THE LONG-TERM WATER ABSORPTION AND DESORPTION BEHAVIOUR OF CARBON-FIBRE / EPOXY COMPOSITES

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Abstract

Long term water absorption tests have been conducted on two different commercial epoxy resin systems along with carbon-fibre composites of one of the resins. Conditioning of samples in water and controlled humidity shows that there is an initial Fickian absorption, followed by a slower second stage that continues for at least 3.6 years. This second stage behaviour occurs in all materials, under all conditions and has a rate that is independent of the presence of fibres. Faster but incomplete drying is seen, along with faster re-absorption after drying. FTIR spectroscopy, optical microscopy and immersion trials in hexane have shown that the primary mechanism for the second stage is one of molecular relaxation, though some chemical degradation of the surface does occur.

1 Introduction

It is well known that composites can be affected by moisture ingress during their service life, leading to plasticisation of the resin and accompanying reductions in some properties. The most common method of accounting for the rate of moisture ingress has been to treat it as a Fickian diffusion process which reaches a fixed saturation. Despite this, it has been quite widely reported that composites based on epoxy resins and some BMI resins can show a slow steady increase in moisture content beyond the initial Fickian period [1-8]. While the behaviour has been widely observed, there is still some debate as to the true mechanism. The mechanisms previously proposed include microcracking [6, 8], chemical degradation [7], molecular relaxation [3, 5] and water becoming bound to specific sites [1]. This paper attempts to shed more light on the most likely mechanism for this behaviour.

2 Experimental measurements of long term absorption and desorption

2.1. Materials

Samples of two unfilled epoxy resins of approximate thickness 4 mm were supplied from separate materials manufacturers. The details of these are not revealed here due to commercial confidentiality, but both were the base resins for commercially available aerospace composites and are designated here as Resin A and Resin B. Carbon fibre / epoxy composite samples based on Resin A were also supplied by Airbus Operations Ltd as a UD and a ±45 layup sheet, both approximately 2mm thick. All materials had been cured using standard autoclave conditions. The volume fraction of the composites had been measured as 62% for the UD and 57% for the ±45 composites. Samples of approximate size 20 mm x 32 mm for the resins and 20 mm x 50 mm for the composites were cut using a diamond saw and dried at 70°C with silica desiccant until no further weight loss was observed and then stored at 23°C above desiccant.

2.2. Conditioning and drying

Samples were conditioned either by immersing in water at temperatures between 23°C and 80°C or in controlled humidity conditions between 45 and 100% RH at 70°C. Weight measurements were taken at regular but decreasing intervals using a balance with a resolution of 0.01mg. All surface water was removed from the sample prior to weighing. The percentage weight increase was plotted against √(time) with the expectation that the samples would show Fickian behaviour and so the first part of this graph would be linear. Initially, two or three samples of each material were conditioned in each environment and the majority of these samples were left to condition for long periods (up to 3.6 years reported here). After 1 year, some samples that had been conditioned at 70 or 80°C in water or 100% RH were removed for drying, which was conducted over silica desiccant either at 23°C or at 70°C. Weight measurements were taken at the intial fast rate once drying had started. After a further 100 days, some of the dried samples were re-immersed in water at 70°C, with fast weight recording re-started.

In addition to weight measurements, FTIR spectroscopy was conducted on some samples of both resins using a Perkin Elmer spectrometer operating in ATR mode. FTIR analysis was performed on both surfaces and cross-sections through the samples. Optical microscopy was also performed using a Reichart-Jung microscope on polished sections taken through the resin samples.

3 Experimental results

3.1. Moisture uptake

Figure 1 shows the weight gain behaviour for Resin A samples, under all exposure conditions. This shows that there is an initial region where the weight increases in a linear manner with √(time). This is then followed by an extended period where the weight continues to increase at a slower rate for the full duration of testing, though there is some suggestion that the samples immersed in water at 80°C are leveling off at a final saturation.
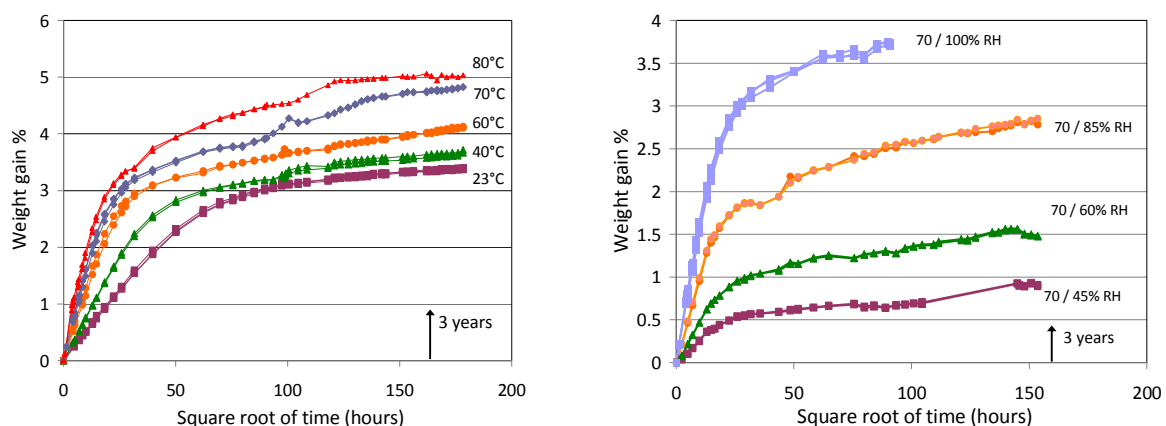

Figure 1. Long term moisture uptake for Resin A immersed in water at different temperatures (left) and at 70°C and different humidities (right).

Figure 2a shows moisture uptake for all the materials immersed in water at 60°C. These figures show that the slow long-term uptake continues for at least 3.6 years, that it is common to all exposure conditions and to both resins and the composites of resin A. It is possible to split the behaviour into a classic Fickian part with an initial linear variation of weight gain with √(time) before reaching 'Fickian saturation' and a long-term behaviour where the weight gain continues to increase with √(time). This is shown in Figure 2b.
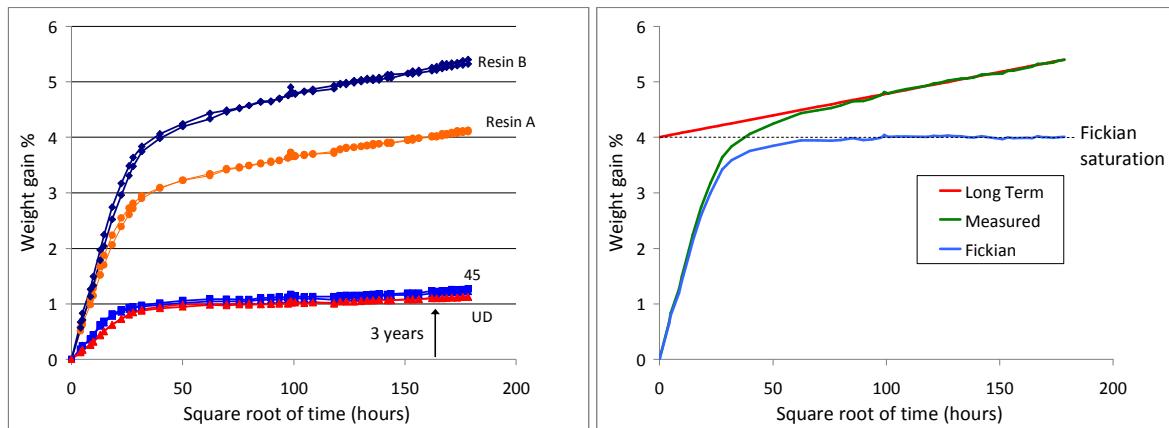

Figure 2. Long term moisture uptake for Resin A, Resin B and the two composite lay-ups of Resin A, immersed in water at 60°C (left) and how the long term and Fickian behaviour are separated (right).

The Fickian saturation (M_F) is plotted against temperature (for the water immersion tests) and against relative humidity (at 70°C) in Figure 3. This shows that the Fickian saturation only varies slightly with temperature, with a small increase, while the increase with relative humidity is more marked. If the Fickian saturation is scaled by the resin weight fraction, then the values for the Resin A and the composites are quite similar for each condition, showing that the Fickian saturation in the resin is not significantly affected by the fibres.
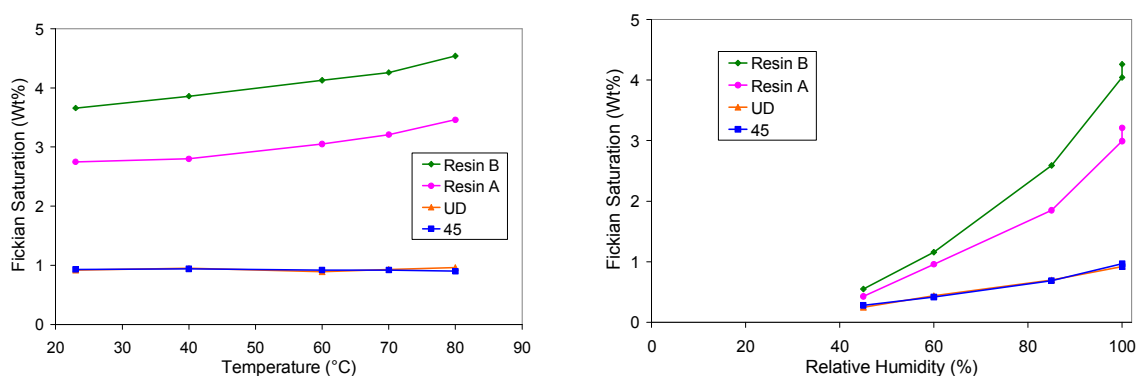

Figure 3. Fickian saturation values for all materials plotted against temperature (left) and against relative humidity (right).

The initial Fickian diffusivity D_F was calculated using the edge effect compensation factor proposed by Starink et al. [9] as formulated in equation 1 where g_{meas} is the initial gradient of the weight uptake / √(time) plot, M_F is the Fickian saturation, h is the sample thickness, W is the sample width and L is the sample length. This assumes D_F is independent of direction for the composites.

$$D_F = \frac{g_{meas}{}^2 h^2}{M_F{}^2 16\pi \left(1 + 0.54\frac{h}{W} + 0.54\frac{h}{L} + 0.33\frac{h^2}{WL}\right)^2} \qquad (1)$$

An Arrhenius plot of ln(D_F) versus 1/T is shown in Figure 4a. This shows that the composites have a significantly lower value of D_F than the resins. Bearing in mind that the primary diffusion direction is across the fibres and that the ±45 material has a higher resin volume fraction than the UD, it is not surprising that the UD has the lowest values of D_F. The activation energies for the different materials are all quite similar in the region of 42 kJ/mol.

It is also possible to define a 'pseudo-diffusion' (D_L) rate from the long-term behaviour. This was done by taking the gradient of the weight uptake vs √(time) graph for the second stage and dividing by the Fickian saturation. This is effectively the rate at which the saturation increases and assumes there is no influence of sample geometry. These values are plotted as ln(D_L) vs 1/T in Figure 4b. This shows that all the materials have similar values, confirming that there is no effect of sample size and also that the composite structure does not affect this long-term behaviour. The activation energy for this second stage behaviour is considerably lower at about 18 kJ/mol.
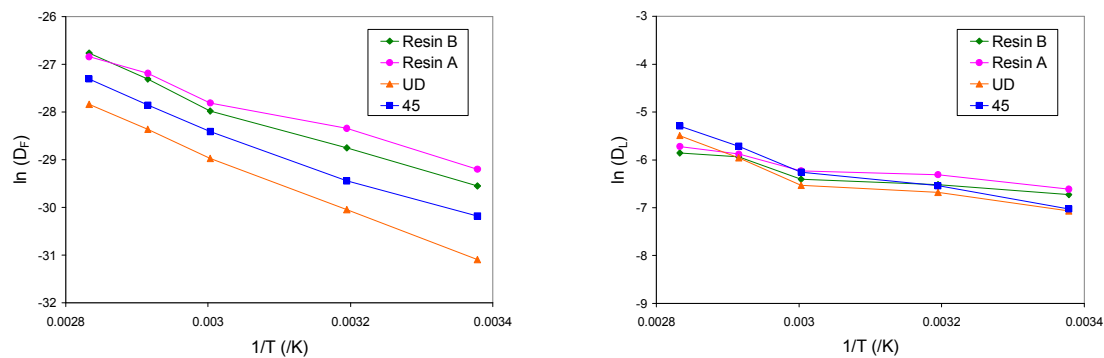

Figure 4. Arrhenius plots for the Fickian diffusion values (left) and the long-term behaviour (right). The y axes are scaled to give the same interval for comparison.

3.2. Drying and re-immersion
Some samples were removed from conditioning (in water at 70 or 80°C or 100% RH at 70°C) after 1 year and were dried above desiccant at 23°C or 70°C. The drying behaviour is shown in Figure 5a for Resin A where the fractional moisture remaining is plotted against the square root of the drying time. This shows that after an initially rapid drying (equivalent to the initial Fickian absorption), drying slows and continues at a slow rate for a long time. For the samples dried at 70°C, there is evidence that some water remains locked in the structure, typically about 10-15% of the original amount. Drying at 23°C seems to be approaching a similar limit. The original Fickian absorption equates to about 0.8 of the original moisture content, so these curves show that some of the long-term moisture is being removed by drying, but that some remains locked into the material.

After 100 days of drying, some of the samples were re-immersed in water at 70°C. The weight gain data for Resin A are plotted against √(time) in Figure 5b. If the re-immersion data are plotted with time starting from zero, then the behaviour is significantly different from the

original weight gain data. If instead the data are plotted against the time since original immersion, then the weight gain behaviour is more straightforward, with the samples quite rapidly re-joining the original weight gain curve. Similar behaviour was seen with all the materials.
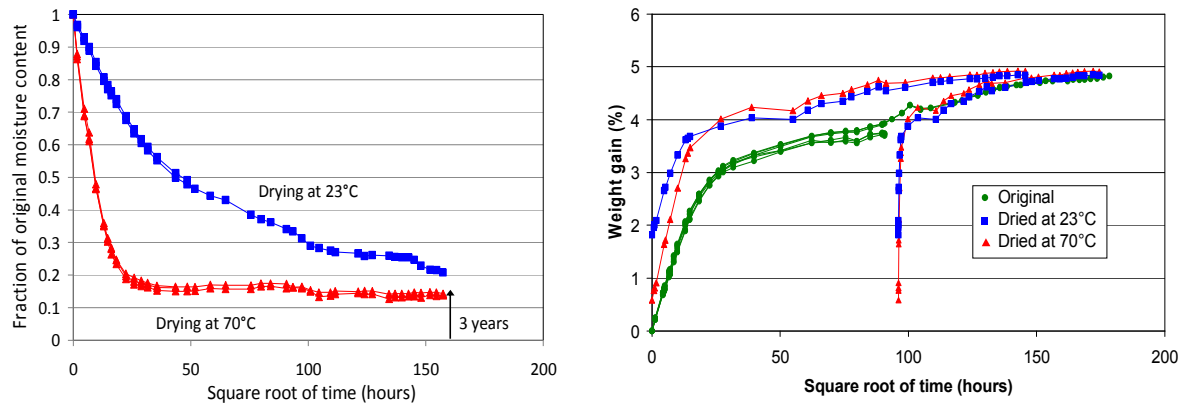

Figure 5. Drying (left) and re-immersion behaviour (right) for Resin A.

3.3. Diffusion coefficients

The diffusion coefficient for the Fickian component of drying and re-immersion can be calculated by using equation 2 for the derivation of g_{meas} and then using the same procedure as above. M is the weight gain at time t (relative to the dry sample weight); M_i is the initial weight gain at the start of drying or re-immersion and M_∞ is the saturation value, again taken by extrapolating the long-term behaviour to the start of the drying or re-immersion time.

$$g_{meas} = slope\left(\left[\frac{M-M_i}{M_\infty-M_i}\right]/\sqrt{t}\right) \qquad (2)$$

The values of D_F are shown for all materials for both drying and re-immersion in Figure 7. This shows that the diffusion rates are somewhat faster for both drying and re-immersion, which is similar behaviour to that seen previously [5].
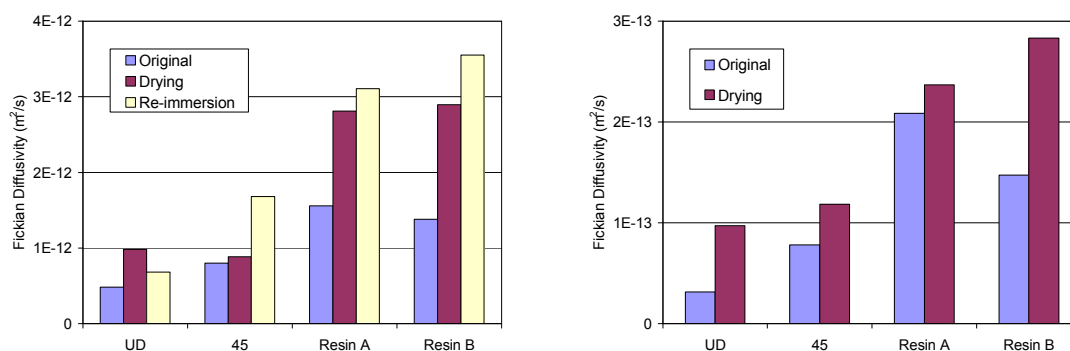

Figure 7. Fickian diffusivities for samples dried and re-immersed compared to the original conditioning. The left hand graph is for samples dried and re-immersed at 70°C; the right hand graph is for samples dried at 23°C.

4   Discussion of two-stage behaviour

It is clear that the slow long-term water absorption is a different process from the initial water absorption; the rate is independent of the composite structure (which slows down the Fickian diffusion due to geometric effects) and it exhibits a lower activation energy. These facts show that the second stage process is a gradual increase in the equilibrium water content for some reason. As it is significantly slower than the initial Fickian diffusion, ingress of additional water from the surface is not the rate-determining step. There are several possible mechanisms for this observed two-stage behaviour, most of which have been proposed before. These include:

- Development of microcracks which open to allow increased absorption.
- Slower diffusion of water molecules to bound sites (such as functional groups remaining from the curing reaction).
- Molecular relaxation of the resin.
- Slow absorption of water into toughening particles.
- Chemical degradation of the resin.

Further tests were conducted to gain more insight as to which mechanisms are most likely.

4.1. Additional experimental evidence

Optical microscopy was performed on sections of both resins and the composites after long-term water immersion at 80°C. No microcracks were seen in any of the samples. FTIR spectroscopy was also performed on both the surface and sections through long-term conditioned samples. There was no significant evidence of any chemical changes. In one or two samples, a slightly larger carbonyl peak at about 1740 cm^{-1} was seen, as shown in Figure 8, but this was not seen consistently.
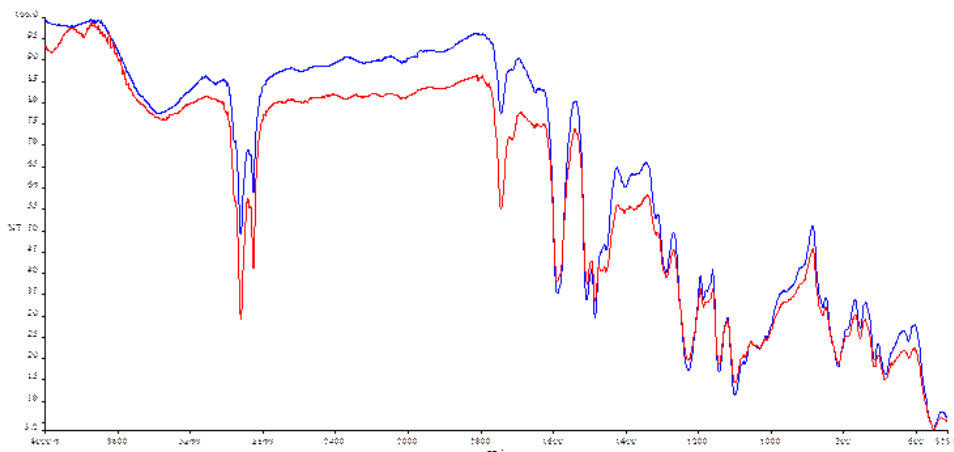

Figure 8. FTIR Spectroscopy results of sections through Resin A on the unconditioned state (blue) and after long term water exposure at 80°C (red).

Immersion and drying of Resin A was also undertaken using hexane at 23°C and 45°C to ascertain whether the same effects are seen in a non-polar liquid that would not be expected to react with the epoxy resin or to bind to active sites. The weight gain during immersion and weight loss during drying (at 23°C) are shown in Figure 9. These show the same type of two stage behaviour, with strong indications of an incomplete drying with about one tenth of the absorbed hexane remaining in the material.
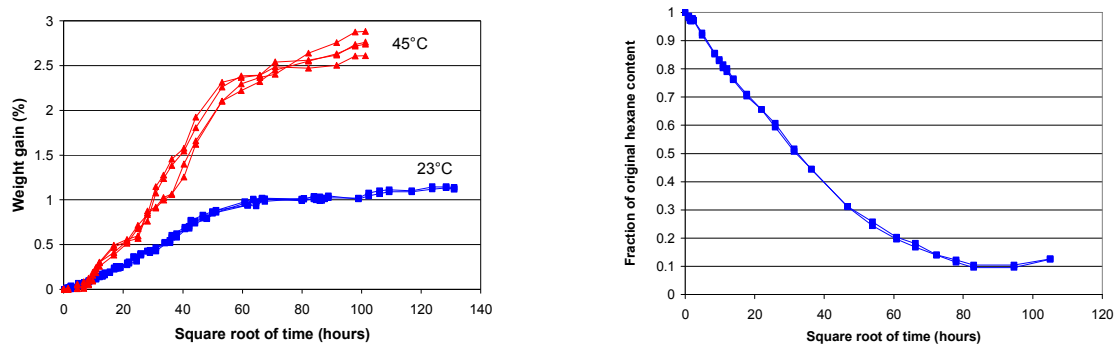
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Figure 9. Weight gain (left) and fractional drying (right) for samples of Resin A in hexane. .

4.2. Mechanism of long-term behaviour

Of the mechanisms suggested above, some can be eliminated reasonably easily. Microcrack formation is unlikely to be the cause as no microcracks were seen microscopically and there is no sensible mechanism by which microcracks would lead to incomplete drying. Slow diffusion into toughening particles can also be effectively eliminated as this long-term behaviour has been seen with epoxy systems containing no toughening particles [3]. The binding of water molecules to certain sites in the epoxy resin is more likely and would explain the incomplete drying, however it is hard to envisage how this mechanism would lead to higher diffusivity on drying and re-immersion. It would also not be expected with a non-polar liquid such as hexane.

Chemical degradation is supported by the observation that the plain resin samples showed some discolouration on the surface after long-term immersion at the higher temperatures. This discolouration was located near to the surface and did not penetrate into the centre of samples, even after 3.6 years exposure. Chemical degradation could also explain the higher diffusivity on drying and re-immersion (as the degradation may open up the epoxy chain structure), as well as accounting for the incomplete drying. To counter this, the FTIR spectroscopy did not point to any significant degradation; the activation energy seen for the second stage process is very low for a typical hydrolysis reaction and the degradation would not be expected to be seen with the hexane immersion. It is quite likely that there is some slight chemical degradation from the surface, probably involving reaction with oxygen dissolved in the water, but this is unlikely to be the main cause of the long-term behaviour.

The mechanism that most completely explains the behaviour is one of slow molecular relaxation allowing additional pockets of free volume for the water (or hexane) molecules to occupy. This process will not depend strongly on the presence or absence of fibres, though the composites show slightly less second-stage water absorption, which may indicate that the fibres provide some additional constraint that limits the relaxation. The relaxation of the network to a more open structure would lead to increased diffusivity on drying and re-immersion. The water (and hexane) remaining in the structure after drying could be explained by the relaxation process causing some liquid molecules to become trapped in molecular holes. The lower activation energy would fit with a secondary chain relaxation process. The fact that the long-term behaviour persists for more than 3.6 years would also fit with a relaxation process. Overall, the only feature that cannot be explained by this mechanism is the

surface discolouration which is most likely to be due to the chemical degradation described above.

5   Conclusions

Long-term conditioning of epoxy resins and carbon-fibre / epoxy resin composites have shown that after an initial Fickian behaviour, there is a slow long-term increase in weight which is common to all the materials studied, under all exposure conditions and persists for at least 3.6 years. This long-term behaviour is attributed to a continued increase in the equilibrium saturation. Analysis of the rate of this increase has shown that it is independent of the presence of carbon fibres and that it does increase with temperature but with quite a low activation energy. Samples dried after conditioning showed a faster initial diffusivity during drying, followed by a slower second stage with some moisture remaining locked into the material even after almost 3 years of drying. Re-immersion after drying showed slightly faster diffusivities and a re-establishment of the slow long-term behaviour. Optical microscopy did not show the presence of any microcracks and FTIR spectroscopy did not show any significant signs of chemical degradation. Immersion and drying trials with one of the resins in hexane showed similar behaviour. It can be concluded from the results that molecular relaxation is the main mechanism for the long-term behaviour, though some surface oxidation was also observed.

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