was also determined. Unlike many other epoxy systems, the maximum moisture content was found to vary appreciably with temperature, as well as with relative humidity, and the initial rate of absorption was found to decrease substantially with increasing relative humidity, especially at higher temperatures. While the maximum moisture content was essentially independent of rubber content and cure treatment, the initial rate of absorption was found to be sensitive to both factors.

1. Introduction

The technique of adhesive bonding of structural components has been widely used for many years. The most commonly used type of adhesives at present are epoxy resins, variously modified and cured. The present investigation was concerned with the properties of bisphenol epoxy adhesives containing rubber particles, which have a higher mechanical toughness than many other adhesives. The toughening is thought to be due to the rubber absorbing energy during its deformation when cracking occurs [1], rather than due to a crack pinning mechanism, which appears to be more important for brittle particle fillers [2].

It is well known that epoxy resins absorb significant amounts of moisture and that this adversely affects their mechanical properties, particularly at higher temperatures, thereby restricting their applications as adhesives and as matrices for reinforced composites. Such considerations are important for their use as structural materials in aircraft which are likely to operate in many different climatic conditions [3].

The aim of the present experimental investigation was to determine the moisture absorption characteristics of a rubber-filled bisphenol epoxy adhesive as a function of time, temperature, relative humidity, rubber content and cure cycle. The study also included measurements of the swelling produced by moisture absorption.

2. Materials studied

The material studied was manufactured by Permabond Adhesives Ltd. It consisted of the basic epoxy resin diglycidyl ether of bisphenol A (DGEBA), made by the reaction of epichlorhydrin with bisphenol A, plus rubber particles at between 8 and 12% by weight. The other ingredients were an aluminium filler and a cross-linking catalyst. The adhesive was supplied in panel form approximately 2 mm thick, prepared on polytetrafluoroethylene (PTFE) plates. The panels had a glossy side and a matt side and it was the glossy side that was exposed to the atmosphere on preparation. Different cure schedules were performed on the panels by the manufacturer.

Eight different panels were studied and the samples taken from them were labelled 1 to 8. The specifications of the samples are shown in Table I.

3. Experimental details

Square samples with nominal side length 25 mm were cut from the panels provided, using a diamond wheel saw, cutting and grinding tools. The edges were ground by hand so as to make them smoother and thereby reducing their surface area.

The samples were degreased with acetone and placed in a vacuum desiccator maintained at 60° C to remove any moisture already present. The initial masses of the samples in this state were recorded and their initial dimensions obtained with a micrometer.

Three samples from each panel were transferred to one of seven conditioning environments, with different relative humidities and temperatures, details of which are shown in Table II. In each case the moisture absorption as a function of time was monitored by weighing the samples periodically. The volume changes

TABLE I The samples and their cure treatment

Sample number	Parts rubber per 100 parts resin	Cure treatments
1	8	3 h at 120° C
2	9	
3	10	
4	11	
5	12	
6	10	1 h at 150° C
7	10	3 h at 120° C + 1 h at 150° C
8	10	3 h at 120° C + ½ h at 180° C

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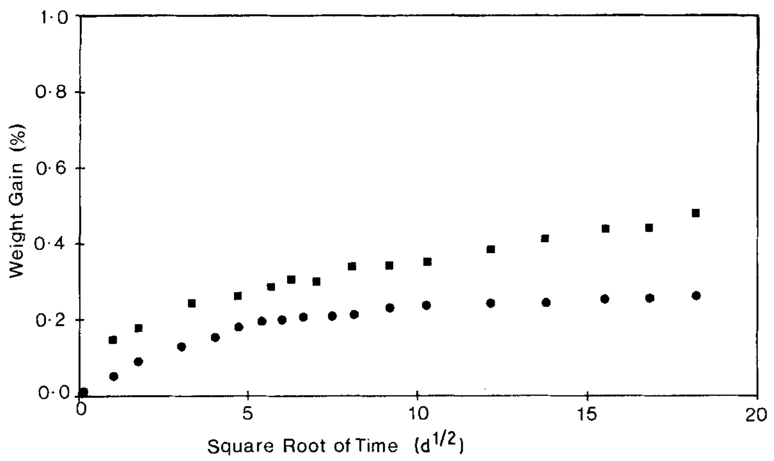

Figure 1 The weight gain in sample 1 resulting from exposure to an atmosphere with a relative humidity of 11 to 12%: (●) room temperature, (■) 60° C.

produced by swelling were determined as a function of time using the Archimedian method.

The samples were weighed on a micro-analytical balance which enabled masses to be determined to within $\pm 2 \times 10^{-4}$ g. Before weighing, the samples were wiped and then air dried for about 5 min.

4. Results

Typical results for the percentage weight gain as a function of the square root of time are shown in Figs 1 to 3. These results, which are for sample 1, illustrate the effects of varying temperature and relative humidity on the moisture absorption, assuming that immersion in water was equivalent to 100% relative humidity. Similar behaviour was found for the other samples.

The weight gain of all the samples has been characterized by an apparent diffusion coefficient, D, and an apparent maximum moisture content, M_m. The latter was taken to be the saturation value or, in cases where it was clear that saturation had not been reached, as the value after one year's exposure. The diffusion coefficient was calculated from the initial linear increase of weight change M with $t^{1/2}$ according to Fickian theory [4]

$$D = \pi\left(\frac{h}{4M_m}\right)^2\left[\frac{\Delta M}{\Delta(t^{1/2})}\right]^2\left(1+\frac{h}{a}+\frac{h}{b}\right)^{-2} \qquad (1)$$

where h is the sample thickness and a and b are the other two sample dimensions. ΔM and $\Delta(t^{1/2})$ are small increments.

The variation of the maximum moisture content with relative humidity for sample 1, at temperatures of 23 and 60° C, is illustrated in Fig. 4. The results for the other samples show similar characteristics.

The dependence of the diffusion coefficient on relative humidity for sample 1 is shown in Fig. 5. Similar results were obtained for the other samples.

It was found that the amount of rubber present in the resin did not have any significant effect on the values of M_m. However, it appeared that the rubber content had more influence on the diffusion coefficients but, as illustrated in Fig. 6, the dependence on concentration and temperature did not vary in any systematic way.

The effects on the moisture absorption of employing different curing procedures for the resins are illustrated in Figs 7 and 8 for the four samples 3, 6, 7 and 8, all containing 10% rubber. From Table I it can be seen that the degree of cure increases in the order sample 6, 3, 7 and 8.

Some typical results for the swelling of the samples immersed in water as a function of the volume of water absorbed are presented in Figs 9 and 10.

5. Discussion

5.1. Influence of temperature and relative humidity

The moisture absorption characteristics of epoxy resins and carbon fibre-reinforced resins have been succinctly reviewed by Wright [5]. It is generally assumed that the equilibrium maximum moisture content, M_m, attained in a resin depends significantly on the relative humidity of its environment, but is essentially independent of the temperature. Conversely, the initial rate of absorption, measured by the diffusion coefficient D, defined by Equation 1, increases markedly

TABLE II Environments used in the experimental programme

Test	Environment	Temperature (° C)	Partial pressure of water vapour (mm Hg)
A	Saturated LiCl, r.h. = 12%	Room temperature (23 ± 3)	2.10 at 20° C 2.84 at 25° C
B	Saturated LiCl, r.h. = 11%	60 ± 1	16.41
C	Saturated NaCl, r.h. = 76%	Room temperature (23 ± 3)	13.31 at 20° C 18.00 at 25° C
D	Saturated NaCl, r.h. = 75%	60 ± 1	111.9
E	Water immersion	Room temperature (23 ± 3)	average barometer reading plus pressure due to water in jar
F	Water immersion	40 ± 1	
G	Water immersion	60 ± 1	

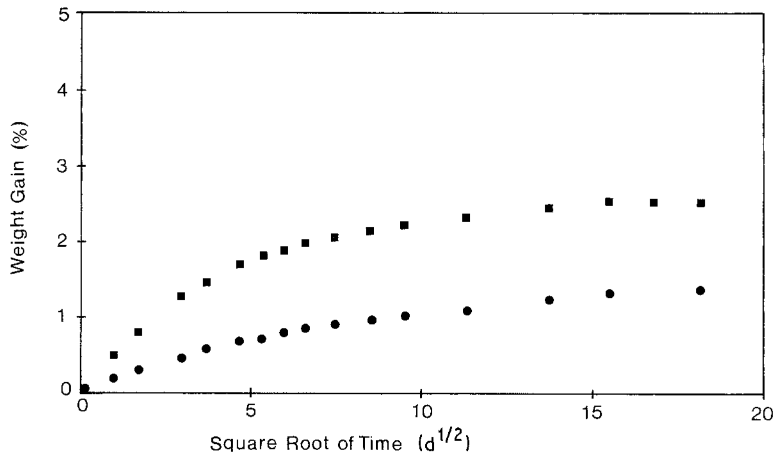

Figure 2 The weight gain in sample 1 resulting from exposure to an atmosphere with relative humidity of 75 to 76%: (●) room temperature, (■) 60° C.

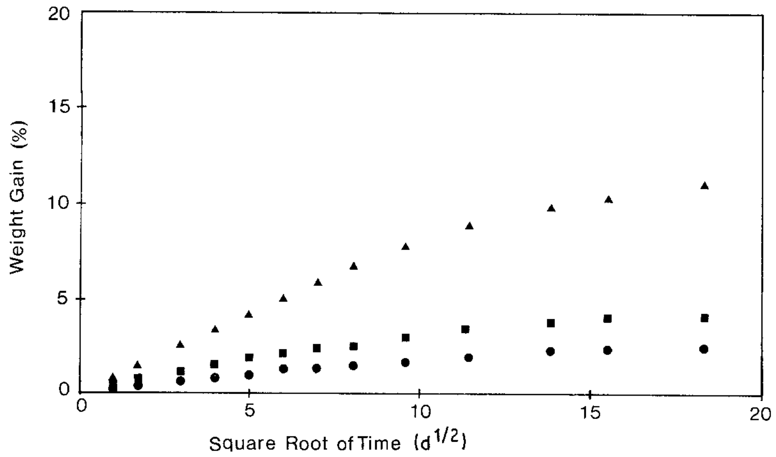

Figure 3 The weight gain in sample 1 resulting from immersion in water: (●) room temperature, (■) 40° C, (▲) 60° C.

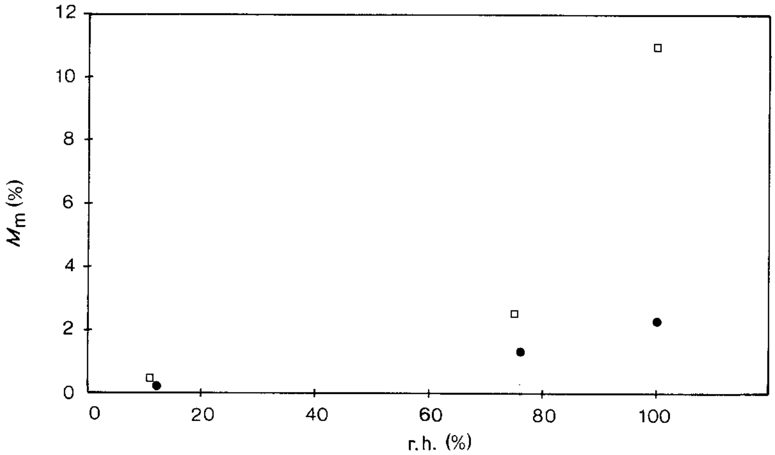

Figure 4 Variation of the maximum moisture content with relative humidity for sample 1: (●) room temperature, (□) 60° C.

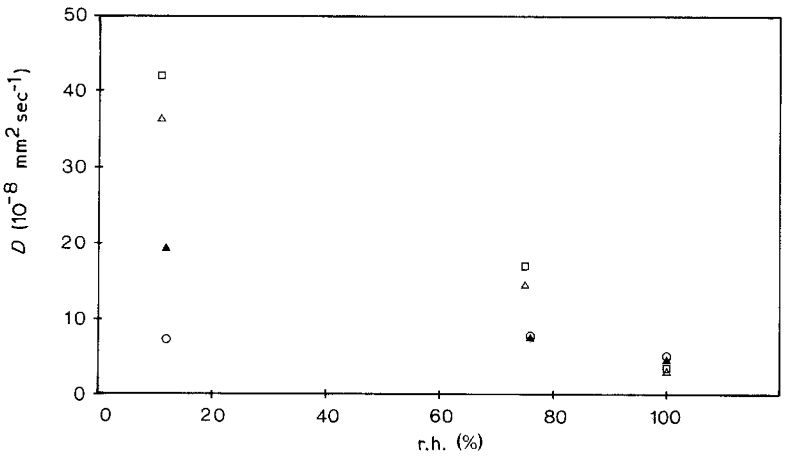

Figure 5 Variation of the diffusion coefficient with relative humidity; sample 1 (8% rubber), (○) 23° C, (△) 60° C; sample 2 (9% rubber), (▲) 23° C, (□) 60° C.

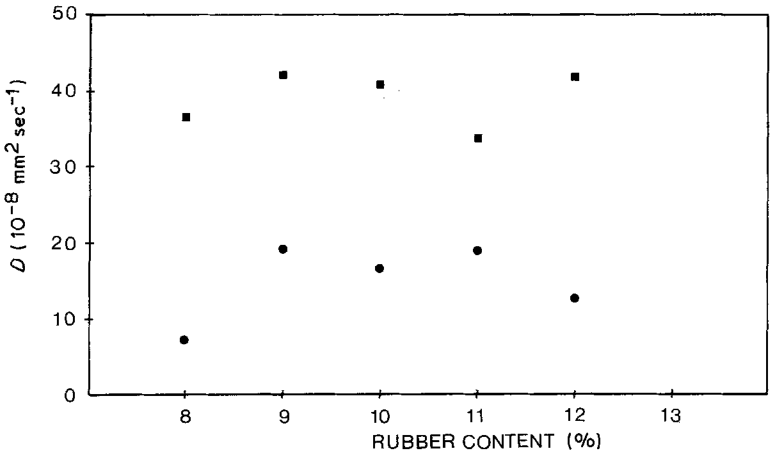

Figure 6 Variation of the diffusion coefficient with rubber content at a relative humidity of 11 to 12%: (●) 23° C, (■) 60° C.

with increasing temperature, but is much less sensitive to relative humidity.

As is clear from the results presented in Figs 4 and 5, the moisture absorption characteristics of the rubber-toughened epoxy resins studied here differ from the general pattern. From Fig. 4 it can be seen that the maximum moisture content varies appreciably with temperature, especially at relative humidity values approaching 100%, where there is a large increase in absorption which is typical of all epoxies. The diffusion coefficient was found to decrease substantially with increasing relative humidity at 60° C, see Fig. 5, but at room temperature the variation with relative humidity depended on the rubber content, compare sample 1 (8% rubber) and sample 2 (9% rubber). Further, it was noted that while D increased with temperature at relative humidities of 12% and 76%, it decreased with increasing temperature for specimens immersed in water. The results for samples 1 and 2 given in Table III illustrate the typical behaviour found for all the samples.

It has often been assumed [3], that the equilibrium moisture content depends on the relative humidity, ϕ, as a power law

$$M_m = 2 \exp(\beta\phi) \qquad (2)$$

The results for sample 1 are presented as a graph of ϕ against log M_m in Fig. 11. Allowing for the scarcity of data, the results for room temperature are a good fit to Equation 2, while those at 60° C are less so.

The rate of moisture absorption was found to be sensitive to the relative humidity for the majority of the samples tested. As remarked earlier, the large decrease of D with increasing ϕ contrasts with the behaviour of other epoxy systems, although Kanellopoulos *et al.* [6] found that for carbon fibre-reinforced Code 69 resin the values of D decreased when the specimens were immersed in water. It has been implicitly assumed above that the environmental conditions during immersion correspond to 100% relative humidity. Experiments of Adamson [7] suggest that the assumption is valid.

The influence of relative humidity on the rate of absorption of moisture from the vapour was discussed by Kanellopoulos *et al.* [6] in terms of kinetic theory. At a constant temperature, the rate at which water molecules impinge on the surface of a specimen is proportional to the relative humidity. On this basis, at ϕ values of 12% and 76%, the rates of arrival of molecules at a surface will be in the ratio 12/76, and the corresponding D values were found to be approximately in this ratio for some carbon fibre reinforced epoxy resins. However, the present results indicate that such a relationship between the molecular bombardment rate and D does not obtain for the rubber-filled epoxies.

5.2. Effects of rubber content

The maximum moisture content was found to be independent of the volume percentage of rubber present in the resin. On the other hand, the initial rate of absorption was sensitive to the rubber content, as illustrated in Fig. 6. In particular, at room temperature there was a large increase in D between 8% and

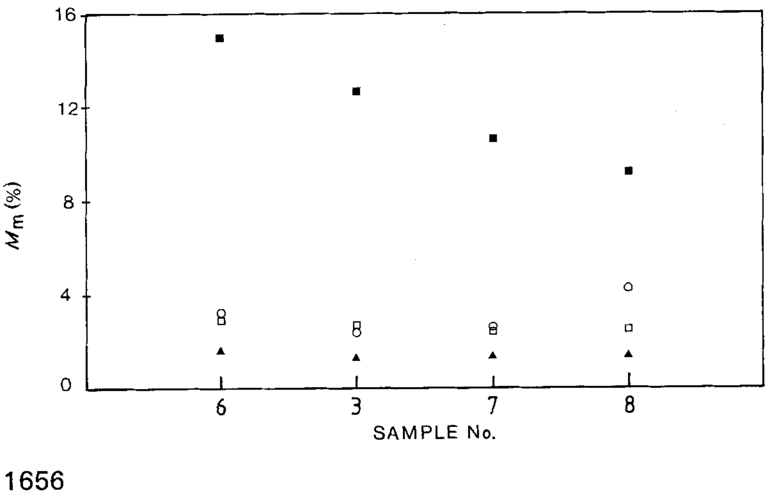

Figure 7 Variation of the maximum moisture content with cure treatment for specimens with 10% rubber content: (▲) room temperature and 75% relative humidity, (○) room temperature and 100% relative humidity, (□) 60° C and 75% relative humidity, (■) 60° C and 100% relative humidity.

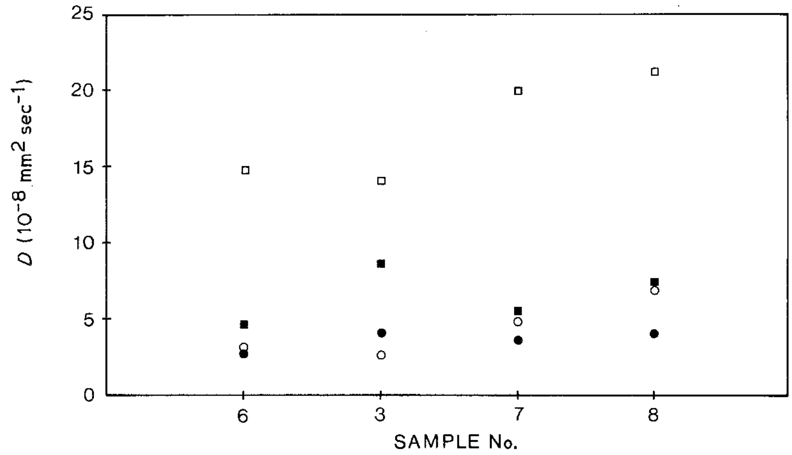

Figure 8 Variation of the diffusion coefficient with cure treatment for specimens with 10% rubber content. (●) Room temperature and 100% relative humidity, (■) room temperature and 76% relative humidity, (○) 60° C and 100% relative humidity, (□) 60° C and 75% relative humidity.

9% content. The effect of relative humidity on D in these two cases was discussed in the previous section.

The effective diffusion constant of a composite consisting of spherical particles in a matrix can be determined using a theory of Maxwell [8]. The theory assumes that the spherical rubber particles are all identical and are sufficiently far apart for their effects on the matrix diffusion to be independent of one another. The steady state spatial distribution of the moisture concentration, under a constant external gradient, satisfies Laplace's equation. Denoting by D_p and D_m the diffusion coefficients of a particle and the matrix, respectively, the boundary conditions at a particle/matrix interface are (i) continuity of concentration, and (ii) $D_p(\partial c/\partial n)_p = D_m(\partial c/\partial n)_m$ where $(\partial c/\partial n)$ is the concentration gradient normal to the particle surface. The appropriate solutions of Laplace's equation are readily determined.

For a large number of particles situated in some local region of the matrix, the moisture concentration can be calculated at a point a large distance from this region, and compared with the result that would have been obtained had the localized region consisted of a homogeneous material with a diffusion coefficient, D. The comparison yields

$$D = D_m \left[\frac{2 - 2v_f + (1 + 2v_f)D_p/D_m}{2 + v_f + (1 - v_f)D_p/D_m} \right] \quad (3)$$

where v_f is the volume fraction of rubber particles. This is the effective diffusivity of the particle/matrix composite. For small values of v_f, such as of interest here, Equation 3 can be approximated to give

$$D = D_m \left[1 + 3v_f \left(\frac{D_p - D_m}{D_p + 2D_m} \right) \right] \quad (4)$$

Although the dependence of D on v_f is linear, the variation with the ratio D_p/D_m is not. In the limit that $D_p/D_m \to 0$ it is readily seen that $D = D_m(1 + 3v_f)$. The variation of D with D_p/D_m is most marked for $0.1 \leqslant D_p/D_m \leqslant 10.0$, as can be seen from Fig. 12. For larger values of D_p/D_m the approximate Equation 4 is not valid at the v_f values of interest.

The results illustrated in Fig. 6 for samples 1 to 5 do not suggest that a simple relationship exists between D and v_f. In terms of the above theory, bearing in mind all the approximations that were necessary, the results suggest that the initial rates of moisture absorption by the rubber and epoxy resin are comparable, i.e. $D_p \simeq D_m$.

No independent measurements were available of D_p for the rubber from which the filler particles were manufactured.

5.3 Influence of cure treatment

Samples 3, 6, 7 and 8, all containing 10% rubber, were subjected to different cure treatments. As indicated in Table I, in terms of temperature and time, the degree of cure increased in the order of samples 6, 3, 7 and 8.

The influence of the cure treatment on the maximum moisture content of these samples is illustrated in Fig. 7. The value of M_m was little affected by the degree of cure, except for the case when the samples were immersed in water at 60° C. In this environment the maximum moisture content decreased substantially with increasing degree of cure.

The dependence of the diffusion coefficients on the cure treatment displayed in Fig. 8 shows some significant variations, but not in a sufficiently systematic way for them to be analysed.

5.4 Swelling

The increased volume of the specimens when immersed in water was monitored for all samples at tempera-

TABLE III Maximum moisture content and diffusion coefficients for sample 1 (8% rubber) and sample 2 (9% rubber)

T (° C)	ϕ (%)	M_m (%)	D (10^{-8} mm^2 sec^{-1})	M_m (%)	D (10^{-8} mm^{-2} sec^{-1})
23	12	0.27	7.49	0.23	19.4
	76	1.38	7.96	1.40	7.88
	100	2.35	5.34	2.35	4.79
60	11	0.48	36.4	0.49	41.9
	75	2.54	14.7	2.65	17.0
	100	10.98	3.38	11.90	3.58

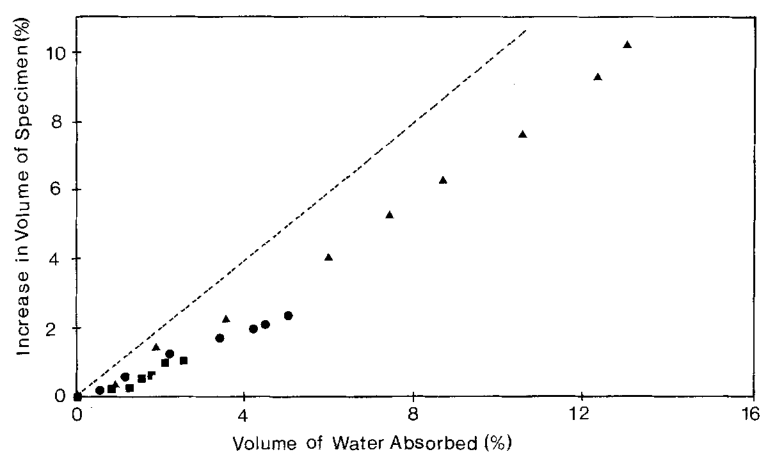

Figure 9 Swelling efficiency of sample 1 (8% rubber) resulting from immersion in water: (■) room temperature, (●) 40° C, (▲) 60° C.

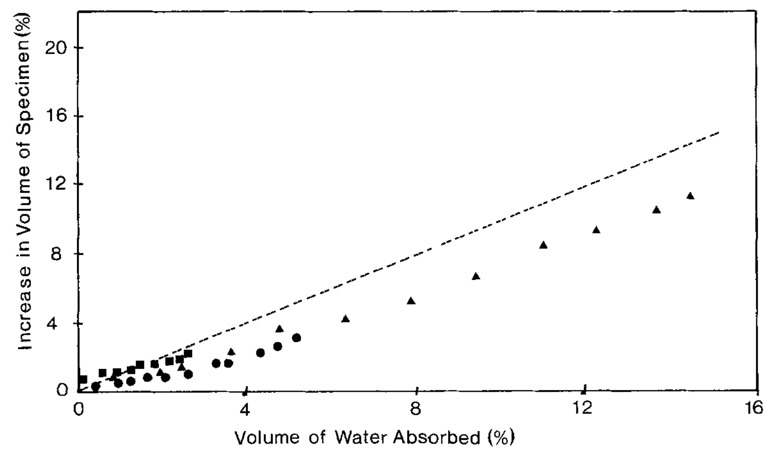

Figure 10 Swelling efficiency of sample 5 (12% rubber) resulting from immersion in water: (■) room temperature, (●) 40° C, (▲) 60° C.

tures of 23, 40 and 60° C. The results for samples 1 and 5 are shown in Figs 9 and 10, where the percentage volume increase is plotted against the volume of water absorbed, as calculated from the mass gain. The general behaviour is similar to that observed by other authors (e.g. [5, 7, 9]), in that the volume of the resin containing the moisture is less than that of the volume of the water absorbed plus the volume of dry resin, the latter being indicated in Figs 9 and 10 by the dotted lines with slope 1.0. Adamson [7] has argued that in the initial stages, most of the water enters vacant sites in the polymer network, filling free volume, and hence does not produce swelling. In later stages, when most of these sites are filled, the absorbed water distorts the polymer network and contributes to the swelling. Adamson also observed a third stage at still higher mass gains, where the swelling was again less than the volume of water absorbed, but this was not found in the present experiments.

Figs 9 and 10 show the swelling produced at three different temperatures, and it is clear that the results do not lie on a universal curve. For a given volume of water absorbed, the swelling is larger at the higher temperatures, an effect which was also noted by Adamson [7]. It is possible from the results from the later stages of absorption to estimate the free volume of the resin available for the initial absorption. The average values obtained are 1.4% at room temperature, 2.3% at 40° C and 2.8% at 60° C. An increase

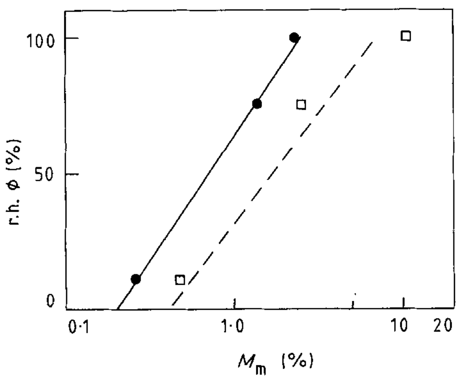

Figure 11 Variation of maximum moisture content with relative humidity for sample 1: (●) room temperature, (□) 60° C.

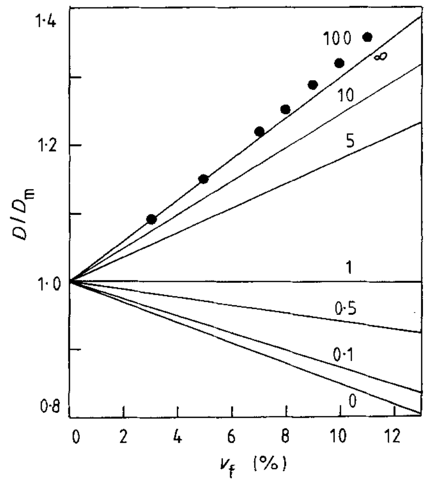

Figure 12 Theoretical calculations for the variation of diffusion coefficient with particle volume fraction: (——) using approximate expression for D, (●) using full formula for D. Numbers are the D_p/D_m ratio.

in free volume with temperature might be expected because of thermal expansion of the resin.

6. Conclusions

The rubber-filled bisphenol epoxy resins studied were found to have moisture absorption characteristics which differ from those of many other epoxy systems. The maximum moisture content varied appreciably with temperature, as well as with relative humidity, and the initial rate of absorption was found to decrease substantially with increasing relative humidity, especially at higher temperatures.

The maximum moisture content was found to be independent of the percentage of rubber present in the resin, in the range 8% to 12% studied, but the initial rate of absorption was sensitive to the rubber content, although not in any simple way. Application of an effective medium-type theory suggested that the rubber and resin have approximately similar moisture absorption properties.

The different cure treatments considered had little influence on the maximum moisture content, except for specimens immersed in water at 60° C, where the moisture content decreased substantially with increasing degree of cure. However, the initial rate of absorption was found to be sensitive to the cure treatment.

The swelling properties were found to be similar to those observed in other epoxy resin systems.

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