

# Diffusion of water into an epoxy adhesive: comparison between bulk behaviour and adhesive joints

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The diffusion of water into a bulk epoxy adhesive at 70°C under ~100% relative humidity has been studied by classic gravimetric analysis. As diffusion progresses, the elastic modulus decreases. This same effect has also been observed with torsional adhesive joints but the phenomenon seems to occur more rapidly. Since gravimetric analysis is not feasible with practical bonded joints, a 'composite' model has been developed in which water ingress may be estimated by changes in overall elastic behaviour of the polymer. Elastic moduli are due to a combination of rigidities resulting from the relative fractions of 'wet' and 'dry' polymer under load. The composite model gives values of the coefficient of diffusion,  $D$ , for the bulk adhesive in satisfactory agreement with those obtained by gravimetric analysis. However, the value of  $D$  for torsional joints is considerably greater. It is proposed that a phenomenon of 'capillary diffusion' exacerbates water ingress. Surface tension effects near the metal(oxides)-polymer interfacial region increase the effective driving force for water penetration.

(Keywords: hygrothermal ageing; capillarity; diffusion; epoxy resin; torsional joint)

## INTRODUCTION

The use of a structural adhesive in place of more established methods of mechanical joining presents many advantages but a major drawback is still the lack of predictability of long-term behaviour, particularly in aggressive environments. Amongst deleterious media, water is the most commonly encountered and it is well known that warm, moist surroundings can lead to a considerable loss in strength of adhesive joints. Reduction in mechanical resistance due to the ingress of water may be related to physico-chemical modifications occurring at the interface (or interphase) between substrate and adhesive<sup>1,2</sup> and/or to degradation of the bulk polymer<sup>3</sup> (or, less commonly, the substrate itself). Whatever the final cause of loss of strength, the effective lifetime of an adhesive joint prone to the effects of humidity is related to the kinetics of diffusion of water molecules within the system. Difficulties encountered in estimating the diffusion kinetics corresponding to various joint geometries complicate matters and can lead to problems in understanding the basic mechanisms involved. Diffusion equations are generally somewhat cumbersome to handle and although successful studies of diffusion have been previously effected with adhesive joints of more

conventional geometries<sup>4,6</sup>, in the present work we have opted to use cylindrical assemblies subjected to a torsional couple. This geometry presents advantages in that the shear stress field is simple and axial symmetry facilitates use of the diffusion equations.

The aim of this study is to compare water diffusion in a bulk structural adhesive with that of the same material used in a bonded joint. Two techniques were employed. The first corresponds to the classical method based on gravimetric results from bulk resin analysis. The second one, more unusual, consists of exploiting mechanical results obtained from the bulk resin and from bonded joints. It appears that exposure of a bonded joint to a hygrothermal environment leads to diffusion within the glue-line thickness and also to interfacial diffusion between metal oxides and polymer.

## EXPERIMENTAL

### Materials

The structural adhesive employed was a modified epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) and tetraglycidylmethylene dianiline (TGMDA) with dicyandiamide (DICY) as the curing agent, already used in an earlier study. A carboxyl-terminated butadiene-acrylonitrile resin (CTBN) served as an elastomeric toughening agent in this material<sup>7</sup>.

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The curing cycle used corresponds to a temperature rise of 3°C min<sup>-1</sup> to 130°C, at which temperature the material was maintained for 90 min.

The substrate material was a stainless steel (0.05% C, 16% Cr, 4% Ni and 4% Cu) which was submitted to the following surface treatment: solvent degreasing followed by sandblasting (with corundum) and cleaning with compressed air<sup>7</sup>.

Two types of bulk specimen of adhesive were employed, corresponding to those used in tensile tests (dimensions 110 × 10 × 2 mm<sup>3</sup>) and those used in compressive (dynamic) tests (15 × 3 × 3 mm<sup>3</sup>). Bonded joints were realized with hollowed-out cylindrical and plate substrates. The two parts were bonded to each other with an annular glue-line; the external and internal radii being respectively  $r_e = 10$  mm and  $r_i = 5$  mm and the adopted thickness 1 mm. The geometry of this test-piece is an adaptation of the 'napkin-ring' first developed by Gillespie and Rideal<sup>8</sup>. Complementary details are given in a recent article<sup>7</sup>.

After curing, specimens were exposed at 70°C to saturated water vapour (~100% relative humidity (r.h.)) for different times.

**Techniques**

Tensile bulk specimens were tested on an Instron apparatus at room temperature and at a crosshead speed of 1 mm min<sup>-1</sup>. A mechanical extensometer was used for recording displacement during the tests.

Compressive bulk specimens were submitted to viscoelasticimetric measurements on a Métravib Viscoanalyser at a frequency of 5 Hz, varying the temperature from ambient to 220°C at 2°C min<sup>-1</sup>.

Bonded joints were loaded in shear at room temperature on an apparatus developed in our laboratory and already described previously<sup>7</sup>.

**RESULTS AND INTERPRETATION**

*Mechanical aspects*

In the context of any diffusion study, data concerning the initial, unaged state of the material should be obtained as a baseline. Young's modulus of the bulk adhesive,  $E$ , was obtained from tensile tests. By viscoelasticimetry, it was possible to estimate an elastic modulus (in compression) at room temperature,  $E_c$ . Values of  $E$  and  $E_c$  were in satisfactory agreement.

From the torsional test effected on bonded joints, an apparent shear modulus of the adhesive,  $G_{app}$ , was obtained. Corrections have been proposed<sup>7</sup> to estimate the true shear modulus of the adhesive,  $G$ .  $G_{app}$  does not allow for deformation of the metallic adherends in the immediate proximity of the joint which is nevertheless measured with the present apparatus.

Acceptable correlations between  $E$ ,  $E_c$  and  $G$  have been obtained by applying equation (1) (Table 1):

$$G = \frac{E}{2(1 + \nu)} \tag{1}$$

**Table 1** Values of elastic moduli of the adhesive before ageing, obtained from results of tests on bulk adhesive and torsional joints

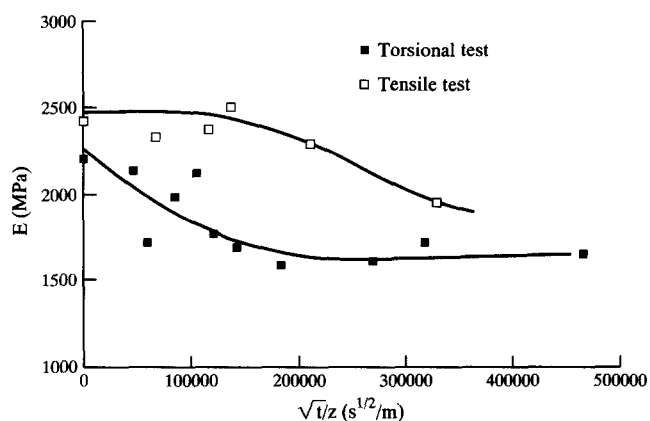
Bulk adhesive	$E = 2430 (\pm 220)$ MPa $(E_c = 2590 (\pm 135)$ MPa) $\nu = 0.38 (\pm 0.01)$	$\xrightarrow{(1)}$	$G = 875$ MPa $(G = 940$ MPa)
Bonded joint	$G = 800 (\pm 40)$ MPa $\nu = 0.38 (\pm 0.01)$	$\xrightarrow{(1)}$	$E = 2220$ MPa

where  $\nu$  is Poisson's ratio. It may be seen that the torsional test can lead not only to an estimation of the interfacial resistance of the bonded joint but also to satisfactory evaluation of the intrinsic elastic properties of the adhesive.

After determination of the elastic properties before ageing, hygrothermal effects were considered. Table 2 gives values of Young's modulus (tensile and dynamic compressive) and shear modulus of the adhesive both in the unaged state and after ageing to saturation. The evolution of Young's modulus values, obtained directly from tensile tests and by using equation (1) in the case of torsional tests, is shown in Figure 1 as a function of the square root of ageing time (corrected for specimen thickness: 2 mm for the tensile test and 5 mm for the bonded joint) at 70°C and ~100% r.h. There is a definite indication that, although values of the modulus are similar for the two systems both before and after ageing to saturation, time-dependent evolution is rather different. The elastic modulus of the adhesive in the torsional joint decreases much more rapidly than that of the bulk.

**Table 2** Values of elastic moduli of the adhesive before ageing and after ageing to saturation

	Young's modulus (MPa)		Shear modulus (MPa)
	Tensile specimen, $E$	Compressive specimen, $E_c$	Bonded joint, $G$
Unaged	2430 (±220)	2590 (±135)	800 (±40)
Aged	1940 (±95)	1880 (±120)	600 (±35)



**Figure 1** Evolution of Young's modulus for bulk and torsional samples (for tensile tests,  $z \equiv h$  (2 mm) and for torsional tests,  $z \equiv (r_e - r_i)$  (5 mm))

Water diffusion

*Gravimetric approach.* The kinetics of water diffusion are based on Fick's two laws<sup>9</sup>. In the case of a sheet of polymer with unidirectional diffusion, Fick's model is often applicable and is associated with diffusion of water molecules in the resin by a unique mechanism. It can be shown that the following equation applies:

$$\frac{m_t}{m_\infty} = \frac{4}{h} \phi \sqrt{\frac{Dt}{\pi}} \quad \text{when} \quad \frac{m_t}{m_\infty} < \sim 0.5 \quad (2)$$

where  $D$  is the coefficient of diffusion of water into the polymer;  $h$  is the thickness of the sheet;  $m_t$  and  $m_\infty$  are, respectively, the masses of water absorbed at time  $t$  and saturation; and  $\phi$  is a geometric factor to allow for finite dimensions<sup>10</sup>.

Considering diffusion in a hollow cylinder, the same equation can be used with negligible error if  $r_e/r_i < \sim 10$  and, with  $h \cong (r_e - r_i)$ , equation (2) then becomes<sup>9</sup>:

$$\frac{m_t}{m_\infty} = \frac{4}{(r_e - r_i)} \sqrt{\frac{Dt}{\pi}} \quad \text{when} \quad \frac{m_t}{m_\infty} < \sim 0.5 \quad (3)$$

(The factor  $\phi$  is simply unity with this geometry if the flat cylinder ends are neglected.)

From gravimetric measurements realized on tensile and compressive specimens,  $D$  can be obtained using equation (2) and was found to be  $1.4 (\pm 0.1) \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ .

*Mechanical approach.* Given the results shown in Figure 1, we wish to obtain data concerning the diffusion of water into the bonded joint. Unfortunately, this cannot be done by gravimetric methods since the relative weight of water compared with the overall weight of polymer plus metal is negligible. We therefore propose an approximate method of evaluation of diffusion properties based on mechanical measurements. This will be applicable both to bulk and torsional specimens and a comparison with gravimetric data can be made in the former case.

1) Bulk adhesive. We consider a parallelepipedic specimen of adhesive (length  $b$ , width  $a$ , thickness  $h$ ). Water diffuses from all faces but since we have dimensions such that ( $b \gg a, h$ ), effects due to the faces of area  $ah$  will be neglected (this renders the following mathematics more tractable). The diffusion front will in reality be a rather gradual transition between a water-free zone and a saturated region (see Figure 2a), but for the purposes of the model we shall assume an abrupt change from saturation concentration  $c_0$  to zero, as shown in Figure 2b.

We represent Young's modulus of the unaged adhesive as  $E_0$  and that of the water-saturated material as  $E'$  (cf. Table 2). Assuming that water has penetrated to depth  $x$  into the adhesive block (but neglecting faces of area  $ah$ ), we may write the effective Young's modulus of the 'composite' material, in the direction of its length  $b$ , approximately as:

$$E = \frac{\sigma}{\varepsilon} = \frac{E'}{ah} [ah - (a - 2x)(h - 2x)] + \frac{E_0}{ah} (a - 2x)(h - 2x) \quad (4)$$

Solution of equation (4) for  $x$  leads to:

$$x = \frac{a + h}{4} \left\{ 1 - \sqrt{1 - \frac{4ah}{(a + h)^2} \frac{(E_0 - E)}{(E_0 - E')}} \right\} \quad (5)$$

With the simple assumed transition at depth  $x$  and referring to equation (2), we have:

$$\frac{m_t}{m_\infty} \cong \frac{ah - (a - 2x)(h - 2x)}{ah} = \frac{2x}{ah} (a + h - 2x) \quad (6)$$

And thus:

$$\frac{x(a + h - 2x)}{\sqrt{t}} \cong \frac{2\phi a}{\sqrt{\pi}} \sqrt{D} \quad (7)$$

when

$$x(a + h - 2x) < \sim \frac{ah}{4} \quad (\text{equivalent to } \frac{m_t}{m_\infty} < \sim 0.5)$$

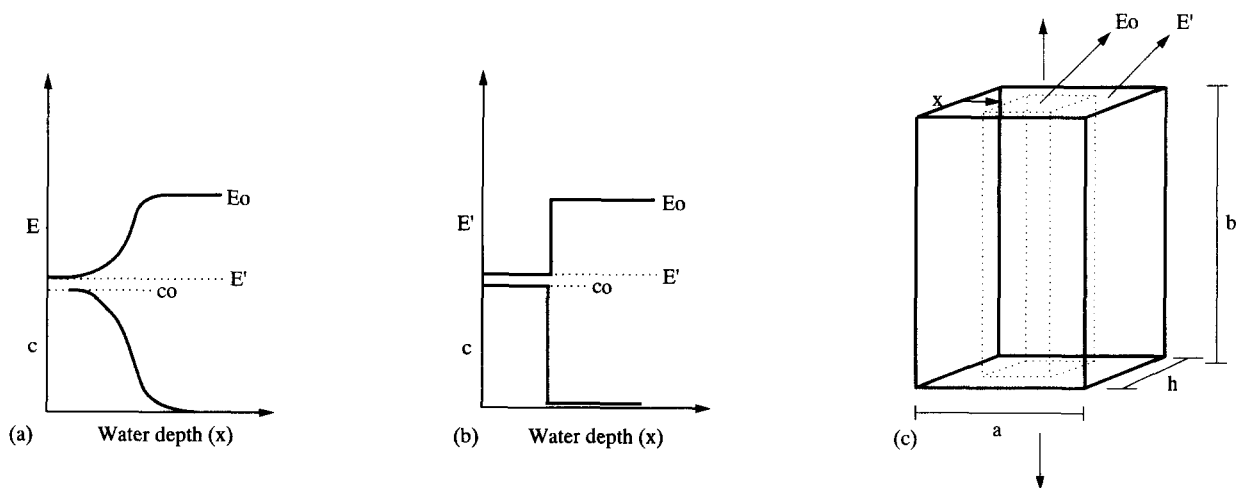


Figure 2 Water diffusion in adhesive block: (a) schematic representation of real water concentration,  $c$ , and resulting modulus,  $E$ , versus penetration depth,  $x$ ; (b) assumed model; (c) 'composite' block with saturated and water-free regions

With the present notation,

$$\phi = \left( 1 + \frac{h}{a} + \frac{h}{b} \right)$$

Using equation (5) to estimate  $x$  from experimental results, we have calculated values of the coefficient of diffusion,  $D$ , from equation (7). Values deduced are somewhat less than those obtained with Fick's model determined from gravimetric measurements ( $1.4 (\pm 0.1) \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ ) (see Table 3). This can be attributed to approximations necessary for the model to be tractable mathematically. Nevertheless, these results furnish a reasonable estimation of the diffusion coefficient and the principles invoked may be used for considering the process of diffusion in bonded joints made with the same adhesive.

2) Torsional joint. The kinetics of water diffusion into the cylindrical bonded joint has been considered assuming that ingress occurs both from the outer exposed surface of adhesive, at radius  $r_e$ , and from the inner surface at radius  $r_i$ . This is shown schematically in Figure 3.

Using the same reasoning as before for the bulk adhesive, we can decompose the measured torque,  $M$ , into three parts (cf. equation (4)):

$$\frac{M}{2\pi} \cong \frac{\theta}{e} \left\{ \int_{r_i}^{r_e} G' r^3 dr + \int_{r_o}^{r_o'} G_0 r^3 dr + \int_{r_i}^{r_o'} G' r^3 dr \right\} \quad (8)$$

where  $G_0$  is the shear modulus of the unaged adhesive;  $G'$  is the modulus after water saturation;  $e$  is the glue line thickness;  $\theta$  is the rotation angle of the adhesive; and radii  $r_o$  and  $r_o'$  refer to transition values from water saturation to dry adhesive for diffusion initiating respectively from  $r_e$  and from  $r_i$ .

It is reasonable to suppose that the quantity of water diffused into each of the two zones,  $r_o < r < r_e$  and  $r_i < r < r_o'$ , will (at a given time) be proportional to the surface area of free adhesive accessible for water ingress. This leads to:

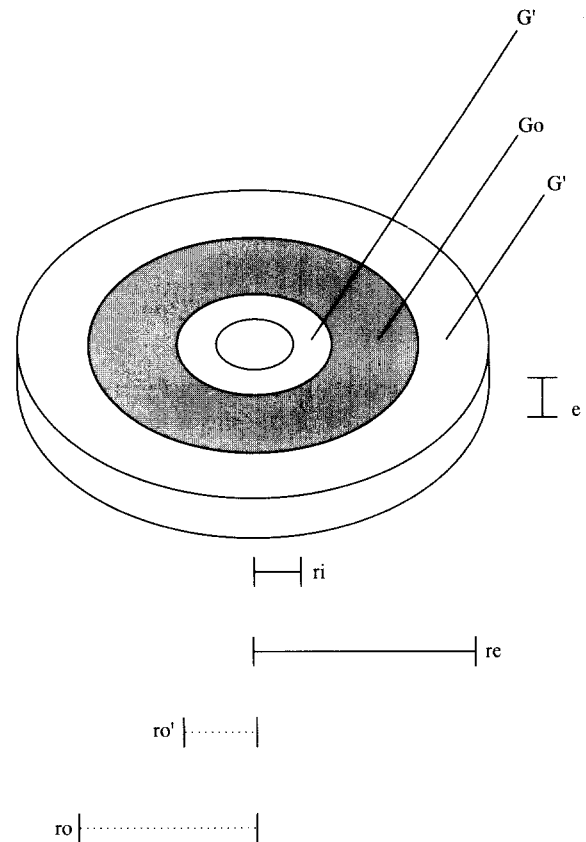
$$(r_e^2 - r_o^2) \cong \frac{r_e}{r_i} [(r_o')^2 - r_i^2] \quad (9)$$

Using relation (9) in equation (8) with appropriate experimental values allows us to determine  $r_o$  and  $r_o'$  as a function of exposure time,  $t$ . By analogy with equation (6), we have:

$$\frac{m_t}{m_\infty} \cong \frac{(r_e^2 - r_o^2)}{(r_e - r_i) r_e} \quad (10)$$

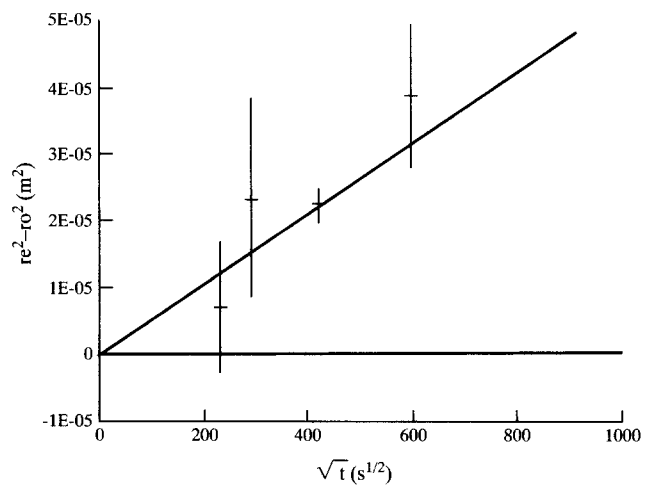
**Table 3** Calculated values of the coefficient of diffusion,  $D$ , obtained from gravimetric and mechanical results

	$D (\times 10^{-12} \text{ m}^2 \text{ s}^{-1})$	
	from gravimetric results	from mechanical results
Tensile specimen	1.4 ( $\pm 0.1$ )	0.8 ( $\pm 0.01$ )
Compressive specimen	1.4 ( $\pm 0.1$ )	0.5 ( $\pm 0.005$ )
Bonded joint		5.3 ( $\pm 0.1$ )



**Figure 3** Process of water diffusion in bonded joint. Water ingress has occurred from both exposed edges  $r_e$  and  $r_i$  up to, respectively,  $r_o$  and  $r_o'$ , whilst the shaded area represents unaged polymer

and making use of equation (3), we may deduce  $D$  in the range corresponding to  $(r_e^2 - r_o^2) < \sim [(r_e - r_i) r_e / 2]$  (equivalent to  $m_t / m_\infty < \sim 0.5$ ). The corresponding graph of  $(r_e^2 - r_o^2)$  as a function of square root of diffusion time is given in Figure 4. Despite some scatter, the linearity of this relation can be seen to be adequate. The value of  $D$  obtained is given in Table 3.



**Figure 4** Estimation of  $D$  in the torsional case using the evolution of  $(r_e^2 - r_o^2)$  as a function of the square root of diffusion time

## DISCUSSION

A standard gravimetric technique has been employed to estimate the coefficient of diffusion,  $D$ , of water into a bulk epoxy adhesive at 70°C and in a water vapour saturated environment. Concomitantly with water diffusion, a reduction of elastic modulus was observed. By testing torsional joints constructed with the same adhesive, it has been shown that the elastic modulus decreases much more quickly in the torsional joints. Since it was not feasible to obtain direct gravimetric data of water uptake from the metal/polymer assemblies, we have developed an indirect method for estimating the diffusion coefficient using a 'composite' model based on mechanical properties. This 'mechanical' model gives quite reasonable agreement between the values of  $D$  obtained from it and those coming directly from gravimetric data for the bulk polymer, although it would seem that the modulus-based estimations are perhaps a little low.

However, when applying the mechanical model to torsional joint data, we obtain a significantly higher value for  $D$  (almost an order of magnitude). We therefore infer that diffusion within the adhesive joint is occurring by another route, as well as by conventional diffusion within the polymer. It would seem that water is entering the system by seepage close to the interface or in the interphase region. Such a mechanism has been reported in the degradation of composite materials, where water enters the system along the interface between matrix and fibre<sup>11</sup>. We propose a phenomenon of 'capillary diffusion'. We imagine the diffusion front near the metal/polymer transition to be analogous to a wetting triple line (see Figure 5). Three 'phases' are present: metal(oxides) (1 in Figure 5), 'wet' adhesive (2) and 'dry' adhesive (3). Since the metallic component represents probably a relatively high energy surface, the interfacial free energy metal(oxides)–'dry' adhesive could well be quite large and, as a consequence, a significant interfacial tension could help to 'pull' the water diffusion front into the system. This can be taken to be analogous to the wetting front of a liquid spreading on a high energy surface, where the solid surface tension provides the motive power for motion. We cannot, as yet, quantify this effect, but schematically

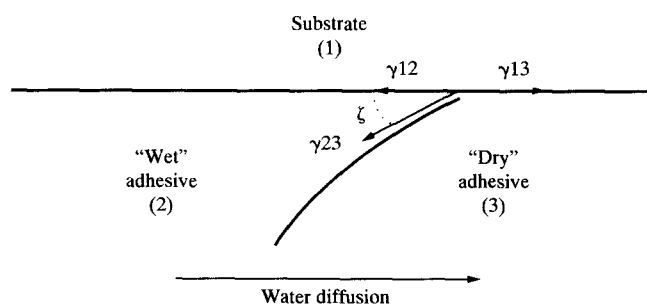


Figure 5 Model of diffusion front near the metal/polymer transition. Terms  $\gamma_{12}$ ,  $\gamma_{23}$  and  $\gamma_{13}$  represent interfacial 'tensions' between the phases metal(oxides), 'wet' and 'dry' adhesive

we may say that the overall diffusion rate is higher since two mechanisms are involved in water ingress. The diffusion mechanism is split into two parts: (1) water diffuses into the thickness of the bulk polymer causing classic ageing and reduction in mechanical properties; (2) water seeps or spreads close to the interface at a faster rate and may then, in turn, diffuse towards the bulk of the glue line. Clearly the second process may play an important role by also provoking the failure of interfacial bonding<sup>7,12</sup>.

It is relevant to note that surface treatment is an important factor in controlling interfacial diffusion. Stainless steel, after sandblasting, has a reactive surface which will almost instantaneously be re-covered by oxides<sup>13</sup>. This nature of the surface state will essentially produce secondary interfacial bonds, rapidly weakened in contact with water<sup>14</sup>. Thus, water penetration through interfaces [substrate–adhesive (or interphase)] is associated with progressive bond breaking and consequently water diffusion in the adhesive through these surfaces. This double process can explain the overestimation of the coefficient  $D$  obtained for bonded joints.

Although 'capillary diffusion' seems to be a quite plausible explanation for the increased value of effective diffusion coefficient and, as mentioned above, a similar mechanism has been suggested in the case of composite materials, another possibility could be linked to the effects of shrinkage stresses. If shrinkage of the adhesive occurs during cure, this will be relatively unconstrained in the bulk polymer. However, in the case of adhesive joints, the interfacial region, or interphase, will be to some extent constrained by the nearby metallic adherend. This could lead to effective dilation of the polymeric material in the vicinity and a less dense structure, possibly facilitating the ingress of water and leading to a higher local (and thus overall) average diffusion coefficient. It is possible that the combined action of water and stress could affect diffusion characteristics.

Another potential reason for enhanced diffusion near the interfacial region could be that the structure and/or orientation of the polymer is somewhat different in the regions contiguous to the substrate.

Clearly, a combination of the above causes could also be responsible for easier water ingress in the proximity of the polymer/metal boundary.

Although the exact cause(s) cannot at present be pronounced with any certainty, probably the most important aspect, as strongly suggested in this study, is that the water diffusion rate in a polymeric adhesive may be increased when it is *in situ* in a bonded joint compared with that observed in the bulk material.

## CONCLUSIONS

A study of water diffusion into an epoxy adhesive has been undertaken both for the bulk polymer and when

it is employed to bond torsional joints. In the former case, standard gravimetric analysis has been used and behaviour found to be reasonably approximated by the Fick model. However, gravimetry could not be used for the bonded systems since weighing precision is insufficient. We have therefore developed a method of estimating the diffusion coefficient,  $D$ , by considering changes in adhesive elastic moduli due to water ingress.

The overall 'composite' elastic modulus is a result of contributions due to 'dry' and 'wet' adhesive, the latter having a lower rigidity than the former. Comparison of values of  $D$  for the bulk polymer obtained by both gravimetric and mechanical analyses shows reasonable agreement but in the case of bonded joints,  $D$  is considerably higher. This has been attributed to an effect of 'capillary diffusion', or seepage of the invasive medium near the metal(oxides)-polymer interface. The combined mechanisms of classic diffusion and that occurring near the interfacial region lead to a considerably higher overall or effective diffusion rate. It would seem that not only can water near the interface provoke interfacial failure, but the existence of this region exacerbates the phenomenon of rapid water penetration.

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