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**Diffusion of Moisture in
Adhesive Bonds**

**B C Duncan, G Pilkington, J
S Nottay, C R G Allen, K
Lawrence, J Urquhart and S J
Roberts**

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J Urquhart and S Roberts

Division of Engineering and Process Control,
National Physical Laboratory

ABSTRACT

Enhanced diffusion through the interface between the adhesive and the adherends may lead to rapid degradation of adhesive joints. Specimens with different types of adherend surfaces were tested and compared with moisture absorption predictions from bulk specimen data. Coated samples, where only one face of the sample was attached to the adherend, behaved the same as bulk specimens. In full joints where only the small area of the edges is available for absorption there was an increased absorption over the predictions. However, some uncertainties about the validity of the models and the input data at low concentrations prevent definitive conclusions from being made.

The feasibility of using a low cost dielectric sensor, which can be embedded within polymeric materials, to monitor moisture concentration was investigated. The measured capacitance was sensitive to moisture concentration and reasonable correlations could be made at low moisture concentrations. However, at high moisture concentrations the results were highly scattered suggesting further development of the technique is needed.

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National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

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Approved on behalf of the Managing Director, NPL,
by Dr M G Cain, Knowledge Leader, Process Materials Team
authorised by Director, Engineering and Process Control Division

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1 INTRODUCTION

Lifetime prediction is an important consideration in the selection of materials systems and the design of structures. The design approach for lifetime prediction of engineering polymeric materials, such as composites or structural adhesives, is developing continuously but still relies on ‘knockdown factors’ or ‘rules of thumb’ generated from mechanical tests on conditioned samples.

Chemical ingress, in particular moisture exposure, is a key mechanism for degradation in polymer systems. An understanding of permeation of degrading species is essential for developing testing methodologies and accelerated ageing protocols for polymeric materials. The process of permeation of chemicals through polymers is a combination of two interrelated processes, dissolution in the polymer and diffusion through the polymer. Dissolution is the process of absorption of the chemical in the polymer and depends on the affinity (interaction energy) of the polymer for the chemical, the volume available for absorption and the concentration of chemical. There is a limit to the amount of the chemical that can be absorbed under any particular set of conditions – the solubility. Diffusion is the concentration gradient driven process whereby the absorbed molecules are transported within the polymer and diffusion properties are characterised via diffusion coefficients. A review [1] of the extensive body of literature on permeation and diffusion in polymers [e.g. 2-6] emphasised the strong need for reliable test methods to measure the diffusion of gases and liquids in polymers. Permeation properties are required under relevant service conditions, which may include transient and varying levels of chemical exposure, temperature and stress [7].

Often, especially in thick sections, the time taken for deleterious species to diffuse in sufficient concentrations to critical regions is the rate-determining step in the ageing process. Accurate modelling of the absorption of moisture into engineering polymers is needed to design exposure procedures and carry out reliable lifetime predictions. This needs to be supported by good quality data obtained under representative conditions. The techniques described in this report focus on diffusion as part of a wider investigation of accelerated ageing of polymer materials [8].

The time dependent concentration of chemical species in a component can be predicted using diffusion modelling approaches [2-6]. A common assumption used in interpreting diffusion measurements is Fickian diffusion - the steady state flux of diffusant per unit area (J) is a function of the concentration gradient and Fick’s first law is expressed:

$$\frac{dJ}{dt} = -D \frac{d\phi}{dx} \quad (1)$$

Where the diffusion coefficient (D) does not depend on concentration then Fick’s second law can be used to determine the time dependence of the concentration (ϕ) of the diffusant in the sample.

$$\frac{d\phi}{dt} = D \frac{d^2\phi}{dx^2} \quad (2)$$

The diffusion coefficient $D(T)$ is temperature dependent, increasing the temperature (T) increases the rate of diffusion and accelerate the ageing of the system [7].

Diffusion in adhesive joints is often estimated from the diffusion properties of the bulk adhesive. These values are then used with a model [e.g. 9] to predict moisture uptake into the joint. If the adherends are also permeable (e.g. composites) then their diffusion properties should be obtained and included in the model. This approach relies on:

- The bulk adhesive having the same properties as the adhesive in the joint;
- The adhesive-adherend interface playing no role in moisture absorption and transport.

It is well established that the properties of materials near the interface, the so-called interphase, differ from those of the bulk material. Therefore, the diffusion properties in the interfacial region may not be the same as the bulk material. Few correlations between bulk adhesive and adhesive joint diffusion have been reported. Bond et al [10] determined diffusion coefficients for an epoxy adhesive as being $6.4 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ when obtained from mass measurements on bulk adhesive specimens and $6.7 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ when determined from measurements of weight gain in lap joints (1 mm thick grit blasted stainless steel adherends). These results suggest a significant contribution from the interface to diffusion. It is well recognised that diffusion of chemicals to the interface degrades bond performance [9-14].

The usual method of determining moisture absorption and diffusion within polymers is to use mass gain measurements [15-17]. These analyse diffusion on the basis of average moisture concentrations. The understanding of diffusion of moisture within complex structures could be improved if measurements of local moisture concentrations could be made directly. Several methods for measuring local moisture concentrations have been suggested [1]. Monitoring moisture concentrations through dielectric properties of polymers appears an attractive method.

The capacitance (C) of a parallel-plate capacitor with two parallel plane electrodes of area (A) separated by a distance (d) is, where d is small compared to the other dimensions of the electrodes:

$$C = \epsilon_m \frac{A}{d} \quad (3)$$

The permittivity of the material (ϵ_m) is:

$$\epsilon_m = \epsilon_r \epsilon_0 \quad (4)$$

Where ϵ_0 is the permittivity of free space ($8.854 \times 10^{-12} \text{ Fm}^{-1}$) and ϵ_r is the relative permittivity or dielectric constant of the material. Water has a dielectric constant (ca. 80) that is very much greater than typical values for a polymer (< 10 and usually between 2-4) [18]. Therefore, changes in the moisture content of a material should lead to measurable changes in the capacitance of the polymer. This approach has

been used for condition monitoring of adhesive joints [19], using the metal adherends as the electrodes, and carbon fibre composites, where the fibres are the electrodes [20]. These techniques could be used to determine the average moisture concentration between the electrodes.

Recently interdigitated capacitance sensors that have a comb-like electrode structure printed on a thin film of plastic, see Section 2.3, have been used to measure chemicals in adhesives [21]. These sensors have also been used for applications such as cure monitoring [22]. The electric field surrounding the two-dimensional sensor has a limited penetration into the surrounding media with the depth of the penetration of the field depending on the electrode separation. Where the inter-electrode separation is small then the electric field will be extremely local to the sensor and the sensor will be sensitive only to changes in the material near the sensor. Thus, interdigitated sensors offer a potential method for determining local changes in moisture concentration.

Determination of moisture concentration from the dielectric properties of polymers is likely to be difficult as there is a frequency dependence of these properties owing to molecular relaxations of the molecular chains [23]. These molecular relaxations are affected by moisture and the dielectric spectra of a polymer absorbing moisture will evolve due to the increasing concentration of the high dielectric constant water and the shifts in peaks in the spectra occurring due to changing molecular mobility. This complexity coupled with the difficulty in quantifying the strength of the fringe electro-magnetic fields within the material are likely to prevent a direct calculation of moisture levels from first principles. However, it may be possible to calibrate sensor systems at a particular frequency using measured capacitance against saturation concentration, achieved by exposing samples to different conditions, and use relative capacitance measurements to monitor moisture concentrations.

2 MATERIALS

2.1 Bulk Epoxy Specimens

A room-temperature curing, rubber-toughened 2-part toughened epoxy adhesive (3M DP460) was used in this work.

Bulk plaques were manufactured by casting the adhesive in a mould designed to minimise the inclusion of voids. The mould, shown in Figure 1, uses a picture frame to control thickness. This can be pressurised or evacuated in order to completely fill the mould and squeeze/draw out voids. The adhesive was cured, under pressure, for 24 hours at 23 ± 2 °C and then post-cured for 60 minutes at 100 °C. The post-cure should minimise further cure of the adhesive during testing. The glass transition temperature, T_g , of the dry adhesive is approximately 80 °C (measured by dynamic mechanical analysis). Absorption of moisture reduces T_g ; for example, a sample containing 2.5% absorbed moisture had a T_g of 75 °C.

Two different picture frames were used to produce plaques of 1 mm and 3.2 mm thickness. Square plaques with sides 50 mm long were machined from the plaques for diffusion measurements.

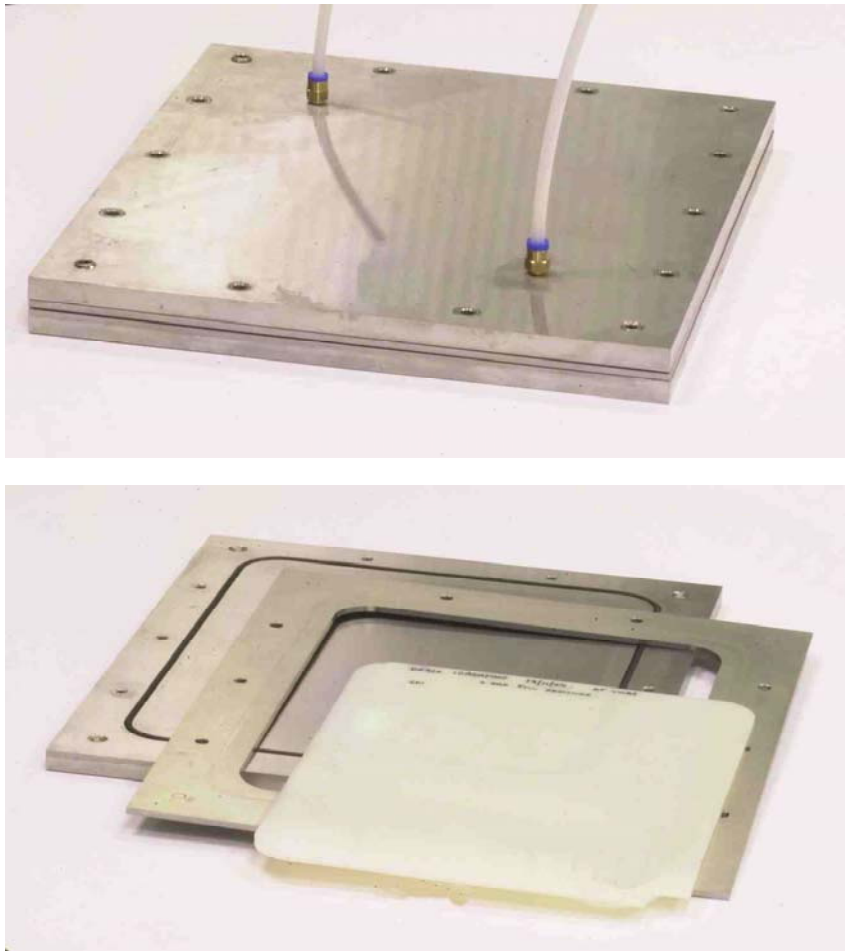


Figure 1: Mould for preparing adhesive samples

2.2 Joint Samples

Square plaques with 50 mm sides were cut from thin sheets of metals with different surface pre-treatments giving different roughness and wettability. Stainless steel and anodised aluminium samples were used as received. The milled aluminium and grit blasted aluminium samples were chromic acid etched to prevent corrosion during exposure [24]. The surfaces used were:

- Stainless Steel
- Anodised Aluminium
- Grit Blasted and Acid Etched
- Milled and Acid Etched

Specimens were prepared as ‘open faced’, i.e. an adhesive coating on a single adherend, or joints, i.e. sandwiched between two adherends, see Figure 2. Moulds were prepared from a flexible silicone compound to control the thickness of the adhesive layer. A set of blanks having the area and thickness required for the combined adhesive-adherend system were placed on a flat base. Silicone compound

was poured around the blanks and left to set. Once the mould had set the blanks were removed leaving square depressions in the mould, Figure 2.

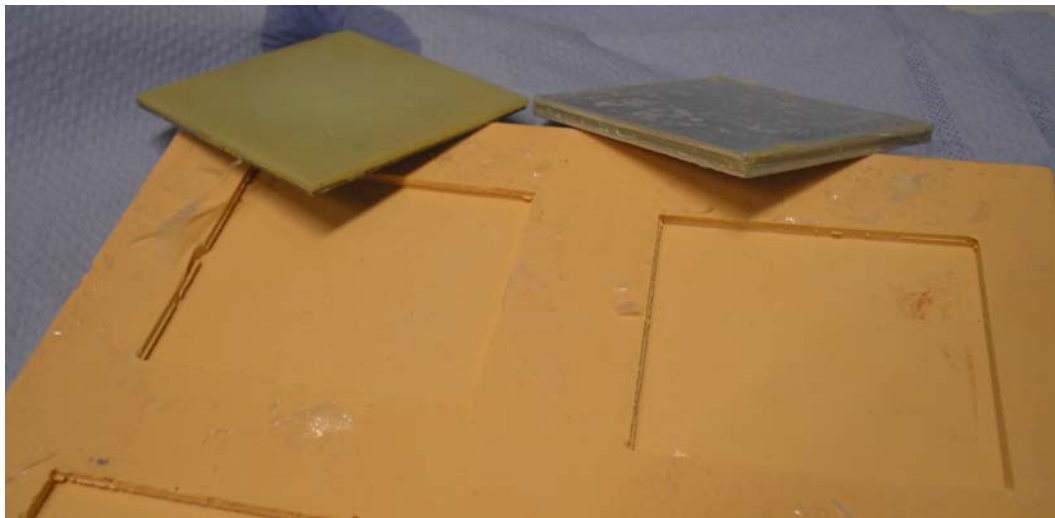


Figure 2: Mould for sample preparation plus ‘open face’ and joint specimens

2.3 Film Adhesives

A film adhesive (3M 6045) was obtained as a system for simplifying the locating and embedding of dielectric sensors. The adhesive contains a carrier cloth and is not intended for use as a bulk material. Film adhesive specimens were made as 50 mm sided square plaques that were cut from a large sheet of film adhesive using a scalpel and template. Bulk samples were prepared as 1-ply, 2-ply or 4-ply. Multiple-ply specimens were prepared by carefully placing and aligning uncured individual squares on top of each other so that the layers overlapped completely. Pressure was applied to the stacked layers to bring the layers into intimate contact.

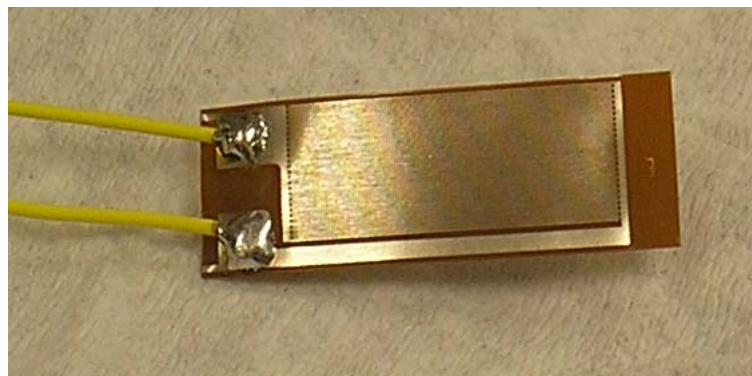


Figure 3: Thin foil dielectric sensor

Thin foil dielectric sensors obtained from Netzsch Instruments, Figure 3, were incorporated in some of the 4-ply samples by inserting the sensor in between two uncured 2-ply samples as shown in Figure 4 and applying pressure to consolidate the sample. The active sensor area is the metal comb, which is approximately 20 mm by 10 mm.

These samples were cured in an oven, which had been preheated to 165 °C, for 40 minutes. Measurements of temperature, made by embedding a thermocouple in one of the specimens, showed that the samples reached 165 °C after approximately 20 minutes.

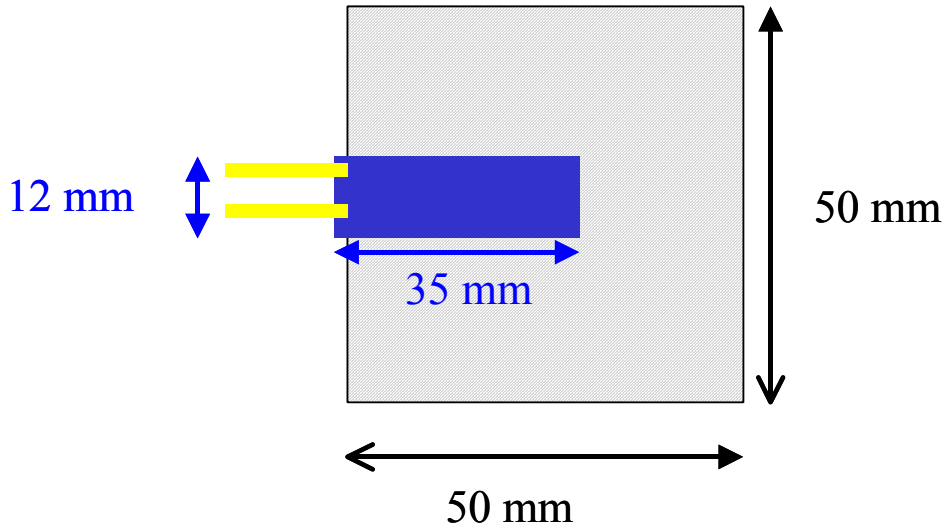


Figure 4: Schematic of specimen with embedded sensor

A 2-ply layer with an embedded dielectric sensor was also prepared using the process describes above. However, this sample was cured for only 20 minutes at 165 °C.

3 EXPERIMENTAL METHODS AND MODELLING

3.1 Moisture Absorption Measurements

The moisture uptake of the epoxy samples (square plaques of bulk adhesive, open faced samples and joints) was measured following the basic method specified in ISO 62 [15]. Samples were fully immersed at different temperatures (4 °C, 23 °C, 44 °C and 64 °C).

There was concern that the embedded sensor or the exposed interface between sensor and adhesive could provide a pathway for wicking of moisture. Therefore, to avoid direct contact of the sensor with water, samples containing embedded sensors were exposed vertically in a rack with the exposed end of the sensor (and connecting wires) uppermost (Figure 5). These were placed in a container of water so that the top edges of the samples were just above the level of the water. Most film adhesive samples without sensors were not racked and were fully immersed, but two of these samples were also racked in order to determine if leaving one edge unexposed affected the absorption of moisture – comparing the results of the two cases suggested the effect was extremely minor and not distinguishable from variability of the measurements.

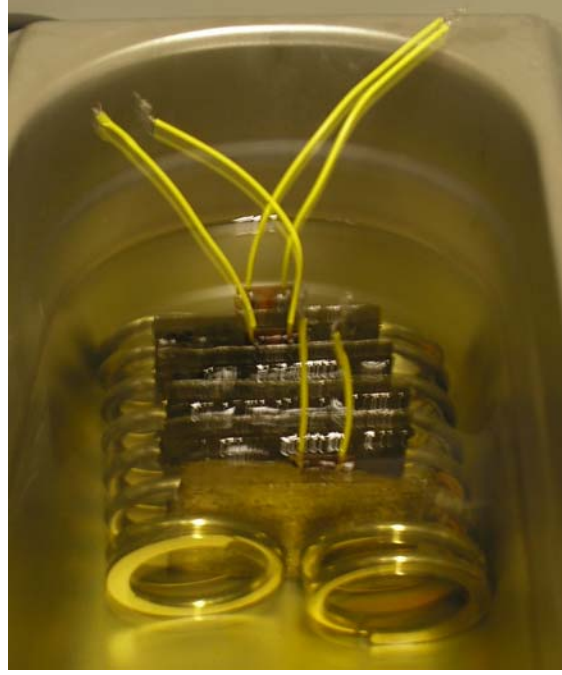


Figure 5: Exposure of samples containing embedded sensors

The apparent diffusion coefficient (D_a) is calculated from the mass gain data, assuming a one-dimensional Fickian process [17, 25], from the mass uptake (M_i) versus time (t_i) measurements and the sample thickness (h):

$$D_a = \frac{\pi}{16} \left[\frac{h(M_2 - M_1)}{M_\infty(\sqrt{t_2} - \sqrt{t_1})} \right]^2 \quad (5)$$

where M_∞ is mass (or percentage) of moisture absorbed at saturation. If the starting point is a dry sample at time zero then t_1 and M_1 can be eliminated and the fractional mass uptake M_2/M_∞ plotted as a function of $\sqrt{t_2}$ has a slope proportional to $D_a^{1/2}$.

$$\frac{M_2}{M_\infty} = D_a^{1/2} \frac{4\sqrt{t_2}}{h\sqrt{\pi}} \quad (6)$$

For Fickian diffusion, this plot is approximately linear until M_2 approaches $0.7M_\infty$. Therefore, D_a can be evaluated from values of M_2 and t_2 if a value for M_∞ is known or can be estimated with reasonable accuracy.

The one-dimensional approximation ignores additional diffusion of moisture through the edges of the sample. This is minimised by ensuring the samples have a large ratio of face area to edge area. Edge effects can also be reduced by sealing the edges.

A correction was derived by Shen and Springer [25] to account for edge effects. The true one-dimensional diffusion coefficient (D_x) can be calculated from the apparent diffusion coefficient D_a and the length (l), width (b) and thickness (h) of the plaques using a correction factor (E).

$$D_x = ED_a = \left(1 + \frac{h}{l} + \frac{h}{b}\right)^{-2} D_a \quad (7)$$

For example, the correction factors for 1 mm and 3.2 mm thick squares with 50 mm sides are 0.925 and 0.786 respectively.

3.2 Dielectric Measurements

Dielectric measurements were made by connecting the sensor to a network analyser (Agilent Precision Impedance Analyser 4249A). Measurements were made of capacitance and resistance as the frequency was swept from 40 Hz to 50 MHz. Figure 6 shows the frequency dependence of resistance and capacitance of a bare sensor (in contact with air). Sensor/instrument effects seem to dominate at high frequencies (> 5 MHz) where negative values for resistance and capacitance are obtained. Therefore, valid measurements could only be made below this frequency. Researchers using parallel plate measurements have reported measurements at much higher frequencies (GHz) [19].

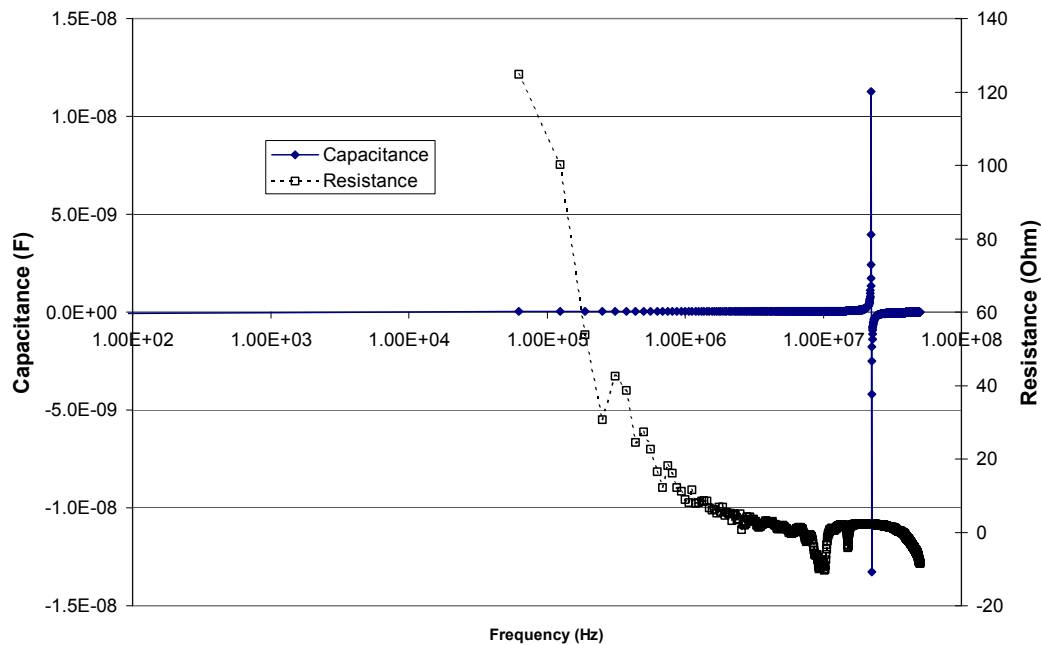


Figure 6: Impedance traces for a bare sensor

3.3 Modelling

To estimate the expected moisture concentration ($\phi(t)$) in the specimens from the saturation concentration (ϕ_∞), the apparent diffusion coefficient (D_a) and the effective specimen thickness (H) the following approximation was used [17]:

$$\phi(t) = \phi_{\infty} \left[1 - \exp \left[-7.3 \left(\frac{D_a t}{H^2} \right) \right] \right]^{3/4} \quad (8)$$

In the bulk specimens, where diffusion occurs through both faces H is equal to the specimen thickness and in open face samples, where diffusion occurs through only one face, H is equal to twice the adhesive layer thickness.

A three-dimensional model using Finite Volume methods has been created for predicting heat and mass transport in solids. The forms of the equations are the same for both heat and mass diffusion. The model for heat diffusion is described in Appendix I.

4 RESULTS FOR EPOXY ADHESIVE

4.1 Diffusion in Bulk Specimens

To obtain base diffusion data for the epoxy adhesive, three samples of each thickness (1 mm and 3.2 mm) were immersed at four different temperatures (4 °C, 23 °C, 44 °C and 64 °C) in deionised water at each temperature, except for 4 °C where only 1 mm samples were used. The samples were weighed periodically with the first measurement taken 8 hours (1 mm thick specimens) or 24 hours (3.2 mm thick specimens) after immersion. Plots of moisture uptake against square root time are shown in Figure 7. Raising the temperature and reducing the thickness increases the rate of moisture diffusion. At 64 °C significant levels of absorption had occurred before the first measurements.

The data suggest that the saturation concentrations at the higher temperatures (44 °C and 64 °C) are lower than at the lower temperature (23 °C). The differences between the saturation values are significant compared to the repeatability of the results from the three replicate samples exposed at each temperature, which was typically $\pm 0.1\%$. The samples at the lowest temperature (4 °C) did not reach saturation in the timescale of the experiments.

The values determined from the data shown in Figure 7 are shown in Table 1. The sample exposed at 4 °C did not reach saturation and the saturation value determined at 23 °C was used for the calculation of D_a .

The thickness appears to have, as expected, little effect on the saturation concentration and variations between different thicknesses fall within the experimental uncertainty. The saturation concentration appears to decrease with increasing temperature. The diffusion coefficient depends strongly on temperature. The plot of logarithm of the averaged diffusion coefficients at each temperature plotted against $1/T$ is linear [7], suggesting that the Arrhenius relationship holds over this range of temperatures.

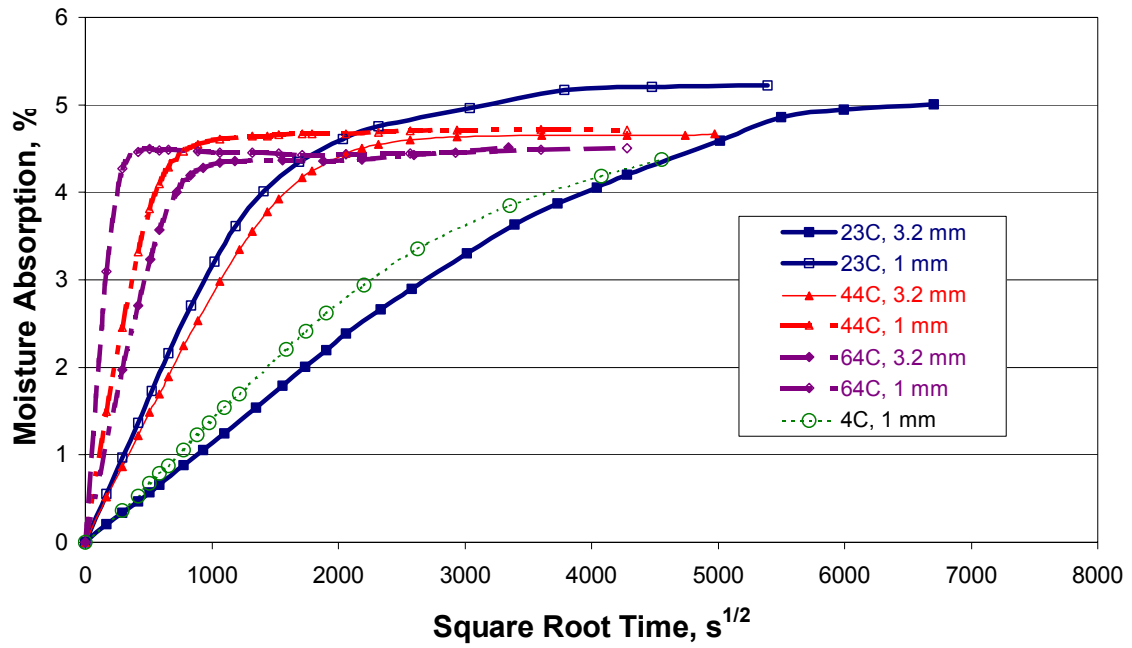


Figure 7: Moisture absorption curves measured by mass uptake

Table 1: Diffusion properties determined from bulk samples

Sample Thickness (mm)	Temperature (°C)	Apparent D_a (m^2s^{-1})	Saturation Concentration (%)	Corrected D_x (m^2s^{-1})
1	4	1.26×10^{-14}	5.2*	1.16×10^{-14}
1	23	6.68×10^{-14}	5.2	6.18×10^{-14}
1	44	4.87×10^{-13}	4.7	4.50×10^{-13}
1	64	3.23×10^{-12}	4.5	2.99×10^{-12}
3.2	23	9.69×10^{-14}	5.2	7.62×10^{-14}
3.2	44	7.23×10^{-13}	4.65	5.68×10^{-13}
3.2	64	3.31×10^{-12}	4.5	2.60×10^{-12}

* Saturation not reached, value for 23 °C used to calculate the diffusion coefficient

4.2 Open Faced Specimens

Moisture absorption in the open face and joint samples was measured through mass gain measurements, following the same methods used for the bulk samples. Samples were immersed in deionised water at 64 °C. The highest temperature was chosen to reduce the duration of the experiments. Since corrosion of the metal adherends could occur, and potentially cause changes in mass, traveller specimens of the adherends were exposed under the same conditions as the specimens. The mass of these travellers was monitored and changes were negligible giving confidence that changes in mass that were observed were due to moisture absorption in the adhesive.

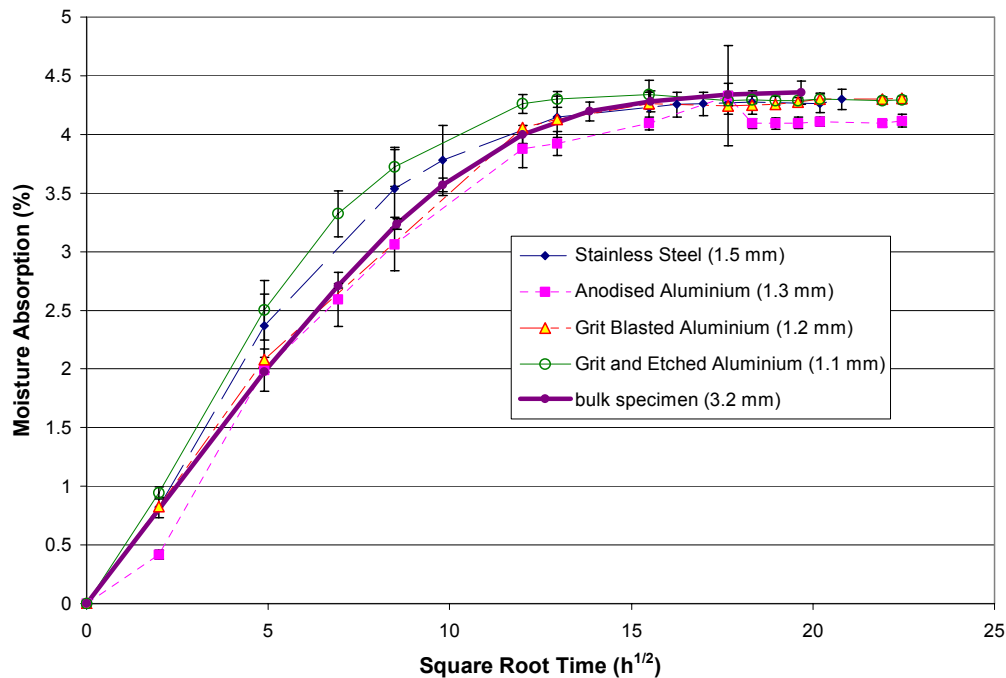


Figure 8: Absorption of moisture in open face samples.

The absorption results are shown in Figure 8. The curves are in reasonable agreement with each other (and the bulk specimen data). The uncertainty bars represent the standard deviation in the results for three replicate samples. At saturation the scatter in the results is small, suggesting consistency in the materials. In earlier portion of the absorption curves the standard deviations in the measurements are larger, most likely reflecting the scatter in the thickness of the adhesive layer. The saturation concentrations in the bulk and open faced specimens are approximately equal and the bulk specimens have slightly higher saturation levels.

Predicted uptake curves, using the analytical approximation and the 3-D Finite Volume method are shown in Figure 9 for the bulk specimen and the open faced specimens with grit blasted and etched aluminium adherends. The adhesive layer on the open faced specimens was 1.1 mm thick (effective thickness $H = 2.2$ mm). The predictions for the bulk specimens agree well with the measurements, expected as the diffusion properties were derived from this curve. Agreement between the predicted values for open face specimen is also good.

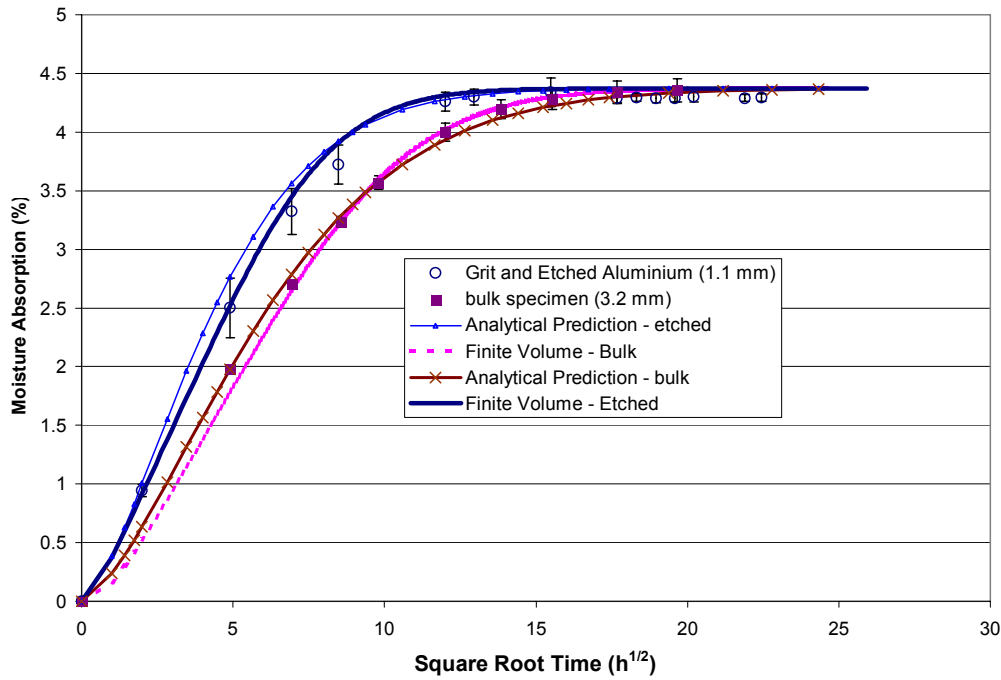


Figure 9: Measured and predicted moisture absorption

4.3 Diffusion in Adhesive Joints

Four samples of each type of adherend (grit blasted and etched or mill finished and etched) were exposed in deionised water at 64 °C. The grit blasted specimens have rougher surfaces ($R_a > 40 \mu\text{m}$) than the milled samples ($R_a < 10 \mu\text{m}$) and are, potentially, more likely to have voids at the interface between the adherend and the adhesive. The adherends were 50 mm squares and the adhesive layers were approximately 1 mm thick. Figure 10 shows that moisture absorption measurements in the different adhesive joints are virtually identical. Scatter in the measurements is reasonably low.

Figure 10 also shows predictions made using the one-dimensional analytical approximation and the three-dimensional Finite Volume model. Since absorption is expected equally through the four exposed edges of the adhesive the assumptions in the one-dimensional approximation are likely to be invalid. The effective thickness of the specimen was taken to be the length of the square divided by $\sqrt{2}$ in order to partially account for the two-dimensional diffusion. The 1-D analytical model is in reasonable agreement with the 3-D Finite Volume model but both predictions are substantially lower than the measurements.

After about a week ($\sqrt{t} \approx 13 \text{ h}^{1/2}$), the plots of measured and predicted moisture absorption curves against the square root of time are linear and all have slopes that are approximately $0.04\% \text{ h}^{-1/2}$. This suggests Fickian diffusion and similar diffusion coefficients. Most of the difference between measured and predicted curves occurs at the start of the tests, suggesting a deviation from theoretical absorption mechanisms that may be due to defects at the edge of the bond.

The analysis of results from the open face and adhesive joint specimens suggests that the different surfaces have very little effect on absorption and diffusion in the joints. Any differences are more likely to be due to experimental uncertainties and differences in adhesive layer thickness (for open face specimens).

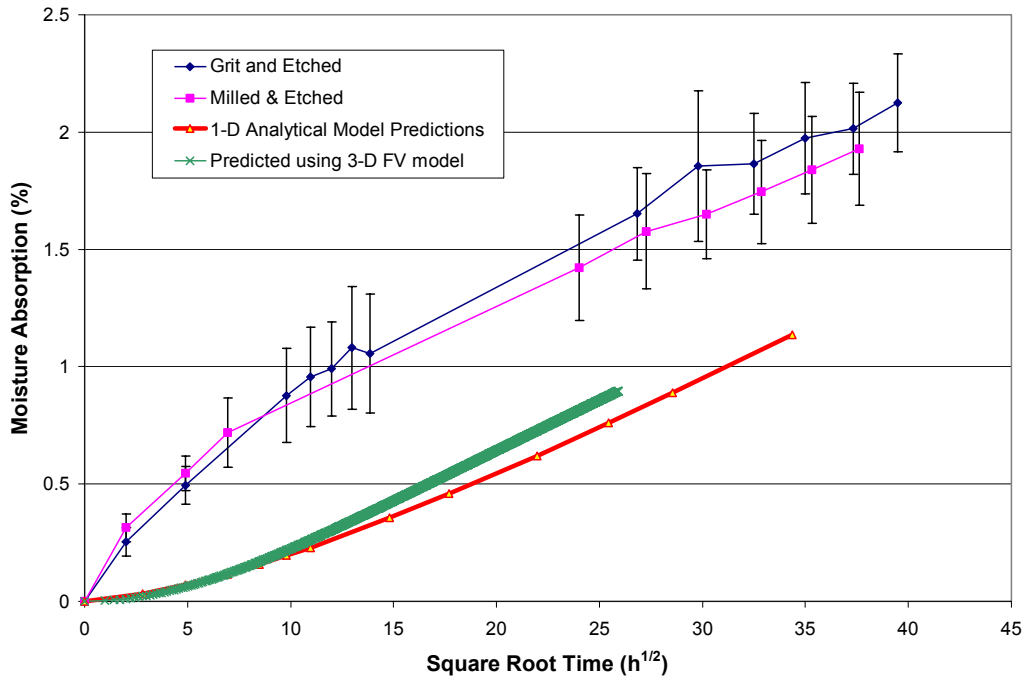


Figure 10: Measured and predicted moisture absorption in adhesive joint samples

Comparing moisture absorption in the open face specimens with moisture absorption in bulk specimens (and predicted moisture absorption based on the properties of the bulk material) shows that the absorption through the open face dominates. The effect of the single interface cannot be distinguished. The comparability of the saturation concentrations suggests that any moisture uptake at the interface or in the interphase region is not significantly different to that in the bulk adhesive.

The absorption of moisture in the joint specimens is significantly greater than predicted from bulk material diffusion properties. Most of the difference arises early on in the absorption measurements where the curves are non-linear with opposite inflections. At longer times, the moisture absorption versus the square root of time curves are linear. The slopes of the measured and predicted curves are very similar suggesting the diffusion properties in the joint are similar to those of the bulk material.

The reasons for the differences between measured and predicted concentration curves at low time are not clear but indicate some deficiency in the models. The models for predicting moisture diffusion are approximations, particularly Equation 8, and, due to the time intervals used in the bulk specimen moisture absorption measurements, no data for low concentrations (< 1.5%) were obtained or used to determine diffusion coefficients. Therefore, the shapes of the predicted curves at small times are open to question. In the Finite Volume method the element size may be an issue, by using a higher mesh density the model may be more sensitive to small concentrations. The

absorption through the edges could be enhanced at the start of the tests by defects at the edges possibly created by removal of fillets (or due to the constraint of the adherends on moisture induced swelling).

5 DIELECTRIC MONITORING OF MOISTURE IN THE FILM ADHESIVE

5.1 Absorption in Film Adhesive by Mass Uptake

Moisture absorption measurements were carried out at 23 °C with 1, 2 and 4-ply specimens of the film adhesive. The results, shown in Figure 11, are highly scattered, significantly more so than the 2-part epoxy. These samples had rough textured surfaces that appeared to be well wetted by water. It took considerably longer to dry the excess moisture from the surfaces of the samples (i.e. until no transfer to the drying cloth was observed) and even then ‘dry’ was subjective. Therefore, the time between removal from exposure and mass measurement was not constant. The film adhesive dried out quickly [17] and therefore the concentration at the point of measurement was more variable.

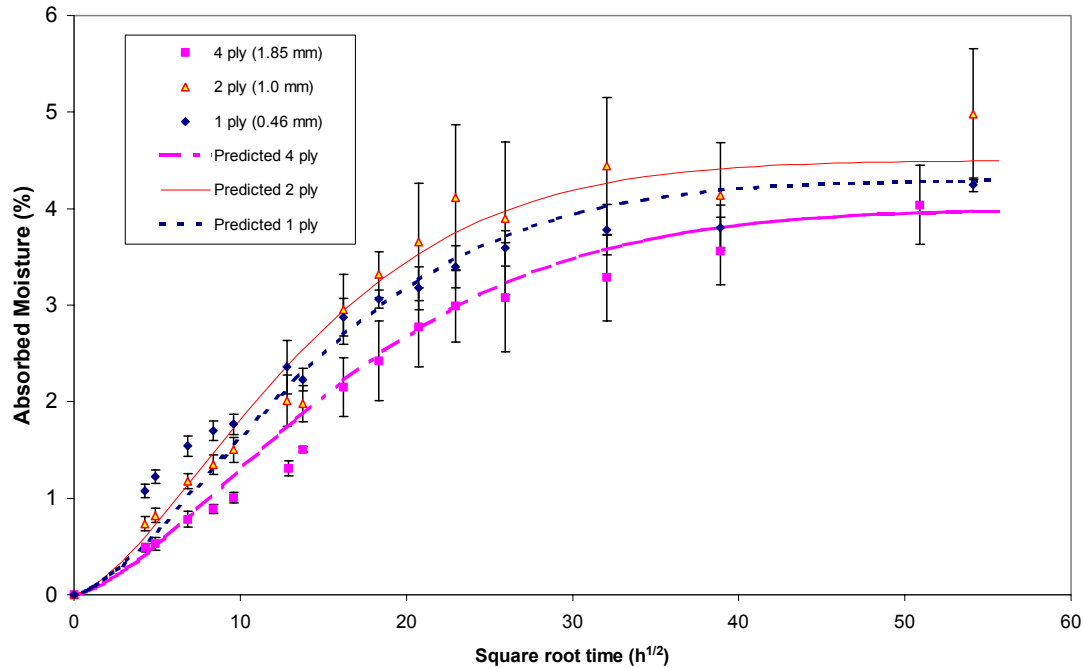


Figure 11: Moisture absorption curves obtained for film adhesive samples, predicted curves were generated using Equation 8

Moisture absorption in the film adhesive was also affected by the cure state of the adhesive. Figure 12 shows moisture absorption in two samples of 2-ply film adhesive that were cured under different conditions. One sample (sample 1) was cured for the shorter cure cycle (20 minutes in an oven preheated at 165 °C). This sample reached 165 °C, as measured by a thermocouple embedded in the mould, towards the end of the cure period. The other sample (sample 2) was cured using the longer cure cycle (a total of 40 minutes in the oven at 165 °C including at least 20 minutes with the sample at 165 °C). Glass transition temperatures, T_g , for samples cured under both conditions

were determined using DSC (differential scanning calorimetry [26]). T_g was 84 °C for sample 1 cured for the shorter time period and 90 °C for sample 2 cured for the longer period. Second and third DSC runs on the samples were carried out and T_g for each sample reached 96 °C, suggesting that neither sample was fully cured.

At equivalent exposure times, there is approximately twice as much moisture absorbed into the sample 1 than into sample 2. It is also apparent that the two samples will have significantly different saturation levels. These major differences exist despite what could be seen as fairly minor differences in cure state.

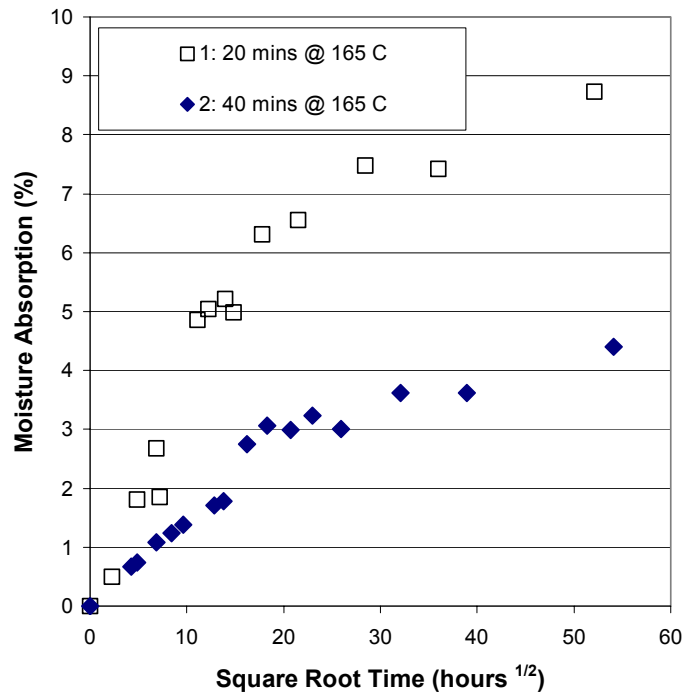


Figure 12: Effect of cure conditions on moisture absorption

5.2 Dielectric Monitoring

The mass of each sensor was measured before embedding so that subsequent mass measurements could be corrected to the mass of adhesive (and absorbed moisture). Dielectric measurements were made in the following sequence:

- Bare sensor
- Sensor embedded in adhesive (pre-cure)
- Sensor embedded in cured adhesive (dry)
- Sensor embedded in cured adhesive after different immersion durations (moisture concentration calculated from mass gain measurements)

Capacitance traces are shown in Figure 13. There are measurable increases in the capacitance readings when the sensor is embedded in the uncured adhesive. The capacitance increases again on curing. As moisture is absorbed, the capacitance increases, with the values increasing more at low frequencies. The frequency dependent drop off in capacitance shifts to higher frequencies with increasing

moisture content. Capacitance values are least affected by frequency around 1 MHz. A curve for a second sensor immersed in deionised water is included for comparison.

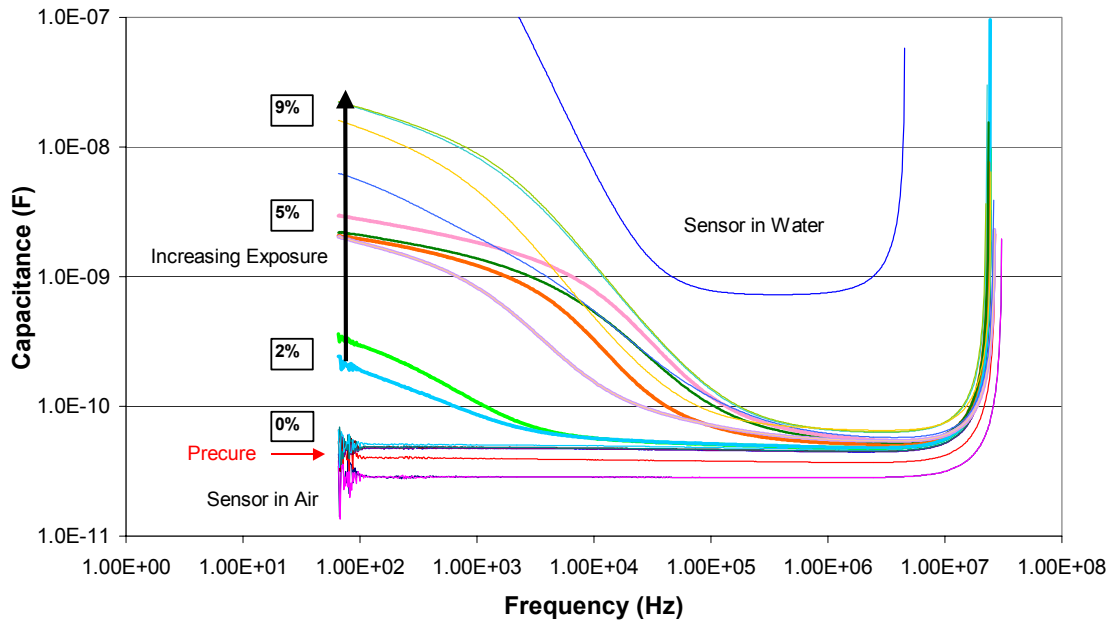


Figure 13: Capacitance curves for film adhesive

The capacitance measurements for different samples were compared by plotting capacitance values at a single frequency against moisture concentration. Figures 14 and 15 show the plots for 12.5 kHz and 1 MHz, respectively. The values have large scatter at high moisture concentrations, the scatter being worse for the lower frequency measurements. This higher scatter is due to the capacitance values being higher but also, as Figure 13 shows, due to the curves crossing each other. The cause of this scatter is unclear but could be due to either moisture condensing on the surface of the sensor from the adhesive or variations in the electrical contact as the exposed ends of the connecting wires deteriorate (due to mechanical damage on connection or exposure to a humid atmosphere). Further work is needed to overcome these problems.

At low moisture concentrations ($< 3\%$) the results are more consistent, the different specimens all lie close together but there appears to be a small but consistent difference between the specimens. A trend line fitted to these data at 1 MHz has a slope of 1.46 pFm^{-1} . Although the data are probably too scattered to determine absolute values, a shift in capacitance could possibly be quantitatively related to a change in moisture concentration.

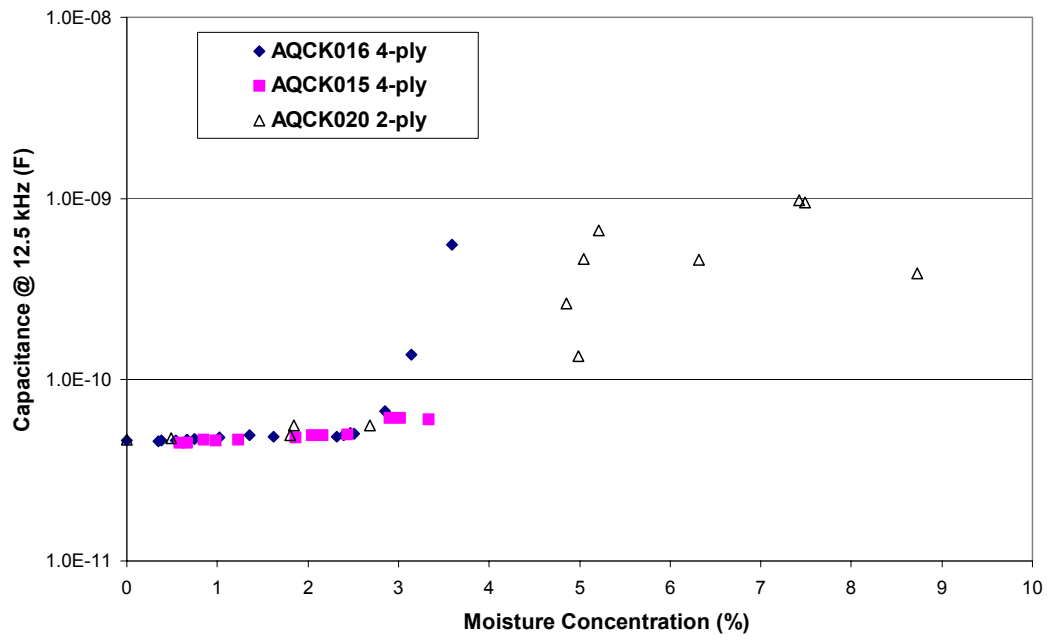


Figure 14: Capacitance versus moisture concentration at 12.5 kHz

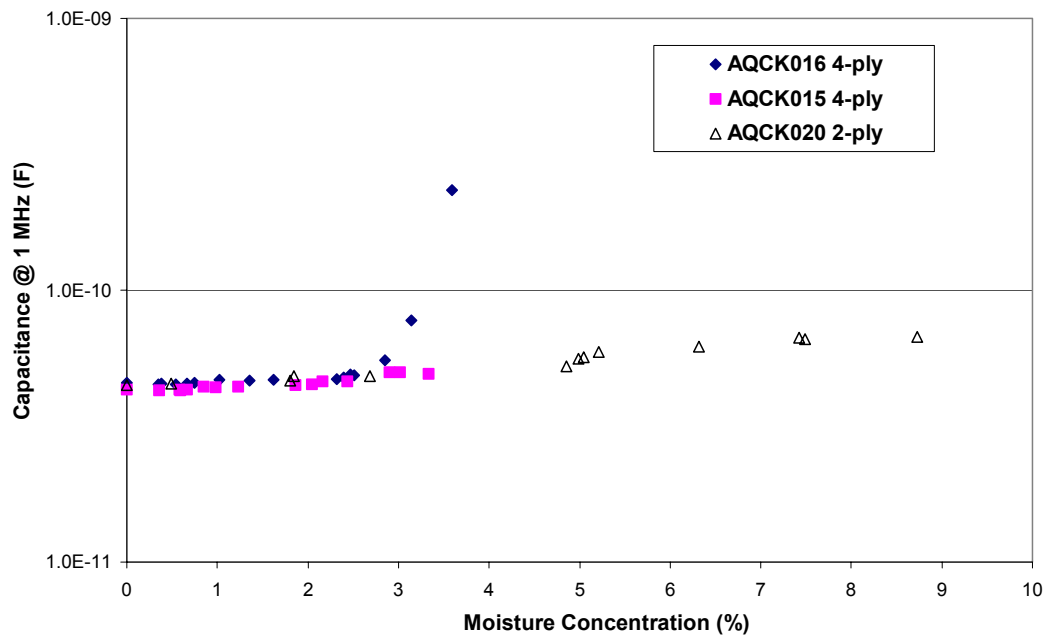


Figure 15: Capacitance versus moisture concentration at 1 MHz

6 DISCUSSION AND CONCLUSIONS

This study investigated evidence for enhanced diffusion due to the interface between the adhesive and the adherends studied but could not find any conclusive evidence. There were no measurable differences between specimens with different types of adherend surfaces. One potential mechanism for enhanced moisture absorption at interfaces is that delaminations occurring at the interface due to poor wetting of rough textured surfaces by the adhesive (e.g. adhesive failing to penetrate the ‘valleys’ of surface features) promote capillary effects. This should have shown up as a difference between rough grit blasted surfaces and the other smoother adherends. However, no differences were seen and it is likely that the low viscosity epoxy adhesive conforms to the surface leaving no gaps.

There were differences observed between moisture absorption in adhesive joints and that predicted from bulk specimen data. In this situation, the small area of edges available for absorption lead to greater significance of the interfaces. The models do not predict the measured uptake correctly and there may be additional mechanisms occurring that are not included in the models. Increased absorption through the edges of the specimens (e.g. possibly due to voids at the edges) may be occurring that is not predicted from either the bulk specimens or the open face specimens where absorption through the faces dominates. However, some uncertainties about the validity of the models and the input data at low concentrations prevent definitive conclusions from being made.

A low cost dielectric sensor that can be embedded within polymeric materials was investigated. The measured capacitance was sensitive to moisture concentration and reasonable correlations could be made at low concentrations but at high concentrations the results were too scattered and further development of the technique is needed.

7 ACKNOWLEDGEMENTS

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APPENDIX I: THREE-DIMENSIONAL TRANSIENT HEAT DIFFUSION IN MULTI-MATERIAL SYSTEMS (CUBIC GEOMETRIES)

I.1 Introduction

Although there exist many analytical solutions to the heat diffusion equation with various boundary conditions, see Carslaw and Jaeger [1], more complicated multi-layered or multi-material structures have to be solved using numerical methods, which is particularly useful for dealing with more complex geometries or problems with more complicated boundary conditions. For determining heat transfer in systems where the geometry is generally static the most suitable approach is to use finite difference or finite volume methods.

Both Incropera and DeWitt [2] and Carslaw and Jaeger [1] have substantial sections on solving heat transfer problems using finite difference numerical methods. The finite difference method is a Taylor series approach that divides the continuum into nodes. The underlying partial differential equation is then approximated node wise using finite differences, which is straightforward for orthogonal grids with simple boundary conditions. In this appendix, solutions of the heat transfer equation are derived using the more popular finite volume approach [3]. This is based on the physical concept of using macroscopic control volumes to numerically solve the conservation laws of heat transfer. The discretisation equations are obtained by integrating over the control volumes surrounding the nodes, after introducing necessary simplifications and assumptions. This often leads to the same discretisation equations as the Taylor series method, however it is much more flexible and has much in common with the Galerkin finite element method [4] but is easier to implement. In the finite volume method, the integration domain is covered by control volumes (cells) where each volume engulfs one node that lies on a grid.

The basic theory necessary to derive three-dimensional transient heat diffusion equations for geometries consisting of cubic elements is outlined. The theory uses standard finite volume approaches [5] for application to multi-materials geometries.

I.2 Finite volume equations for Three-Dimensional Transient Heat diffusion

I.2.1. Integral form of the energy balance

The energy balance is a principle that must be obeyed in addition to those for momentum and species. Energy may enter and leave a given volume due to transport across the surface. The same energy may also be generated within the volume (for example from chemical reactions) and accumulated within the volume. The well-known rate equation describing the conservation of energy [5] is

$$\frac{\partial}{\partial t}(\rho c_v T) = -\nabla \cdot \mathbf{q} + \hat{E}, \quad (\text{A.1})$$

where T is the temperature, $\mathbf{q}$ is the heat flux vector, ρ is the density and c_v is the specific heat at constant volume and $\hat{E}$ is a source term that describes the rate of

increase of temperature due to chemical reactions. Now consider a region V bounded by a closed surface S across which heat may flow. Integrating A.1 over the region leads to

$$\int_V \frac{\partial}{\partial t} (\rho c_v T) dV = - \int_V \nabla \cdot \mathbf{q} dV + \int_V \hat{E} dV. \quad (\text{A.2})$$

Applying the divergence theorem to A.2 yields

$$\int_V \frac{\partial}{\partial t} (\rho c_v T) dV = - \int_S \mathbf{n} \cdot \mathbf{q} dS + \int_V \hat{E} dV, \quad (\text{A.3})$$

where $\mathbf{n}$ is the outward unit normal to the surface S bounding the region V . The relation A.3 is the integral form of the energy balance equation and defines the relationship between rate of change of temperature within the volume, the temperature flux across the boundary and the rate of production of energy within the volume. We now consider a control volume in the form of a rectangular parallelepiped whose sides are parallel to the Cartesian coordinate axes x , y and z and are of lengths Δx , Δy and Δz respectively, such that the volume of the cell is simply

$$\Delta V = \Delta x \Delta y \Delta z. \quad (\text{A.4})$$

If we assume that the cell size is small enough for the rate change of temperature, density and specific heat to be regarded as uniform throughout the control volume, then the left hand side of A.3 may be written

$$\int_V \frac{\partial}{\partial t} (\rho c_v T) dV = \int_z^{z+\Delta z} \int_y^{y+\Delta y} \int_x^{x+\Delta x} \frac{\partial}{\partial t} (\rho c_v T) dx dy dz = \frac{\partial}{\partial t} (\rho c_v T) \Delta x \Delta y \Delta z. \quad (\text{A.5})$$

The source term in A.3 is integrated in a similar fashion leading to

$$\int_V \hat{E} dV = \int_z^{z+\Delta z} \int_y^{y+\Delta y} \int_x^{x+\Delta x} \hat{E} dx dy dz = \hat{E} \Delta x \Delta y \Delta z. \quad (\text{A.6})$$

The surface integral in (2.3), when applied to the control volume, can be written

$$\begin{aligned} - \int_S \mathbf{n} \cdot \mathbf{q} dS &= \int_z^{z+\Delta z} \int_y^{y+\Delta y} (q_x - q_{x+\Delta x}) dy dz + \\ &\quad \int_z^{z+\Delta z} \int_x^{x+\Delta x} (q_y - q_{y+\Delta y}) dx dz + \\ &\quad \int_y^{y+\Delta y} \int_x^{x+\Delta x} (q_z - q_{z+\Delta z}) dx dy, \end{aligned} \quad (\text{A.7})$$

where q is a scalar term describing the components, indicated by respective subscripts, of the heat flux vectors across the boundaries at x , y , z , $x+\Delta x$, $y+\Delta y$ and

$z+\Delta z$. Assuming the flux components are uniform across each boundary of the control volume, the integration of A.7 yields

$$-\int_S \mathbf{n} \cdot \mathbf{q} dS = (q_x - q_{x+\Delta x}) \Delta y \Delta z + (q_y - q_{y+\Delta y}) \Delta x \Delta z + (q_z - q_{z+\Delta z}) \Delta x \Delta y. \quad (\text{A.8})$$

It is sufficient in most applications of heat conducting through solids to use Fourier's law [6], which defines, for any point within the system, the flux vector as

$$\mathbf{q} = -\lambda \nabla T, \quad (\text{A.9})$$

where λ is the thermal conductivity coefficient that usually depends upon the temperature T . This form assumes that there are no temperature or stress gradients in the system. The use of A.9 is thus an approximation for many practical applications. Using A.9, equation A.8 can be rewritten as

$$\begin{aligned} -\int_S \mathbf{n} \cdot \mathbf{q} dS = & \left(\lambda_{x+\Delta x} \frac{\partial T}{\partial x} \Big|_{x+\Delta x} - \lambda_x \frac{\partial T}{\partial x} \Big|_x \right) \Delta y \Delta z + \\ & \left(\lambda_{y+\Delta y} \frac{\partial T}{\partial y} \Big|_{y+\Delta y} - \lambda_y \frac{\partial T}{\partial y} \Big|_y \right) \Delta x \Delta z + \\ & \left(\lambda_{z+\Delta z} \frac{\partial T}{\partial z} \Big|_{z+\Delta z} - \lambda_z \frac{\partial T}{\partial z} \Big|_z \right) \Delta x \Delta y, \end{aligned} \quad (\text{A.10})$$

where the subscripts $x, y, z, x+\Delta x, y+\Delta y$ and $z+\Delta z$ refer to the values of the thermal conductivities and derivatives at the respective control volume boundaries.

1.2.2 Finite volume representation of the conservation of energy

Any multi-material structure can be described approximately by a collection of discrete cells, where each cell represents a homogeneous material block. A simple orthogonal grid is constructed where each node represents the centre of each cell as shown in Fig. I.1. The finite volume equations are obtained by integrating (A.1), over the cell volume surrounding each grid node, for a discrete time interval. For each time interval it is assumed that the temperatures internally and at the boundary are fixed.

We take this opportunity to introduce the notation to be used in this report. From now on, a variable associated with the $(i,j,k)^{\text{th}}$ node will have the subscript (i,j,k) . For example, the temperature *at* the $(i,j,k)^{\text{th}}$ node would be denoted by $T_{(i,j,k)}$. Similarly values of other parameters associated with the $(i,j,k)^{\text{th}}$ node would also have the (i,j,k) subscript, for example the size of the $(i,j,k)^{\text{th}}$ cell in the x -direction would be notated as $\Delta x_{(i,j,k)}$. The notation is extended to the heat fluxes *across* the cell boundaries. The flux at the interface between the $(i-1,j,k)^{\text{th}}$ node and the $(i,j,k)^{\text{th}}$ node, in the direction *towards* the $(i,j,k)^{\text{th}}$ node (in the positive x -direction) would be $q_{(i-1,j,k) \rightarrow (i,j,k)}$. Generally the symbols $\rightarrow, \uparrow, \bullet$ indicate the values of fluxes in the positive x, y and z

directions respectively. The symbols $\leftarrow$, $\downarrow$, $\otimes$ will be used to indicate the values of fluxes in the negative x, y and z directions respectively. Finally the superscripts p and $p+1$, where $p = 0, 1, 2, \dots$ will represent the values of the state variables at the p^{th} and $(p+1)^{\text{th}}$ time steps when the time has values t_p and t_{p+1} respectively, where the size of each time step is denoted by $\Delta t_{p+1} = t_{p+1} - t_p$, and where it is assumed that $t_0 = 0$.

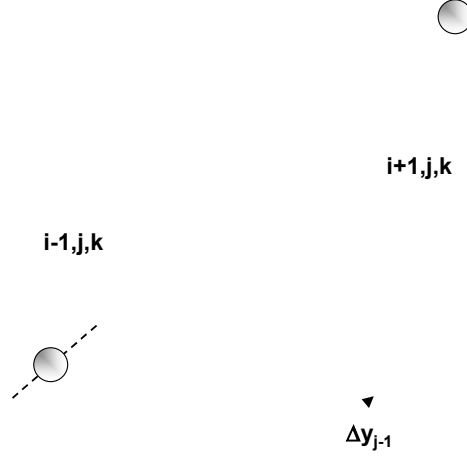


Fig. I.1: Three-dimensional node and cell structure.

At the $p+1^{\text{th}}$ time step, let $\tilde{E}_{(i,j,k)}^{p+1}$ be the rate of thermal energy accumulated and stored in the $(i,j,k)^{\text{th}}$ cell, $\vec{E}_{(i,j,k)}^{p+1}$ be the rate of thermal energy entering and leaving the cell due to temperature across the surface from neighbouring cells and $\hat{E}_{(i,j,k)}^{p+1}$ be the rate of thermal energy generated within cell. For the $(i,j,k)^{\text{th}}$ cell at the $p+1^{\text{th}}$ time step, the conservation of energy may be written (corresponding to the form A.3) as

$$\tilde{E}_{(i,j,k)}^{p+1} = \vec{E}_{(i,j,k)}^{p+1} + \hat{E}_{(i,j,k)}^{p+1}. \quad (\text{A.11})$$

In A.11, the energy transfer rate *into* the $(i,j,k)^{\text{th}}$ cell from the surrounding cells (Fig. I.1) is obtained using A.10 so that

$$\begin{aligned} \vec{S}_{(i,j,k)}^{p+1} = & (q_{(i-1,j,k) \rightarrow (i,j,k)}^{p+1} + q_{(i,j,k) \leftarrow (i+1,j,k)}^{p+1}) \Delta y \Delta z + \\ & (q_{(i,j-1,k) \uparrow (i,j,k)}^{p+1} + q_{(i,j,k) \downarrow (i,j+1,k)}^{p+1}) \Delta x \Delta z + \\ & (q_{(i,j,k-1) \bullet (i,j,k)}^{p+1} + q_{(i,j,k) \otimes (i,j,k+1)}^{p+1}) \Delta x \Delta y, \end{aligned} \quad (\text{A.12})$$

Using an approach where fluxes from neighbouring cells are defined in a direction into the $(i,j,k)^{\text{th}}$ cell is useful as it enables a reduction of the number of different equation forms needed for computation analysis. The rate of change of energy stored in the control volume is simply (see A.5)

$$\tilde{E}_{(i,j,k)}^{p+1} = \frac{\partial}{\partial t} (\rho c_v T) \Delta x \Delta y \Delta z. \quad (\text{A.13})$$

For a small time step Δt the thermal properties ρ and c_v are assumed to be constant, so the time differential of the temperature in A.13 can be approximated using finite differences, such that

$$\tilde{E}_{(i,j,k)}^{p+1} \cong \rho c_v \frac{(T_{(i,j,k)}^{p+1} - T_{(i,j,k)}^p)}{\Delta t^{p+1}} \Delta x \Delta y \Delta z. \quad (\text{A.14})$$

Inserting A.14 in A.11 and rearranging gives a finite difference representation of the temperature at a time period $p+1$

$$T_{(i,j,k)}^{p+1} = T_{(i,j,k)}^p + \frac{1}{\rho c_v} \left(\frac{\Delta t^{p+1}}{\Delta x \Delta y \Delta z} \right) (\tilde{E}_{(i,j,k)}^{p+1} + \hat{E}_{(i,j,k)}^{p+1}), \quad (\text{A.15})$$

where $\tilde{E}_{(i,j,k)}^{p+1}$ is calculated using A.12 from the temperatures of neighbouring cells, each of which must be derived taking account of the type of surrounding node.

1.2.3 Heat fluxes at the material cell interface

In this model, material cells are defined as cells that contain a homogeneous material for temperature to flow through. The nodes at the centre of these cells are referred to as material nodes. The boundary between two adjacent cells is referred to as a material cell interface. Heat fluxes at the interface of material cells can be estimated using Fourier's law where the flux between the material cells is proportional to the gradient between the temperatures. For a multi-material system where neighbouring material cells could have different properties, an effective thermal conductivity is to be calculated to ensure continuity of the heat fluxes at the cell interfaces.

It is assumed that the $(i,j,k)^{\text{th}}$ cell has different thermal conductivity rates along different principal axes x , y and z . Assume that thermal conductivity is uniform within each of the cell volumes and let the superscripts x , y and z represent cell conductivities in the x , y and z planes respectively. Continuity of flux across the interface between the $(i,j,k)^{\text{th}}$ cell and the $(i+1,j,k)^{\text{th}}$ cell requires the following equations to be satisfied

$$\lambda_{(i,j,k)|(i+1,j,k)} \frac{(T_{(i+1,j,k)} - T_{(i,j,k)})}{\Delta x_{(i+1,j,k)} + \Delta x_{(i,j,k)}} = \lambda_{(i+1,j,k)}^x \frac{(T_{(i+1,j,k)} - T_{(i,j,k)|(i+1,j,k)})}{\Delta x_{(i+1,j,k)}}, \quad (\text{A.16})$$

$$\lambda_{(i,j,k)|(i+1,j,k)} \frac{(T_{(i+1,j,k)} - T_{(i,j,k)})}{\Delta x_{(i+1,j,k)} + \Delta x_{(i,j,k)}} = \lambda_{(i,j,k)}^x \frac{(T_{(i,j,k)|(i+1,j,k)} - T_{(i,j,k)})}{\Delta x_{(i,j,k)}}, \quad (\text{A.17})$$

where $\lambda_{(i,j,k)|(i+1,j,k)}$ and $T_{(i,j,k)|(i+1,j,k)}$ are the effective thermal conductivity and temperature at the interface between the $(i,j,k)^{\text{th}}$ and $(i+1,j,k)^{\text{th}}$ cells as shown in Fig. I.2.

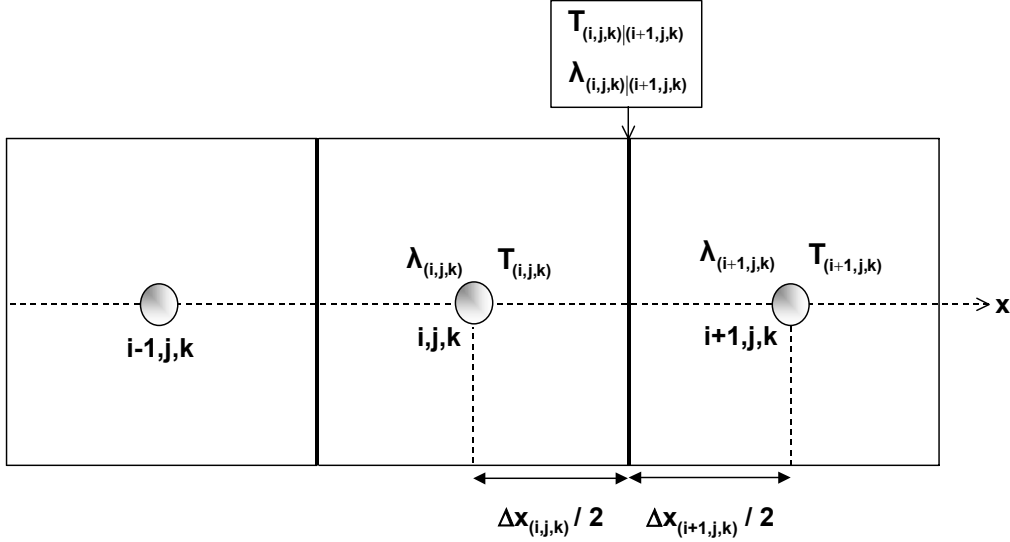


Fig. I.2. The effective thermal conductivity and temperature at the interface between the $(i,j,k)^{\text{th}}$ and $(i+1,j,k)^{\text{th}}$ cells

Eliminating $T_{(i,j,k)|(i+1,j,k)}$ from A.16 and A.17, and making $\lambda_{(i,j,k)|(i+1,j,k)}$ the subject of the equations leads to the result

$$\lambda_{(i,j,k)|(i+1,j,k)} = \frac{\lambda_{(i,j,k)}^x \lambda_{(i+1,j,k)}^x (\Delta x_{(i+1,j,k)} + \Delta x_{(i,j,k)})}{\lambda_{(i,j,k)}^x \Delta x_{(i+1,j,k)} + \lambda_{(i+1,j,k)}^x \Delta x_{(i,j,k)}} = \lambda_{(i+1,j,k)|(i,j,k)}. \quad (\text{A.18})$$

In general for a solid cell that is completely surrounded by solid cells of different material diffusivities (Fig. 2.1), the thermal conductivities are

$$\lambda_{(i,j,k)|(i\pm 1,j,k)} = \frac{\lambda_{(i,j,k)}^x \lambda_{(i\pm 1,j,k)}^x (\Delta x_{(i\pm 1,j,k)} + \Delta x_{(i,j,k)})}{\lambda_{(i,j,k)}^x \Delta x_{(i\pm 1,j,k)} + \lambda_{(i\pm 1,j,k)}^x \Delta x_{(i,j,k)}}, \quad (\text{A.19})$$

$$\lambda_{(i,j,k)|(i,j\pm 1,k)} = \frac{\lambda_{(i,j,k)}^y \lambda_{(i,j\pm 1,k)}^y (\Delta y_{(i,j\pm 1,k)} + \Delta y_{(i,j,k)})}{\lambda_{(i,j,k)}^y \Delta y_{(i,j\pm 1,k)} + \lambda_{(i,j\pm 1,k)}^y \Delta y_{(i,j,k)}}, \quad (\text{A.20})$$

$$\lambda_{(i,j,k)|(i,j,k\pm 1)} = \frac{\lambda_{(i,j,k)}^z \lambda_{(i,j,k\pm 1)}^z (\Delta z_{(i,j,k\pm 1)} + \Delta z_{(i,j,k)})}{\lambda_{(i,j,k)}^z \Delta z_{(i,j,k\pm 1)} + \lambda_{(i,j,k\pm 1)}^z \Delta z_{(i,j,k)}}. \quad (\text{A.21})$$

It should be noted that if neighbouring cells have the same value of thermal conductivity (as would be the case if they were material constants), then $\lambda_{(i,j,k)|(i\pm 1,j,k)} = \lambda^x$ where λ^x is the common value. Also, when a cell is located at an external boundary, the correct thermal conductivity arises from A.19-A.21 if the neighbouring (fictitious) cell is taken to have a zero thickness. Cells of zero thickness do in fact offer a convenient method of imposing a fixed temperature at external boundaries. Such cells partake in the incremental process of advancing time, but their temperature values are not updated.

The fluxes *into* the $(i,j,k)^{\text{th}}$ cell from the surrounding cells, for the $p+1^{\text{th}}$ time step, can be simply approximated using Fourier's law [6] to give

$$q_{(i-1,j,k) \rightarrow (i,j,k)}^{p+1} = \lambda_{(i,j,k)|(i-1,j,k)} \frac{2(T_{(i-1,j,k)}^p - T_{(i,j,k)}^p)}{\Delta x_{(i,j,k)} + \Delta x_{(i-1,j,k)}}, \quad (\text{A.22})$$

$$q_{(i,j,k) \leftarrow (i+1,j,k)}^{p+1} = \lambda_{(i,j,k)|(i+1,j,k)} \frac{2(T_{(i+1,j,k)}^p - T_{(i,j,k)}^p)}{\Delta x_{(i,j,k)} + \Delta x_{(i+1,j,k)}}, \quad (\text{A.23})$$

$$q_{(i,j-1,k) \uparrow (i,j,k)}^{p+1} = \lambda_{(i,j,k)|(i,j-1,k)} \frac{2(T_{(i,j-1,k)}^p - T_{(i,j,k)}^p)}{\Delta y_{(i,j,k)} + \Delta y_{(i,j-1,k)}}, \quad (\text{A.24})$$

$$q_{(i,j,k) \downarrow (i,j+1,k)}^{p+1} = \lambda_{(i,j,k)|(i,j+1,k)} \frac{2(T_{(i,j+1,k)}^p - T_{(i,j,k)}^p)}{\Delta x_{(i,j,k)} + \Delta x_{(i,j+1,k)}}, \quad (\text{A.25})$$

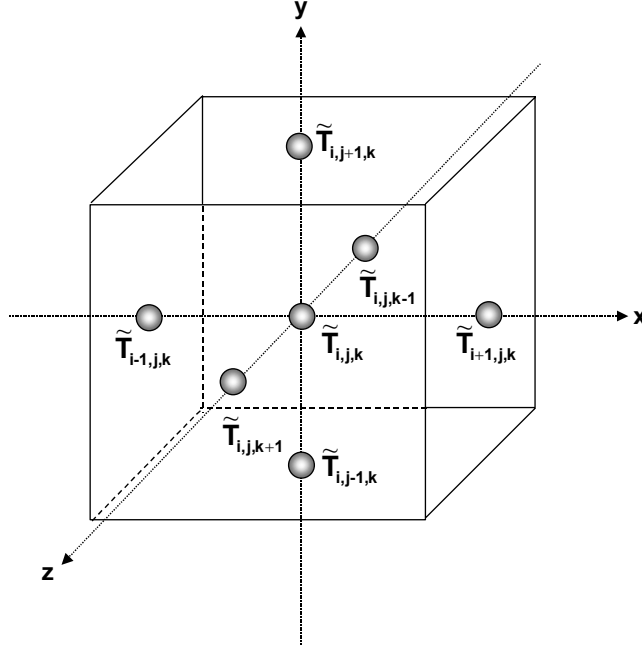
$$q_{(i,j,k-1) \bullet (i,j,k)}^{p+1} = \lambda_{(i,j,k)|(i,j,k-1)} \frac{2(T_{(i,j,k-1)}^p - T_{(i,j,k)}^p)}{\Delta z_{(i,j,k)} + \Delta z_{(i,j,k-1)}}, \quad (\text{A.26})$$

$$q_{(i,j,k) \otimes (i,j,k+1)}^{p+1} = \lambda_{(i,j,k)|(i,j,k+1)} \frac{2(T_{(i,j,k+1)}^p - T_{(i,j,k)}^p)}{\Delta x_{(i,j,k)} + \Delta x_{(i,j,k+1)}}. \quad (\text{A.27})$$

The fluxes in A.22-A.27 are inserted into A.12 to calculate the energy transfer rate *into* the $(i,j,k)^{\text{th}}$ cell. The advantage of this definition is that all temperature gradients are now of the same form, which is useful when designing efficient algorithms for computational analysis. The temperature over time may then be calculated in an incremental fashion using A.15.

2.4. Heat fluxes at the material cell boundary

When using the relations A.12 and A.15 to update the temperature distribution during its evolution, it is necessary to estimate the fluxes at the external boundary where a fixed temperature value has been imposed as a boundary condition. Boundary nodes, that can be associated with the nodes of additional boundary cells having zero thickness, are used to describe *fixed temperature* boundary conditions at the edge or boundary of a material cell. Values of temperatures at the boundary nodes, whose values are denoted by tilde, are used to calculate the temperature of a material cell in the vicinity of a boundary. It is useful to deal with boundary conditions of this type by considering a system having a single cell, so that all its boundaries are external surfaces at which a fixed temperature is imposed, as shown in Fig. I.3. The relations that will be derived from the single cell model will apply also to systems of interest that have many cells on a grid.

Fig. I.3. Temperatures at the boundaries of the i,j,k^{th} cell

Consider the material cell (i,j,k) with temperature $T_{(i,j,k)}^p$ at time p in the absence of surrounding material cells. The boundaries are the edges of the cell and are set as *fixed temperature* boundary conditions with temperatures $\tilde{T}_{(i+1,j,k)}^p$, $\tilde{T}_{(i-1,j,k)}^p$, $\tilde{T}_{(i,j+1,k)}^p$, $\tilde{T}_{(i,j-1,k)}^p$, $\tilde{T}_{(i,j,k+1)}^p$ and $\tilde{T}_{(i,j,k-1)}^p$, as shown in Fig. 2.3. The effective heat fluxes from the boundaries are simply

$$q_{(i-1,j,k) \rightarrow (i,j,k)}^{p+1} = \lambda_{(i,j,k)}^x \frac{2(\tilde{T}_{(i-1,j,k)}^p - T_{(i,j,k)}^p)}{\Delta x_{(i,j,k)}}, \quad (\text{A.28})$$

$$q_{(i,j,k) \leftarrow (i+1,j,k)}^{p+1} = \lambda_{(i,j,k)}^x \frac{2(\tilde{T}_{(i+1,j,k)}^p - T_{(i,j,k)}^p)}{\Delta x_{(i,j,k)}}, \quad (\text{A.29})$$

$$q_{(i,j-1,k) \uparrow (i,j,k)}^{p+1} = \lambda_{(i,j,k)}^y \frac{2(\tilde{T}_{(i,j-1,k)}^p - T_{(i,j,k)}^p)}{\Delta y_{(i,j,k)}}, \quad (\text{A.30})$$

$$q_{(i,j,k) \downarrow (i,j+1,k)}^{p+1} = \lambda_{(i,j,k)}^y \frac{2(\tilde{T}_{(i,j+1,k)}^p - T_{(i,j,k)}^p)}{\Delta y_{(i,j,k)}}, \quad (\text{A.31})$$

$$q_{(i,j,k-1) \bullet (i,j,k)}^{p+1} = \lambda_{(i,j,k)}^z \frac{2(\tilde{T}_{(i,j,k-1)}^p - T_{(i,j,k)}^p)}{\Delta z_{(i,j,k)}}, \quad (\text{A.32})$$

$$q_{(i,j,k) \otimes (i,j,k+1)}^{p+1} = \lambda_{(i,j,k)}^z \frac{2(\tilde{T}_{(i,j,k+1)}^p - T_{(i,j,k)}^p)}{\Delta z_{(i,j,k)}}. \quad (\text{A.33})$$

The results A.28-A.33 apply also at the external cells of a system having multiple cells. When a boundary is encountered, the heat fluxes in A.35-A.39 are inserted into A.12, as before, and the temperature over time may then be calculated in an

incremental fashion using A.19, together with values generated by the initial temperature distribution (usually uniform throughout the system). When considering updating the temperatures of internal cells, the relations A.22-A.27 involving effective thermal conductivities are used. It should be noted that the expressions in A.28-A.33) can be obtained from A.22-A.27 by setting the cells surrounding the $(i,j,k)^{\text{th}}$ to have zero cell size.

Transient solutions for the temperature at the $(i,j,k)^{\text{th}}$ cell can easily be constructed by using the appropriate equation for the heat fluxes depending on whether the edge of the cell is an interface with another material cell A.22-A.27 or a boundary with a fixed temperature A.28-A.33. When applying a *fixed heat flux* at the boundaries, the values for the imposed flux are substituted directly into A.12 at the appropriate boundary.

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