Characterising moisture ingress in adhesively bonded joints using nuclear reaction analysis

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Abstract

The moisture ingress in bonded structures is usually characterised by gravimetric experiments on bulk adhesive samples. This is a relatively economic and convenient method. However, this approach poses a problem as only the total amount of moisture in the specimen can be determined and not the moisture concentration distribution throughout the adhesive layer. In this study, the moisture profile at two different ageing times (43 and 96 hours) in a bonded joint has been determined by use of Nuclear Reaction Analysis (NRA). The moisture ingress profile, which was found to be Fickian in the bulk adhesive sample, was dominated by apparent Case II kinetics in the bonded joint specimens. The ingress in the laminates was seen to be much faster than if the moisture transport had been governed by Fickian diffusion.

Keywords: Epoxy/epoxides; Aluminium and alloys; Durability; Case II diffusion, Interfacial diffusion

1. Introduction

The main advantages of adhesives are their ability to bond dissimilar materials and their more efficient load transfer in comparison with other joining techniques such as, rivets and bolts. Their major disadvantage is their susceptibility to humid environments. It is hence of major importance to be able to characterise the ingress of moisture accurately. Reliable knowledge of the mechanisms of the moisture ingress would lead to greater confidence and thus increase the use of adhesives in industry.

Diffusion coefficients derived from film uptake experiments have been used by many researchers to determine the moisture profile in bonded joints [1-4]. However, the ingress profile of moisture may be different in a free standing film than it is in a bonded joint.

The sorption of water into polymers can, in most cases, be described by Fick's second law [5]. A range of non-Fickian sorption curves have however been observed as, for example, two-stage [6], sigmoidal [7] and Case II sorption [8]. Fickian diffusion is generally assumed to occur when the diffusion is much slower than the polymer relaxation and moisture transport is then governed by the diffusion. Whereas, in Case II moisture ingress, the diffusion is much faster than the relaxation and the ingress is governed by the advancing front between the swollen and the un-penetrated polymer [8,- 11].

The mass uptake in polymer films can, for shorter times scales, be described by Eqn 1 [12]:

$$\frac{m_t}{m_\infty} = kt^n$$

For Fickian diffusion the uptake will be proportional to the square root of immersion time ($n=0.5$) whereas for Case II diffusion the mass uptake will be directly proportional to the immersion time ($n=1$). For the other non-Fickian uptake curves the coefficient n ranges between 0.5 and 1.

Modelling has however showed that non-Fickian behaviour also can occur due to residual stresses arising from the non-uniform distribution of the absorbed penetrant [13-15]. Other researchers have developed models for Case II diffusion which included history dependent diffusion coefficients [16, 17].

It has also been observed that large plastic strains increase the tendency for Case II diffusion [18, 19]. Sanopoulo and Stamatialis [20] observed that Case II kinetics occurred for the uptake of a polymer constrained from expansion between two glass plates when the swollen polymer was sufficiently plasticised in order to deform plastically along the penetration axis to overcome the constraints imposed in the thickness direction.

A schematic drawing the moisture profile in a material governed by Case II kinetics can be seen in Figure 1 (after Zhou et al [21]). It has been noted that the Case II diffusion front is always preceded by a Fickian precursor. This precursor can be described by Eqn 2 as suggested by Peterlin [22]:

$$c = c_0 \times \exp\left(\frac{-x'v}{D}\right) \quad (2)$$

where x' is the distance ahead of the moving front, v the front velocity and D the Fickian diffusion coefficient. Both the Case II front velocity and the Fickian diffusion coefficient can hence be determined if the moisture profile in the sample has been determined.

There is also some evidence that moisture penetration may be faster in the interfacial region [23-27]. This implies that the actual moisture content throughout the adhesive layer will be underestimated and hence the durability overestimated.

Wahab et al. [23] have investigated the moisture uptake for various configurations of bulk and laminated adhesive resin diffusion discs to study the effect of the interfacial moisture diffusion. It was found that, during the early stages, the flux in the laminated disc was about 50% higher than that in the bulk epoxy disc of the same exposed area. This indicated that there might be a faster interfacial diffusion which contributed to the more rapid overall uptake.

Linossier et al. [24] have studied water transport along the interface of polymer/substrate systems using Fourier transform infrared multiple internal reflection (FTIR-MIR) spectroscopy. Their results indicated that the water migration along the polymer/substrate interface was the governing transport process for untreated substrates. Plasma treatment of the substrate greatly reduced the rate as well as the amount of water accumulated at the interface. Wapner and Grundmeier [25]

have measured the diffusion of D₂O in adhesive joints by spatially resolved FTIR-transmission spectroscopy. A significantly faster diffusion was found in the joints than in bulk specimens.

The absorption of acetone at room temperature into an adherend-pressure sensitive adhesive tape was measured by applying the techniques of impedance spectroscopy and utilising interdigitated electrode sensor design [26]. The results showed that the absorbance was faster in the interfacial regions. Wilken et al. [27] have determined the moisture content along the interface of an aluminium epoxy laminate by ToF-SIMS (time of flight secondary ion mass spectroscopy). After immersion in D₂O the substrate was peeled off, analysed and the moisture profile quantified. The diffusion was found to be about 6 times faster along the interface than in the bulk material.

In this study an experimental method has been developed to determine the moisture profile in bonded joints. In previous works [24-27] by other researchers, the profile in an adhesively bonded joint has only been measured at one point through the adhesive thickness. In this work, the profile across the adhesive thickness as well as along the overlap length has been determined. The methodology described is an important step towards a better understanding of the moisture ingress in bonded joints.

2 Experimental methods

2.1 Gravimetric experiments

Unidirectional Fickian transport in bulk adhesive films is described by Eqn 3:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \quad (3)$$

where c is the concentration, t the time, x the distance along the penetration direction and D is the diffusion coefficient. Assuming a constant diffusion coefficient, the equation above can be integrated over the whole specimen and the equation for mass uptake is given in Eqn 4 [15]:

$$\frac{m_t}{m_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\{-D(2n+1)^2 \pi^2 t / 4l^2\} \quad (4)$$

where m_t is the current mass at time t , m_∞ is the saturation mass uptake and l is the half specimen thickness.

The bulk Fickian diffusion coefficient for an adhesive can hence be determined by submerging a thin sample in a moist environment and recording the weight increase with time and then fitting this data to equation (4).

2.2 Nuclear reaction analysis for moisture measurement

Bulk diffusion for the adhesive has been determined by gravimetric experiments. However this does not address the moisture concentration profile throughout the joint. The aim of this work was to investigate the moisture diffusion by using an ion beam technique to determine the moisture concentration across and along the adhesive

thickness of aged aluminium epoxy laminates. The laminate sample was cured and then immersed in water.

With ion beam techniques it is difficult to profile water (containing hydrogen and oxygen) in polymers, which contain both these elements. The diffusion of heavy water (D₂O) has been shown to be equivalent to the ingress of ordinary water [28]. Hence heavy water was used as a representative diffusant in all experiments in order to determine the moisture profile. After ageing, the samples were cooled in liquid nitrogen to retain the absorbed moisture and cut into two (Figure 2). Further details of this process are given in Section 3. The samples were held between two copper blocks on a sample plate. This plate was attached vertically to a liquid nitrogen cooled cold stage in the Surrey micro-beam line [29]. A 1560keV, 150pA ³He⁺ microbeam from the High Voltage Engineering Europe 2.0MV Medium Current Plus Tandetron™ accelerator was used to raster scan in the sectioned plane over adjacent areas. The set up is shown schematically in Figure 3.

The fusion reaction with deuterium (*d*) produced protons (*p*) and alpha particles (*α*) by the reaction given in Eqn 5:

where *Q* is the energy released during the reaction. The energy of protons (which identify the reaction) at an angle to the beam where the detector was situated can thus be determined from the available energy in the system. The detector was an array of 15 mm×15 mm×3 mm CdZnTe, which can absorb the full energy of protons up to more than 15 MeV [30]. The array is located 10 mm upstream of the target and

subtends a solid angle of $\pi/2$ steradians. A scanned specimen with high moisture concentrations results in many counts when scanned, while a lower moisture concentration results in fewer counts. The moisture distribution throughout the laminate can thus be determined.

3 Sample preparation and ageing

The approach developed was applied to thin bulk samples and sandwich specimens consisting of thin aluminium plates (specification 1050) bonded with DP490 by 3M. This is a two-part epoxy adhesive. Bulk samples and laminates were cured for 24 hours at 23°C followed by 1 hour at 80°C. The aluminium-adhesive laminate was 100 mm long, 13.5 mm wide and the total thickness was 2.0 mm. The thickness was 1.5 mm and 0.25 mm for the adhesive layer and the substrates respectively. The substrates were wiped with acetone prior to bonding. It should be noted that the acetone wipe is not a surface treatment that will provide high durability. It has been used only to remove surface grease. The interface integrity and eventual interfacial diffusion might well be different if a different surface treatment were used.

After cure both bulk samples (1.4 mm thick) and the laminates were immersed in pure D₂O at 50°C. The bulk samples were removed periodically and the weight was recorded.

After laminates had been aged for an appropriate time they had to be sectioned to expose the surface of interest for analysis. The difficulty with the technique was that the sample had to be sectioned whilst maintaining a temperature below zero. Initial

attempts were undertaken by simply cooling the samples in liquid nitrogen to freeze in the moisture and section them along the mid plane with a jewellers saw. The initial specimens had a rough surface that was not ideal for analysis (as a rough and not perfectly straight surface will be partly shadowed from the beam). Polishing the surface after the cutting was not feasible as the moisture would desorb rapidly or be distorted by any cooling fluid. The possibility of using cryo-microtoming to obtain an improved surface at a temperature below zero was thus investigated.

The cutting has to be undertaken under cryogenic temperatures to maintain the moisture profile in the sample. The MSSU (Micro Structural Studies Unit) at the University of Surrey has an LKB 2288-050 CryoNova [31]. CryoNova is a cryoultramicrotome system specifically designed for frozen sectioning. CryoNova is an addition to the room temperature microtome, Ultratome NOVA [32].

Usually very thin samples are cut. Thus it was necessary for a custom chuck to be designed and manufactured to clamp the laminate specimen. The cryochamber where the knife and the specimen were situated during the sectioning was kept cold by supplying liquid nitrogen by a pump from a floor-standing dewar vessel. In the cryochamber, a foil heater boiled the nitrogen to produce a cold nitrogen atmosphere in the chamber. The cutting temperature was -50°C . A diamond knife had to be used as one of the materials being sectioned was aluminium. During sectioning, the knife was advanced forward by use of the thermal feed.

The epoxy-aluminium laminate could be cut using the CryoNova and a smooth surface was achieved (Figure 4).

After the cryo-microtoming, the sample was kept in liquid nitrogen until the testing. Upon testing the sample was placed in a clamp and placed in the scattering chamber, again under a cryogenic condition.

4 Results

4.1 Fickian diffusion coefficients determined from gravimetric experiments

The experimental data and the Fickian fit are shown in Figure 5. From this figure it can be seen that the moisture ingress was Fickian (concentration gradient driven) as the initial uptake was proportional to the square root of time (equation (1)). The diffusion coefficient was found to be $1.61 \times 10^{-12} \text{ m}^2/\text{s}$. It was assumed that nothing was leached from the adhesive into the water and from the shape of the uptake curves this seems to be a reasonable assumption.

4.2 Moisture distribution throughout the adhesive layer using NRA

The surface area that can be analysed for each scan is approximately $0.8 \times 0.8 \text{ mm}$. The spot size was $10 \text{ }\mu\text{m}$ and the distance between each scan point was about $3.25 \text{ }\mu\text{m}$. After the scan was finished the sample was moved and a new area was scanned. Data was collected for about 30 minutes for each scan. The counts from the detection of the deuterium were normalised with the intensity of the Rutherford backscattering spectra (RBS) on the copper clamp to account for any small differences there may have been in the beam current when analysing the different samples

Samples aged for 43 and 96 hours were analysed. Multiple (8) scans were employed to cover a larger part of the sample as seen in Figure 6, which had been aged for 43 hrs. The sample was scanned over the interface regions but not over the centre of the adhesive layer (see Figure 6). Visually, a slight moisture profile from the interface may be inferred.

Similar characteristics were also found for the sample aged for 96 hours. On this sample, a moisture profile from the interface could be determined by summing the counts in the longitudinal direction as seen in Figure 7. In this figure, it can be seen that the moisture concentration in the interfacial region compared with that at the centre of the bondline is higher and there is an apparent flux from the interfacial region towards the centre. (Peaks on the underlying slope are due to bubbles present in the resin). This characteristic would be expected if the interfacial diffusion was faster than in the bulk material.

Counts were summed in the transverse direction to get 1D diffusion data. The results are given in Figure 8 and 9 for the samples aged for 43 and 96 hours respectively. In Figure 9 information from distances between 0 and 0.5mm is missing as the cryo-microtoming during sample preparation did not extend back far enough to expose a flat surface the full width of the sample (beyond the initial saw cuts). This left an extremely coarse region at the edge of D₂O ingress ~0.5mm wide, behind the flat plane, from which accurate NRA data could not be obtained. It can be seen that the moisture concentration is apparently Case II with its characteristic sharp front. The rates of the advancement of the fronts for the two specimens aged at different times are given in Table 1. The rate of advancing front is consistent for the two specimens

which indicate that the ingress is indeed driven by Case II diffusion. The Fickian diffusion coefficient was determined by fitting equation (2) to the precursor part of the measured profile. The determined Fickian diffusion coefficient was consistent for the two specimens and was also in good agreement with the coefficient determined from the gravimetric experiments. These results are also given in Table 1. The computed saturation to 90% is also given in Table 1. It can be seen that this level of moisture concentration would be achieved 14 times faster in the bonded joints compared with a bulk adhesive specimen with the same diffusion path.

4. Conclusions and future work

Bulk diffusion for the adhesive used has been determined by gravimetric experiments. An experimental technique was used that enabled spatial distribution of moisture within a joint to be measured. A profile of moisture concentration across the thickness of the adhesive layer was clearly discernable in one of the specimens. However, the mechanisms for the ingress of the moisture in the bulk and the bonded joint were apparently very different. The diffusion was Fickian in the bulk samples whereas it showed clear characteristics of Case II diffusion in the bonded joints. The ingress was also very much faster in the laminates compared with the bulk adhesive. This might have serious implications on the durability if this also is true for other structural adhesives used in the aerospace industry.

More work is required to assess if the apparent Case II diffusion is caused by the constraints imposed by the substrates against swelling or if this might have been induced by a higher ingress along the interface. This could be assessed by repeating

the experiment with different surface preparations of the substrates. It would also be interesting to determine the moisture distribution in a bulk specimen using the NRA technique. This would give even higher confidence when analysing the data obtained from the NRA of the laminates.

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Table 1 Moisture ingress properties for DP490

Specimen	Fickian diffusion coefficient ($\times 10^{-14} \text{m}^2 \text{s}^{-1}$)	Case II front rate ($\times 10^{-9} \text{ms}^{-1}$)	Time required for 90% saturation* (days)
Bulk adhesive	161	0.0	278
Laminate, 43 days	161	4.5	16
Laminate, 96 days	173	4.1	20

*for a diffusion path of 6.75 mm

Figure 1 Diagram of the moisture profile in a specimen governed by Case II kinetics

Figure 2 Diagram of the specimen and locations measured with neutron reaction analysis

Figure 3 Diagram of the experimental set-up for the NRA analysis

Figure 4 Surface after ‘polishing’ with the microtome

Figure 5 Fickian fit to the bulk uptake measurements

Figure 6 Results from the NRA for the sample aged for 43 hours

Figure 7 Measured moisture profile (summed counts in the longitudinal direction) for the laminate specimen aged for 96 hours

Figure 8 Measured normalised moisture profile (summed counts in transverse direction) and Case II fit for the laminate specimen aged for 43 hours

Figure 9 Measured normalised moisture profile (summed counts in transverse direction) and Case II fit for the laminate specimen aged for 96 hours

Fig. 1

Fig. 2

Fig. 3

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Fig. 6

Fig. 7

Fig. 8

Fig. 9