

# Assessment of moisture absorption in marine GRP laminates with aid of nuclear magnetic resonance imaging

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The diffusion of water in an isophthalic polyester glass reinforced composite laminate, typical of marine applications, has been studied through accelerated water uptake tests involving total immersion in seawater at 40 and 60°C. Gravimetric analysis has shown that at 40°C, a Fickian type diffusion is operative with a saturation level of 0.8% whereas at 60°C, a two stage Langmuir type diffusion is operative. The nuclear magnetic resonance technique has also been used in an attempt to image the diffused water and determine its position within the composite. This has revealed that the water concentrates on the fibre/matrix interface and the concentration there is twice that of bulk of the matrix. The diffusion process appears to be aided by 'wicking' along the fibre/matrix interface.

**Keywords:** Polyester, Laminates, Diffusion, Interface, NMR

## Introduction

Aqueous environments diffusing into the bulk of glass reinforced plastics (GRPs) can, over time, degrade the mechanical properties of the polymer matrix, the fibre/matrix interface and in some cases, the reinforcement itself.<sup>1-5</sup>

Fibre reinforced polymer composites comprise of three distinct phases (fibre, matrix and matrix/fibre bonding layer) which have considerably different physical and chemical properties. These phases are affected in different ways when water enters the material from the environment. The reinforcement is normally impervious to moisture. Water molecules sit at the surface where they form bonds of the type X-OH. This bond is acidic or basic depending on the molecule X of the surface and initiates a process of surface corrosion. This may produce corrosion pits on the surface and weaken the material. However, this damage has a negligible effect on the strength of the reinforcement.

Water is chemically very reactive because it has a polar molecule H-OH and dissociates readily giving a proton and a hydroxyl ion. When the moisture enters the bulk of the matrix, it reacts chemically with the polymer chain, saturates the intermolecular bonds and dissects the side branches of the polymer chain. These effects allow the chains to slide more freely over each other. In addition, the water molecules lubricate the sliding motion of the chains. As a result, the shear strength of the polymer decreases.

The breaking of the side chains impairs molecular packing and swelling occurs, which reduces the compressive strength. Moisture absorption also facilitates the stretching of intermolecular bonds, which reduces the elastic moduli.

It has long been hypothesised that diffused water in a composite material does not advance with a uniform profile, but accumulates in preferential sites or propagates along the reinforcement network. Conclusive proof to support these hypotheses does not exist to date. This work makes use of the nuclear magnetic resonance (NMR) imaging technique to assess the process of moisture absorption in a glass reinforced polymer composite, used typically in marine and offshore applications, subjected to accelerated aging by immersion in seawater at elevated temperatures.

The NMR technique was developed as a result of observations that many atomic nuclei interact with magnetic fields, and the strength of this interaction varies between the nuclei of different isotopes and even between different nuclei (of the same type) within a molecule. The first practical applications of NMR were made in the medical field in the early 1970s based on the work of Damadian<sup>66</sup> who observed a variability in nuclear magnetic relaxation times of the hydrogen nuclei in different cellular environments and Lauterbur<sup>77</sup> who demonstrated that the spatial distribution of hydrogen containing fluids in an object can be mapped out by NMR.

Since then, many advances have been made in the field of NMR imaging (also known as MRI) which led to uses outside the medical field such as studies of the structure of molecules, dynamic or chemical changes in molecules, or the distribution of atoms throughout an object.

Generally, the nuclei imaged by NMR are mobile protons (hydrogen nuclei), as in water, and also protons

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in rigid structures, although many other nuclei can be imaged. An NMR image can therefore be thought of as a two-, or more, dimensional representation of the density of nuclei throughout an object. Although, superficially, an NMR image may resemble an optical image, the means of acquiring it and the data it produces are completely unrelated. In the late 1970s, Gummerson *et al.*<sup>8</sup> demonstrated the use of NMR to follow the dynamics of water diffusion in several porous inorganic materials. NMR imaging was therefore thought to be a very useful tool in determining the position of diffused water molecules within polymer resins. The recent development of specialist scanners with sufficient resolution has raised the possibility of imaging water molecules in composite samples. Since hydrogen atoms belonging to the rigid polymer matrix have extremely short nuclear magnetic transverse relaxation times, they could be removed from the observed NMR image so that an image displaying only the diffused water molecules could be produced. The position of water in the composite and its concentration profile could therefore be determined.

## Experimental

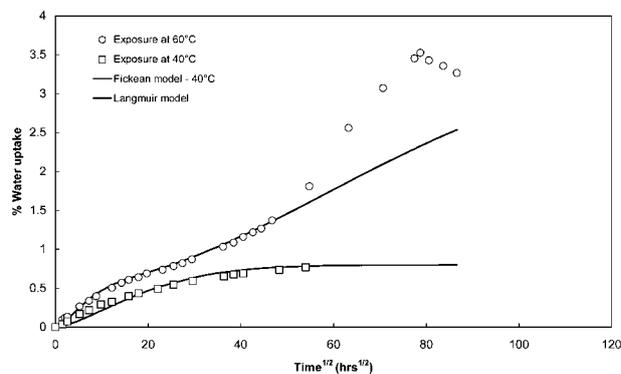
A glass reinforced isophthalic polyester laminate, typical of marine applications, was investigated in the present study. The composite was made up of a Crystic 489PA polymer matrix (supplied by Scott Bader) and YO530 (780 g m<sup>-2</sup>) woven roving glass reinforcement (0/90°, by Fothergill). There was no special treatment of the glass fibre surface. The laminate was made up of 9 plies of glass reinforcement and was manufactured by hand lay-up. The volume fraction  $V_f$  was ~0.55 wt-%. The average thickness of laminate panel was 7 mm.

Moisture absorption was studied by accelerated water uptake tests involving immersion of small coupons in seawater maintained at elevated temperatures of 40 and 60°C for a period of up to 10 000 h (416 days). Gravimetric analysis was carried out to determine the percentage water uptake over time and calculate the diffusion coefficients at the two immersion temperatures.

Small coupons were removed at certain time intervals from the conditioning tanks and placed in the NMR scanner to image the position of the diffused water. NMR images were obtained using a Bruker DPX300-Avance spectrometer, resonating at 300 MHz fitted with a Bruker microimaging accessory and using a 25 mm resonator. Data were acquired using a single point imaging (SPI) pulse sequence and processed using the Paravision suite of MR processing software supplied by Bruker BioSpin.

A 'dry' sample (coupon placed in an oven at 60°C for three days to remove any moisture present) was also placed in the NMR scanner for calibration, i.e. to eliminate imaging of hydrogen nuclei from sources other than the diffused water.

The duration of each NMR scan was between 24 and 36 h. Because undoubtedly, there would be moisture loss by water diffusion out of the samples during the scanning period, the samples were wiped dry and wrapped in polythene film as soon as they were removed from the immersion tank. The samples remained sealed in the polythene film for the duration of the NMR scans.



1 Water uptake (%) with respect to time for isophthalic polyester glass reinforced composite immersed in seawater at 40 and 60°C

## Results

The gravimetric results are shown in Fig. 1 where a difference in the water uptake behaviour of the GRP for the two immersion temperatures is evident. At 40°C, the water uptake increases linearly with the square root of the immersion time and then, levels off at ~0.8% water content, i.e. no further water diffusion takes place with increasing immersion time.

Immersion at 60°C on the other hand resulted in a three stage water uptake behaviour. At first, the water uptake increased linearly with respect to the square root of time appearing to level off at ~0.8% water content but then, a second stage of water absorption was observed up to ~1.4% water content. Following that, a third stage of water absorption was observed peaking at 3.5% water content. Further immersion beyond this time led to mass loss being observed, indicative of severe damage (decomposition) taking place in the composite.

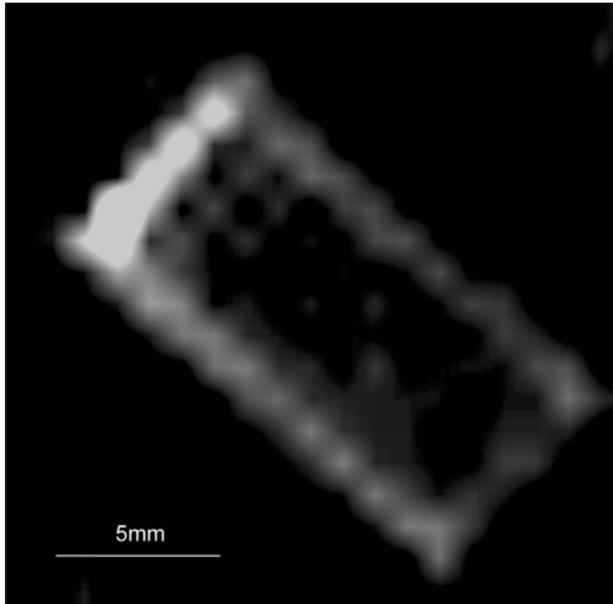
Optical inspection of specimens removed from the 60°C conditioning tanks during the third stage of water absorption revealed that these contained microcracks, suggesting that the rapid weight gain was not due to diffusion but due to water ingress through capillary action.

Figures 2–4 are images of NMR scans carried out on composite samples exposed in seawater at 40 and 60°C for up to ~7000 h. These images show the distribution of the diffused molecular water, where the brightness of the image is a measure of the molecular water concentration (the brighter the image, the higher the concentration). Figures 5 and 6 are images of physical (liquid) water which has penetrated deep into the composite by capillary action through microcracks formed in the GRP after prolonged immersion at 60°C. The images show severe delamination and large voids within the material. It has to be noted that only physical (liquid) water is imaged in Figs. 5 and 6.

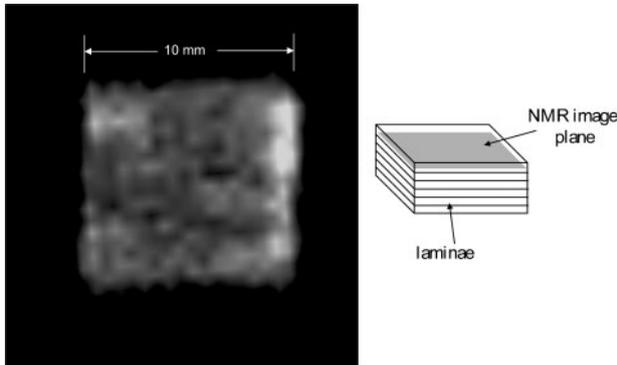
## Discussion

### Diffusion kinetics

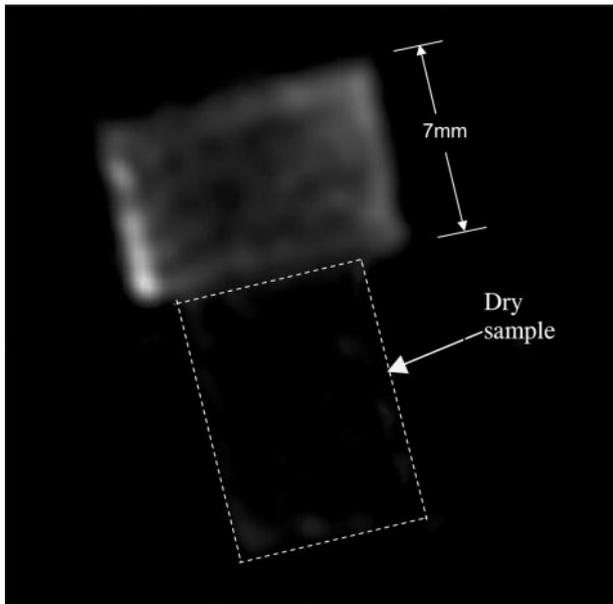
The gravimetric analysis results in Fig. 1 show that the weight of the material increases initially, in direct proportion to the square root of time and when the material is saturated, the curve levels out. This is typical of a Fickian diffusion, which suggests that the diffusion is caused by the water concentration gradient and is



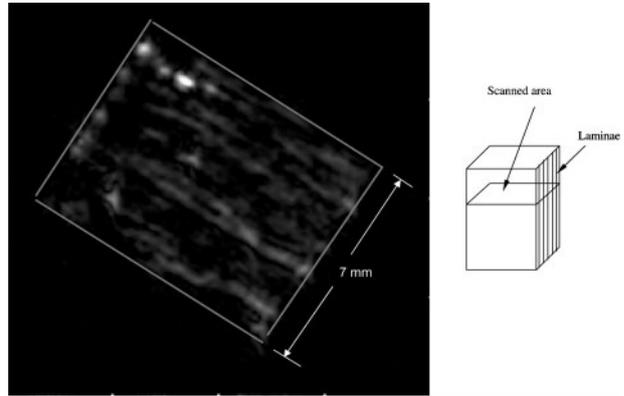
2 Nuclear magnetic resonance image of composite laminate exposed in seawater at 40°C for 1000 h



3 In plane NMR image, 0.7 mm below surface, of sample exposed in seawater at 40°C for 6000 h



4 Transverse NMR image of composite laminate samples exposed in seawater at 60°C for 7000 h (top) and dry (bottom)



5 Through thickness NMR image of 'liquid' water in UK laminate exposed at 60°C for 7000 h

described by the equation

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} \tag{1}$$

where  $c$  is the moisture concentration at distance  $x$ ,  $D_x$  is the mass diffusivity and  $t$  is the exposure time. The solution to equation (1) for an infinite plate was provided by Springer and Shen,<sup>9</sup> from which the diffusion coefficient could be obtained. For the GRP used in this work immersed at 40°C, this was determined as  $D_{40} = 1.1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ .

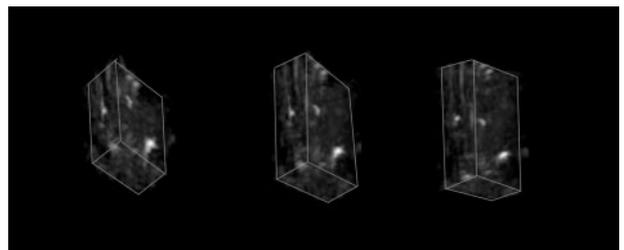
It has to be mentioned that a correction equation, to account for the finite size and unsealed edges of the specimens, has been used for the calculation of the diffusion coefficient. This expression is described as

$$D_x = D \left( 1 + \frac{l}{w} + \frac{l}{h} \right)^{-2} \tag{2}$$

where  $l$  is the specimen length,  $w$  is the specimen width and  $h$  is the specimen thickness.

Although Fick's law is widely accepted to describe water diffusion in polymer resins, it cannot be applied universally. Immersion at 60°C has shown a two stage water uptake behaviour (the observed third stage was determined not to be diffusion related) which has been observed in other systems.<sup>22</sup> Such behaviour can be described by the Langmuir model,<sup>10</sup> which assumes that the water does not enter the material freely but a number of water molecules become bonded to the resin (or become trapped within the polymer chain) and can no longer diffuse. The number of bonded and free molecules varies over time until equilibrium is reached. This is described by the following equations

$$D_x \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} + \frac{\partial c}{\partial t} \tag{3}$$



6 Rotated NMR image of sample in Fig. 5, exposed in seawater at 60°C for 7000 h

$$\frac{\partial c}{\partial t} = C\gamma - c\beta \quad (4)$$

$$\gamma C_{\infty}(H) = \beta c_{\infty}(H) \quad (5)$$

where  $C$  and  $c$  are the bonded and free water concentrations respectively,  $c_{\infty}$  and  $C_{\infty}$  are the free and bonded water concentrations at saturation,  $\beta$  is the probability of bonding (the concentration of free molecules greater than the concentration of bonded molecules) per unit time,  $\gamma$  is the probability of release (the concentration of free molecules lower than the concentration of bonded molecules) per unit time and  $H$  is the relative humidity. It is evident that if the quantity of bonded water can be neglected, then the model becomes equivalent to Fick's law.

Analysis of the data in Fig. 1 for the 60°C immersion tests using the Langmuir model resulted in a diffusion coefficient of  $D_{60} = 5.5 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ .

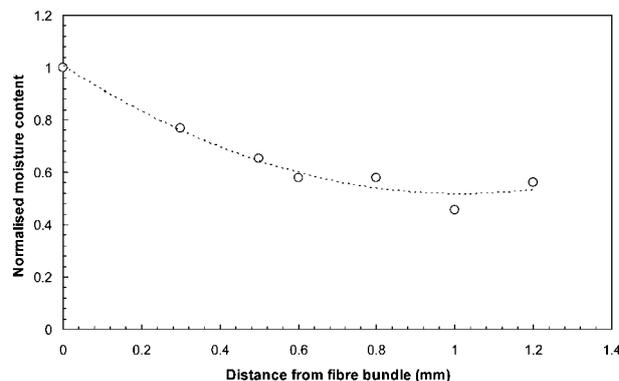
The diffusion coefficients determined in this work, for both immersion temperatures, are very close to values quoted in the literature for other isophthalic polyester resins.<sup>2</sup>

### Nuclear magnetic resonance imaging

It is clear from the NMR images that the water does not diffuse uniformly into the material but concentrates along the fibre/reinforcement interface, which is widely recognised as playing the most important role in the performance of composites. The bonding layer, which is present as a thin film, is extremely reactive because of its large surface area per unit volume and therefore, would be a preferential site for water molecules. The moisture concentration is expected to further increase at the interface because of 'wicking' effects. For these reasons, the degradation of the interfacial bond mechanical properties is more rapid than the other two phases (matrix and fibre).

Because the NMR image contrast is very dependent on the rates at which nuclei, excited in the experiment, relax to equilibrium, the intensities of the different proton types are related to their real density (concentration). Figures 2–4 confirm that the concentration of water at the matrix/fibre interface is much higher (higher intensity – brighter image) than that of the bulk of the resin. Figure 2 also appears to confirm that a 'wicking' process is operative as it shows the water tracing the reinforcement geometry. This behaviour is similar in both the 40°C and 60°C immersed samples. Detailed analysis of the variation of proton intensities at a region near a fibre bundle (Fig. 7) has shown that the ratio of water concentration between the matrix/fibre interface and the bulk of the matrix was ~2:1. The increase in water concentration at the far right of the graph is due to the influence from the adjacent fibre bundle.

Prolonged exposure at 60°C (i.e. >6500 h) has resulted in microcracking of the resin and absorption of water through capillary action. Figure 5 is an image of 'liquid' water present in the sample exposed at 60°C for 7000 h. Severe cracking is evident from this image, which shows the trace of the liquid water penetrating deep into the GRP through capillary action. Figure 6 is a rotated image of the same sample showing extensive delamination and large voids within the sample, the latter being evidence of material loss.



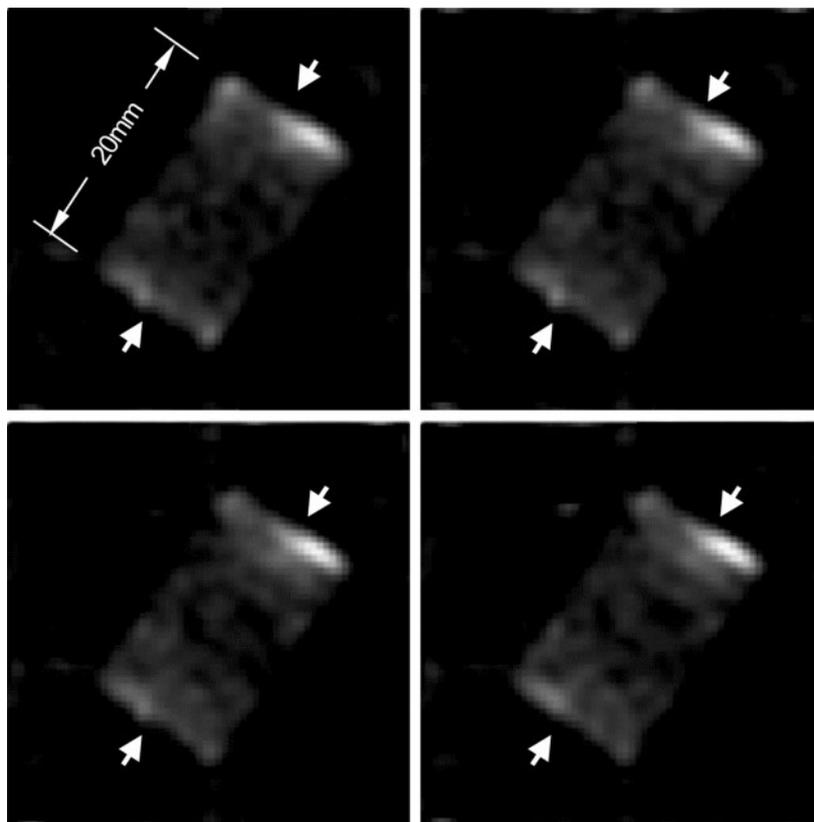
7 Variation of water concentration in composite laminate sample exposed in seawater at 40°C for 8000 h

Since the samples used for the NMR scans did not have the edges sealed from water ingress, it was thought that this might have encouraged 'wicking' by allowing water to diffuse through the ends of the exposed fibres, thus obscuring the mechanism by which the water diffuses into the material. A sample was therefore extracted from the centre of a 300 × 300 × 20 mm panel immersed in seawater at 40°C for 8000 h. Figure 9 (four transverse scans ~1.0 mm apart) shows that even in this case, the water is still attracted to the matrix fibre interface and diffuses preferentially along it (the arrows indicate the face exposed to the environment).

It was mentioned previously that the intensities of the different proton types are related to their real density (concentration). This is not strictly true because in many cases, they are not necessarily in exact correspondence. Some nuclei, very tightly bound within a matrix, may be very difficult to image or may not be observable at all. Although this makes exact quantification very difficult, it also opens an avenue to separate nuclei in different environments, e.g. 'bound' and 'free'.

Molecular water absorbed in the polymer matrix may exist either in the 'free' or 'bonded' state. In the current work, the Langmuir type diffusion observed for the samples immersed at 60°C indicates that this may be the case here. A sample of GRP exposed for 6000 h at 60°C was removed from the conditioning tank and allowed to dry in lab air at 22°C over a period of three days. During this time, the sample was placed periodically in the NMR scanner and measurements of the proton densities (concentration) were taken. Figure 8 is the plot of the relative proton densities of the sample for two slices ~5 mm apart, with respect to drying time. The result shows that there was a reduction in proton density, followed by a levelling off to an almost constant proton density over time, indicating that no more water molecules diffused out of the composite beyond the 70 h. This result could be an indication of the presence of two phases of water being present, i.e. 'free' water (molecules which are mobile within the polymer chain and can easily diffuse in and out) and 'bound' water (molecular water which has been trapped by the polymer chain).

On the other hand, this is not an absolute proof because there is uncertainty whether the remaining water will also escape after longer drying times or at a higher drying temperature. Clearly, further work is needed in this area.



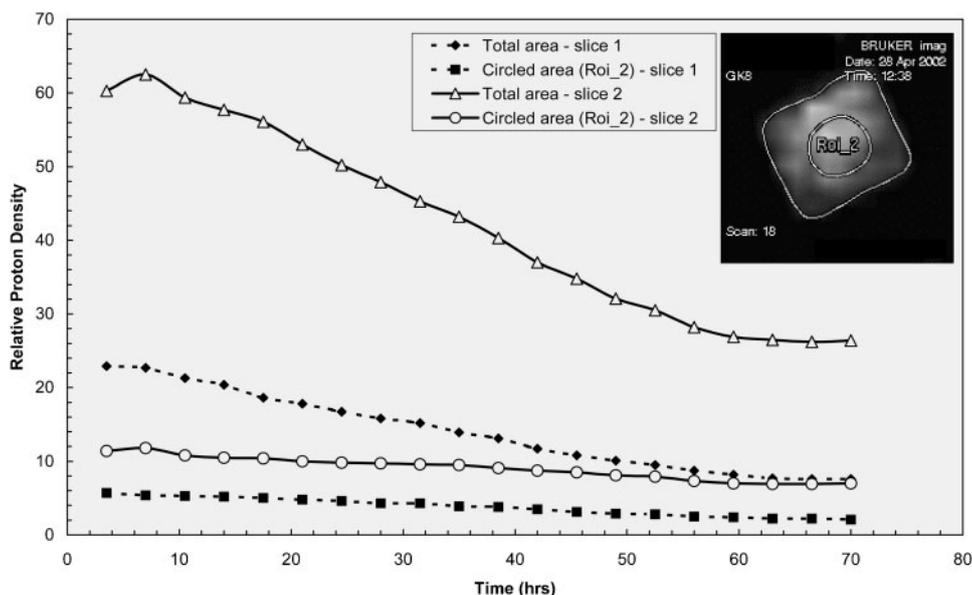
8 Nuclear magnetic resonance images of through thickness sections of 20 mm thick GRP laminate exposed in seawater at 40°C for 8000 h

### Conclusions

Accelerated water absorption tests on an isophthalic polyester glass reinforced composite by immersion in seawater at 40 and 60°C have been carried out and the diffusion coefficients have been determined.

Aging tests at 40°C indicate a Fickian type water absorption behaviour for the material whereas at 60°C, a two stage Langmuir type of diffusion takes place.

The NMR technique has been used to image the diffused water in the composite successfully. The NMR imaging has demonstrated that the diffused water concentrates at the matrix/reinforcement interface and the concentration of the diffused water is about three times higher there than the bulk of the resin. It has also been shown that the diffusion of water in the material is aided by ‘wicking’ along the interfacial bond region.



9 Plot of proton density v. time for drying laminate samples at 25°C in air, previously exposed in seawater for 6500 h at 60°C

The NMR technique is a useful tool for the study of water absorption in composite materials.

## Acknowledgements

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