

THE LONG TERM EFFECTS OF WATER ABSORPTION, DESORPTION AND RE-ABSORPTION IN CARBON-FIBRE / EPOXY COMPOSITES

Ebelechukwu P. Otaluka^{*}, Cris Arnold[†], Sue Alston[†]

^{*}Materials Research Centre, College of Engineering, Swansea University, UK
SA2 8PP
605837@swansea.ac.uk

[†]Materials Research Centre, College of Engineering, Swansea University, UK
SA2 8PP
j.c.arnold@swansea.ac.uk, s.alston@swansea.ac.uk

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Summary: *Water absorption and desorption in polymer composites is important for long term performance, especially in outdoor applications. The epoxy and BMI resins used in many composites absorb water which leads to resin softening, swelling and loss of mechanical performance. At longer times and higher temperatures absorbed moisture can induce degradation in the polymer. To predict this effect, better understanding of the absorption behaviour of water is needed, especially over long times. It is well established for these resin systems that there is a continued slow increase in water content with time, beyond the initial Fickian behaviour. Various mechanisms for this have been proposed including molecular relaxation, chemical degradation and a Langmuir diffusion mechanism. This paper presents new information on this area for carbon fibre / epoxy composites utilising some test samples that had been previously conditioned for long times (up to five years) in water and humid environments.*

Long term water absorption, desorption and re-absorption tests have been carried out on unidirectional and $\pm 45^\circ$ carbon-fibre reinforced epoxy composites. Samples had been previously exposed to various cycles of conditioning, drying, then re-conditioning over a period of five years. Drying and reconditioning cycles were then carried out over a further period of a year. The slow continued increase in water content was evident over the whole time-range. Faster re-absorption was observed after drying with samples attaining equilibrium within a short time and showing a Fickian response. Dynamic mechanical tests were conducted to determine the effects of moisture on the glass transition temperature (T_g) and molecular relaxation of the material. Investigations revealed that the T_g values of the re-immersed samples were lower both in the UD and $\pm 45^\circ$ materials. Annealing was performed at 180°C to assess the influence of annealing on the effects of water absorption and a decrease in the height of the peak was seen when compared to those subjected to absorption only. The T_g values correlated quite well with the water content, though for some

long-term tests, a second relaxation peak developed as a result of molecular changes during conditioning. There was no significant change seen with annealing the samples after drying or before re-immersion. A post peak plateau appeared at about 180°C, and FTIR spectroscopy and microscopy have suggested that this and the depression in the glass transition temperature were caused by some chemical degradation and plasticizing effect. From the results, it seems that both molecular relaxation and some chemical degradation at higher temperatures play a role and that the slow increase in water content continues for at least five years. There is a need for these to be included in any design analysis or modelling of the effects of water on long term composite performance.

1 INTRODUCTION

Polymer composites are gaining wide use in aerospace applications due to their excellent performance characteristics such as high strength and high stiffness at low weight [1]. These composites are usually exposed to a range of environmental conditions, therefore the determination of the mechanism of liquid diffusion, degradation mechanism and level of performance retention are critical for designers. The epoxy resins often used have a high affinity for moisture and so absorb moisture from the atmosphere quite quickly at high temperatures which over time can cause the polymer to lose some of its properties. Moreover, water molecules can migrate into the polymer matrix even at room temperature and alter their physical properties. It is well established that epoxy resins do absorb a significant amount of water which leads to swelling, plasticisation and loss of mechanical performance with the matrix dominated properties being mostly affected [2], [3], [4], [5]. A Fickian diffusion process is commonly used to determine the rate of moisture uptake which reaches a fixed saturation level. Notwithstanding, composites based on epoxy and BMI resins can show a slow continuous increase in moisture content beyond the initial Fickian behaviour [3], [6], [7].

In this paper, moisture absorption, desorption and re-absorption effects on unidirectional carbon fibre / epoxy composites have been studied by hygrothermal ageing. The effect of moisture on the mechanical properties of the composites has been studied by dynamic mechanical analysis, for the saturated, desorbed and re-saturated samples with all conditioning at 70°C.

2 EXPERIMENTAL MEASUREMENTS

2.1 Materials and conditioning

The materials used in this study were commercial unidirectional and ± 45 carbon fibre / epoxy composites produced using standard autoclave processing into sheets nominally 2mm thick with a unidirectional and ± 45 symmetrical lay-up cured in an autoclave. The volume fraction of the composites was measured to be 62% and 57% for the UD and ± 45 composite respectively. Samples used for the tests had originally been prepared as follows: firstly, samples were sectioned to 20mm x 50mm using a diamond saw, and then dried at 70°C in an oven until no further weight loss was observed.

This was followed by conditioning some samples (labelled a samples) at 70°C/100%rh for a year. These were then removed and dried over a silica desiccant at either 23°C or 70°C. The drying was conducted for a period of three months before re-immersion in water at 70°C.

Long term water re-absorption continued for 3.8 years and so samples reached higher water content and are ageing. Before the conditioning considered in this study took place these samples were sectioned to 25mm x 10mm to create new samples labelled a45 and aud.

The second sets of samples were labelled B samples (± 45 and UD) and were initially conditioned either in water at 80°C or 100% RH at 70°C for one year. They were then dried over a silica desiccant at 70°C for four years. These samples were then also sectioned to 25mm x 10mm to create B45 and BUD samples, which were therefore in the dry but aged state. All weight measurements were carried out using a balance with 0.01mg resolution at regular but decreasing intervals. All surface water was removed with clean tissue paper prior to weighing.

The following further long term conditioning was then performed on the samples. The A45 and AUD samples (after 3.8 years of re-immersion) were dried again over a silica desiccant at 70°C. After 84 days, the dried samples were re-immersed in water at 70°C and weight uptake was monitored for another 9 months. Samples B45 and BUD (which had been drying over a desiccant for 4 years in a 70°C oven) were re-immersed in water at the same temperature.

Weight measurements were taken at an initial faster rate when each re-conditioning was commenced, followed by an increasing time interval. The percentage weight increase was plotted against square root of time with the sample showing Fickian behaviour at the initial stage. The samples were found to attain saturation level within a short time.

Additional tests carried out included annealing some samples at 180°C for two hours at various points in the conditioning process. DMA tests were conducted on some samples using a Perkin Elmer DMA 8000 operating in a single cantilever mode. The temperature was scanned from room temperature to 220°C set at a heating rate of 10°C/min and measurements taken at 1Hz. FTIR spectroscopy was performed on unreinforced epoxy resin using a Perkin Elmer spectrometer operating in ATR mode. Annealing performed on some of the samples is shown in table 1.

| Sample conditioning (for both UD and ± 45 samples) | | | | | | | |
|--|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| A1,2 | A3,4 | A5,6 | A7,8 | B1,2 | B3,4 | B5,6 | B7,8 |
| Dry | Dry | Dry | Dry | DMA | Immerse | Anneal | Anneal |
| DMA | Immerse | Anneal | Anneal | | DMA | DMA | Immerse |
| | DMA | DMA | Immerse | | | | DMA |
| | | | DMA | | | | |

Table 1 Conditioning summary for both UD and ± 45 samples.

3 RESULTS AND DISCUSSION

3.1 Desorption and re-absorption

The drying behaviour of the A45 and AUD samples is shown in Figures 1 and 2 where the % change in weight is plotted against square root of time. This graph shows that there is an initial rapid drying which corresponds to the initial Fickian absorption after which drying slows and continues at a slow rate for a long time.

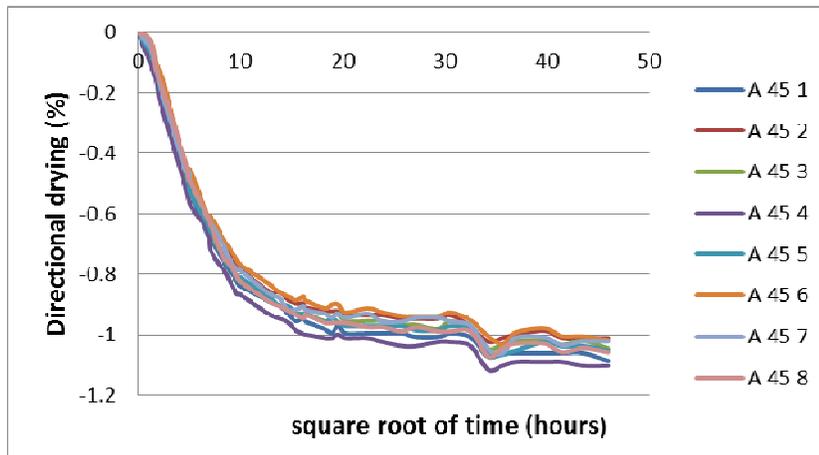


Figure 1 Drying behaviour of A45 samples

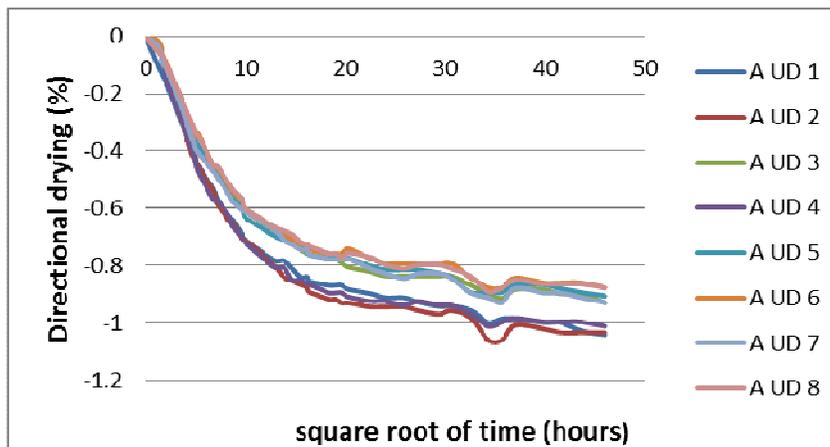


Figure 2 Drying behaviour of AUD samples

After drying for three months, some of the samples were re-immersed in water at 70°C. The weight gain curves for A45 and AUD are plotted against square root of time represented in Figure 3. Moisture uptake behaviour for the second re-immersion corresponds with Fickian behaviour for the initial part of weight gain although the curve was quite different between the ± 45 and UD samples. The ± 45 absorption curves lie on top of the graph which shows that the samples absorbed more water than the UD samples and likewise shows that

the slow long term moisture uptake continues for 9 months in both the ± 45 and UD.

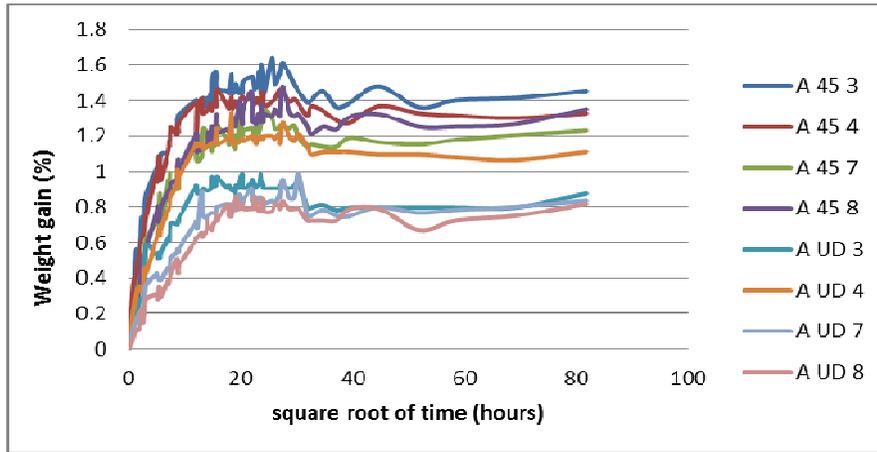


Figure 3 Re-absorption behaviour of the A (45 and UD) samples at 70°C

The re-absorption behaviour for the B samples plotted against the square root of time is shown in Figure 5 for both ± 45 and UD samples. Again, the absorption curves for the ± 45 samples lies above the graph while the UD's lie below except for one with higher moisture content. Generally, it had shown that the ± 45 samples absorbed more water than the UD which could be due to their lower fibre volume fraction.

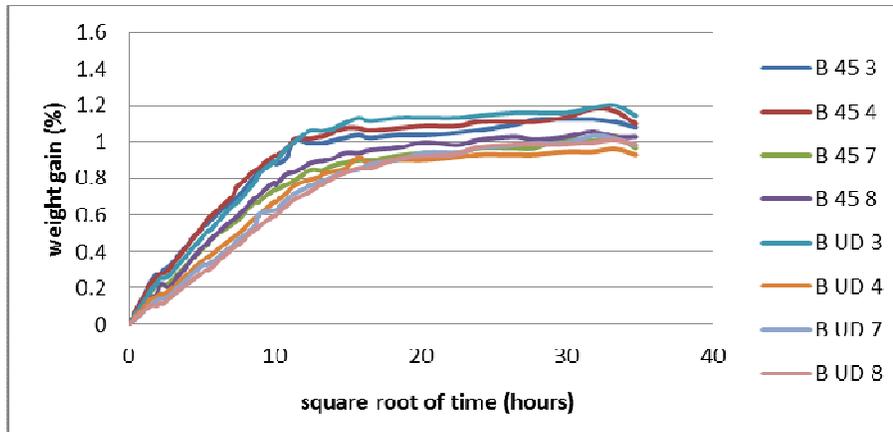


Figure 4 Re-absorption curves for B samples (45 and UD) at 70°C

3.2 Diffusion coefficients

The diffusion coefficient for the Fickian part of the re-immersion can be calculated using the Starink, Starink and Chambers equation, formulated for the z direction on the largest face: [8].

$$\frac{H}{\sqrt{t}} = \sqrt{\frac{16}{\pi}} \left[\frac{\sqrt{Ez}}{c} + \frac{0.54\sqrt{Dy}}{b} + \frac{0.54\sqrt{Dx}}{a} + \frac{0.23z}{ab} \sqrt{DyDxDz} \right] \quad (1)$$

$\frac{H}{\sqrt{t}}$ is equal to the gradient/ M_{∞} where M_{∞} is the equilibrium moisture content. Dz is the

diffusion coefficient across the fibres and c is the dimension of the samples across the fibres. D_y is the diffusion coefficient along the fibres and b is the dimensions of the samples through the layers and D_x and a is the diffusion coefficient through thickness and dimensions of the samples along the layers.

The diffusion coefficients of the ± 45 samples were determined and compared to that of the UD samples. The results obtained are represented in Figure 6. This shows that the ± 45 material has a higher value of diffusion coefficient than UD; this is because the ± 45 has easier diffusion pathways leading to higher diffusion rates a result which is being investigated further. It also indicates a big difference between the ± 45 and small variations between the UD.

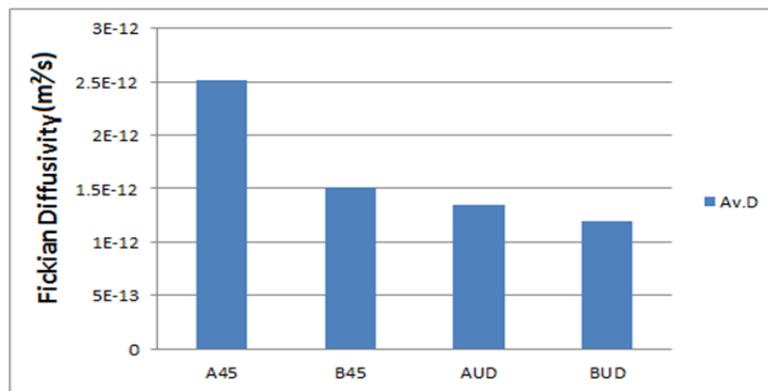


Figure 5 Comparison of average Fickian diffusivities for A and B samples.

3.3 Additional experimental work

Dynamic mechanical analysis was conducted to determine the effects of moisture on glass transition temperature of the materials. The result of the T_g obtained are clearly represented in Figures 6-9, showing data from A45, AUD, B45 and BUD respectively. Each graph compares annealed with unannealed samples, with the left hand graph showing samples after re-immersion, and the right hand graph samples before re-immersion. These evidently show that there was no significant change observed between the annealed samples and the unannealed samples. The ± 45 samples have slightly higher T_g values compared to the UD samples. The T_g values of the dried A samples are slightly lower than those of the dry B samples; since the A samples had previously been immersed for a much longer period this could be as a result of moisture which has caused the structure to be broken up and degradation to occur.

In the case of the UD re-immersed samples, a decrease in height of the peak was seen as a result of annealing. After immersion, two peaks can be clearly seen with the ± 45 samples and a post peak plateau observed with the UD samples, which is similar to behaviour seen previously [3]. This could be as a result of more crosslinking occurring during test, however, this effect is being investigated further. It can be seen in all samples that re-immersion leads to low glass transition temperatures at about 140°C and 150°C for B and A samples respectively. The high T_g values of about 200°C and 180°C were noticed with the annealed and unannealed B and A samples before immersion.

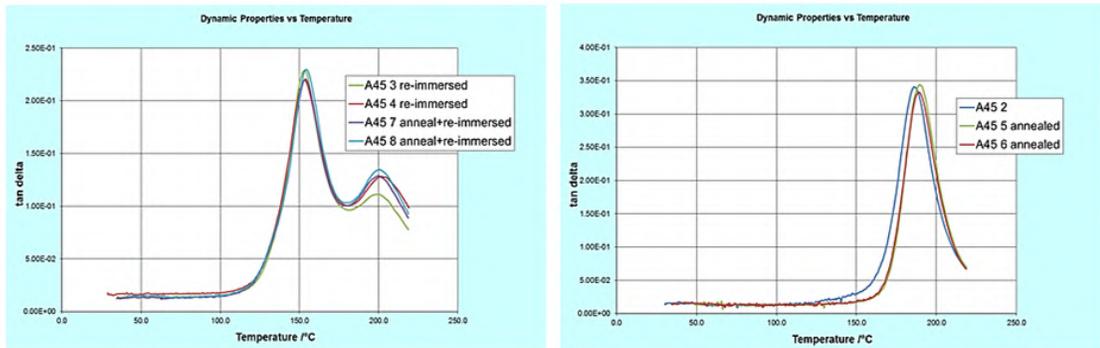


Figure 6 Tg value of unannealed and annealed A45 samples after re-immersion (left) and before re-immersion (right).

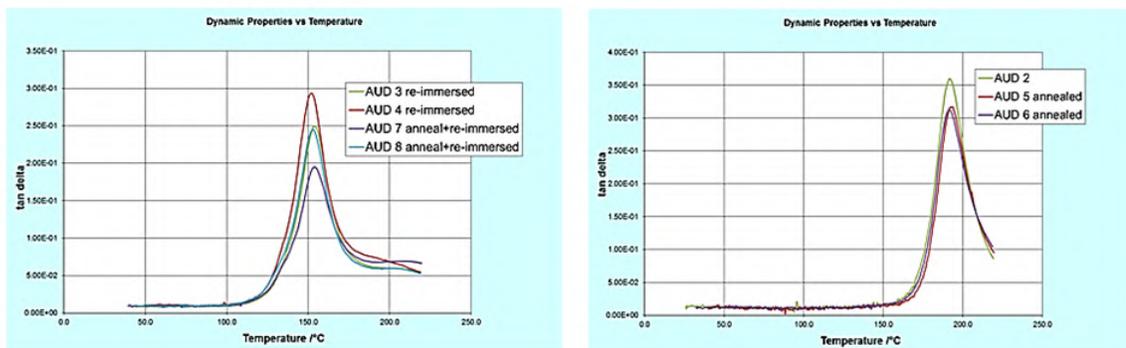


Figure 7 Tg values of annealed and unannealed AUD samples after re-immersion (left) and before re-immersion (right).

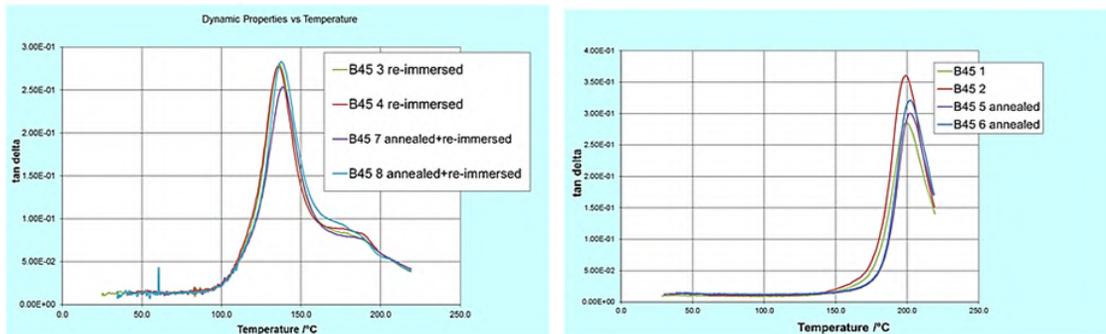


Figure 8 Tg comparison for B45 samples re-immersed, annealed and re-immersed (left) and annealed and unannealed (right).

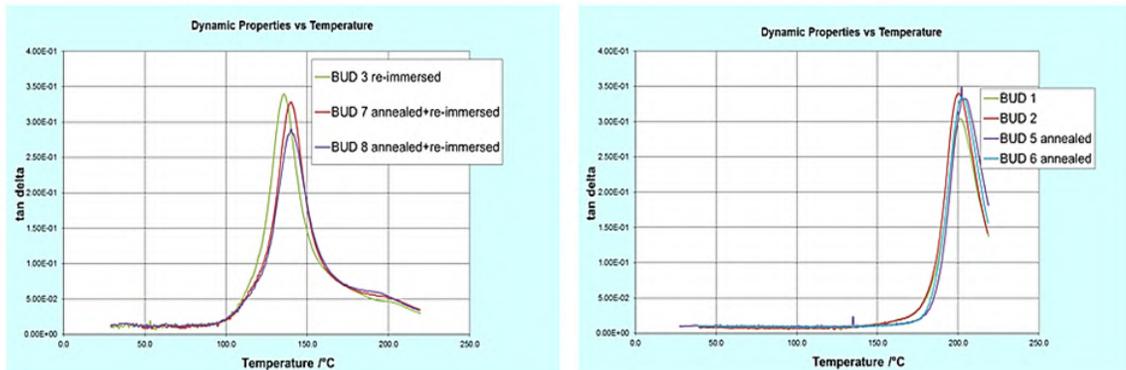


Figure 9 Tg comparison for BUD samples re-immersed, annealed & re-immersed (left) and annealed and unannealed (right)

Optical microscopy was performed on resin and composite samples conditioned at 80°C in water but which were not used for the re-immersion test. The result obtained showed no microcracks, except some physical discolouration which can be seen without the microscope. Some whitish discolouration was noticed on the composite samples and the resin samples had become darker due to long term immersion. FTIR was performed on the surfaces and cut sections of resin samples conditioned in water at 80°C but not used for the re-immersion test, and an unconditioned sample. The result obtained revealed that the conditioned resin sample has a broad O-H peak at around 3200-3600cm⁻¹ showing the influence of water on the samples as seen in Figure 8. A large carboxylic group was observed around 1700-1730cm⁻¹ on the unexposed resin. At this point, it indicates that the C-O and the O-H vibrations are highly characteristic.

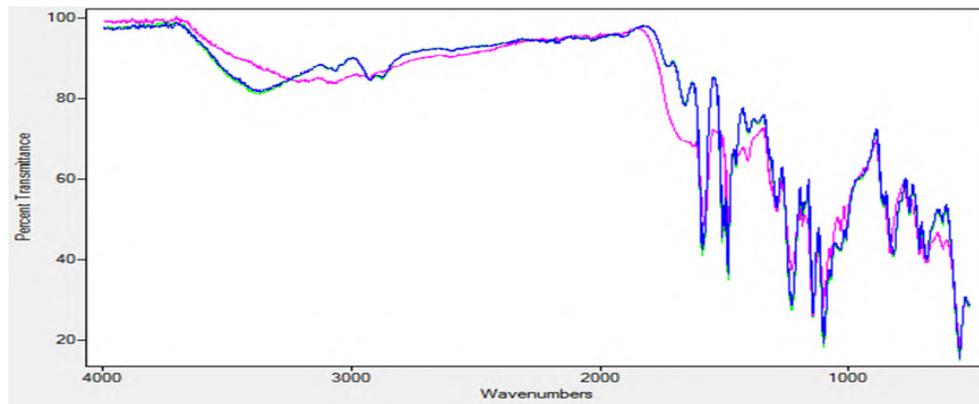


Figure 10 FTIR spectroscopy of the sections through the resin of unconditioned (pink) and after long term conditioning in water at 80C (blue).

4 CONCLUSION

Moisture absorption, desorption and re-absorption characteristics of unidirectional and ±45 carbon fibre /epoxy composites have been investigated by hygrothermal ageing. Long

term conditioning has shown that after initial Fickian behaviour, there is a slow increase in weight common to all materials studied which continues for 5 years. Samples re-immersed after drying for 4 years showed a rapid weight uptake followed by re-establishment of the slow long-term behaviour. The faster rate of the reabsorption process showed that structural relaxation was irreversible and that annealing at 180°C did not reverse this. Investigations revealed that the ± 45 has higher diffusivities and Tg results showed double peaks which was not seen with the UD samples. The dynamic mechanical tests carried out also revealed a depression in the glass transition temperature. Optical microscopy did not show any sign of microcracks and FTIR spectroscopy revealed that moisture absorption causes structural change in the polymer. The plasticising effect causes rearrangement of atoms resulting in a change in the network structure.

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