Article Title:

An investigation of the long-term water uptake behaviour and mechanisms of carbon fibre / 977-2 epoxy composites

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Abstract

The long-term water absorption behaviour of UD and ±45 carbon fibre / 977-2 epoxy composite and unreinforced 977-2 epoxy resin has been studied at different environments with various temperatures and relative humidities. Fickian behaviour was noticed initially followed by a slight and continuing increase in saturation with time, a behaviour that continues for at least 4 years. Fickian saturation and diffusion coefficients of all materials were derived using graphical method. Initial Fickian equilibrium moisture contents were found not to be dependent on temperature but the long-term increase in solubility increased with temperature. Absorption rates showed strong dependency on temperature and relative humidity. The activation energy values for all materials in the initial stage found to be much higher (40 kJ/mole) than the long-term stage (10 kJ/mole). Ea values of the neat resin were observed to be slightly lower than the composites. The slow continued weight gain in the long-term absorption experiments has been seen to be coupled with an incomplete drying and a higher diffusion rate on drying and subsequent re-conditioning. The possible reasons and mechanisms for the long term gradual increase in moisture absorption was further investigated. It was found that molecular relaxation is the most likely dominant mechanism.

1. Introduction

Composite materials have been used for many years in many engineering applications due to their superior properties. Polymer composites are often used in contact with liquids and vapours, either organic or aqueous (liquids or vapours), and such environments can affect the immediate or the long-term performance of the material [1]. Polymer matrix composites normally absorb small but potentially damaging amount of moisture from the surrounding environments [2]. Typically, the moisture flow into or out of the bulk of the composite interior is slow while the external surfaces absorb and desorb moisture almost immediately. Desorption in general takes longer than absorption and some materials may never completely dry because of bound sites for the water. The diffusion mechanism, rate of diffusion and maximum moisture content are dependent in general on the temperature and relative humidity of the conditioning environments [3].

The majority of polymeric composites follow Fickian diffusion kinetics. On the other hand, in many cross-linked and glassy polymers, when molecular relaxations or morphological effects dominate the movement of diffusing species in polymers, deviations from Fick's law can be noticed which may be associated with resin deterioration, or structural changes [4]. The long term water absorption in carbon fibre / epoxy composites was studied by Arnold et al [5] and Korkees et al [6]. The weight gain behaviour was noticed to deviate from Fickian behaviour and it followed the two-stage behaviour. The first stage followed Fickian diffusion while the second stage was slower and continued for long time. The moisture absorption curves of CF/epoxy specimens studied by Qian et al [7] also displayed two-stage (diffusion-controlled and relaxation-controlled) diffusion behaviour. The moisture absorption of UD CF/Epoxy composite laminates was also studied by Perrez-Pacheco et al [8] at several relative humidities at a constant temperature of 25˚C. For the 25% and 55% RH, dual-mode absorption was observed with rapid increase in the first stage followed by slow absorption in the second stage stabilized.

The main object of the moisture absorption experiments was to understand the long term moisture uptake behaviour of carbon fibre/epoxy composites, to study the effect of temperature on moisture absorption, to see how the diffusion coefficients of CFRP and epoxy resin vary when the specimens are subjected to moisture uptake as a function of time. The test parameters that affect water absorption in all cases are time, relative humidity and temperature

2. Methodology

2.1. Materials

The 977-2/HTS composite was manufactured from pre-pregs by Airbus Operations Ltd (at Filton-UK) into sheets generally of 2 mm thickness with either a unidirectional or ±45˚ (symmetrical) lay-up and cured in an autoclave. The volume fraction of the composites had been measured as 62% for the *UD* and 57% for the ±45˚ composites, in line with Cytec's datasheet for CFRP 977-2, where a typical V_f value of 57% to 63% can be expected. All specimens were received from the manufacturers already cut with the dimensions 50x19.90x2 mm, so no preparation was done on these materials.

2.2. Water uptake

The samples were dried in an oven at 70°C and were weighed periodically until the sample weights stabilized. Specimens were then immersed in distilled water at 23°C 40, 60, 70 and 80°C. For humidity experiments, other samples were exposed to moisture uptake at different relative humidity 45%, 60%, 85%, 100% at 70°C. The percentage of moisture weight gain versus time was monitored by gravimetric methods for all specimens until the specimens approached effective moisture equilibrium. Two to three specimens of each material type were conditioned to get averaged results.

3. Water Uptake Results

The weight gain of specimens exposed to water at different temperatures of 23, 40, 60, 70, 80℃ and to various relative humidity of 45%, 60%, 85%, and 100% at 70°C are shown in Figures (1), and (2) for 977-2 epoxy resin, UD and ±45˚ composite, respectively. Figure 1 shows initial Fickian behaviour followed by a continued increase in moisture content with time in contrast to the curve predicted by Fickian diffusion behaviour which should reach a constant value. This two stage diffusion behaviour, where initial behaviour is Fickian, has been seen before and the second stage has been attributed either to polymer chain relaxation opening more spaces, or water molecules binding to specific sites, or to the effects of long term chemical degradation.
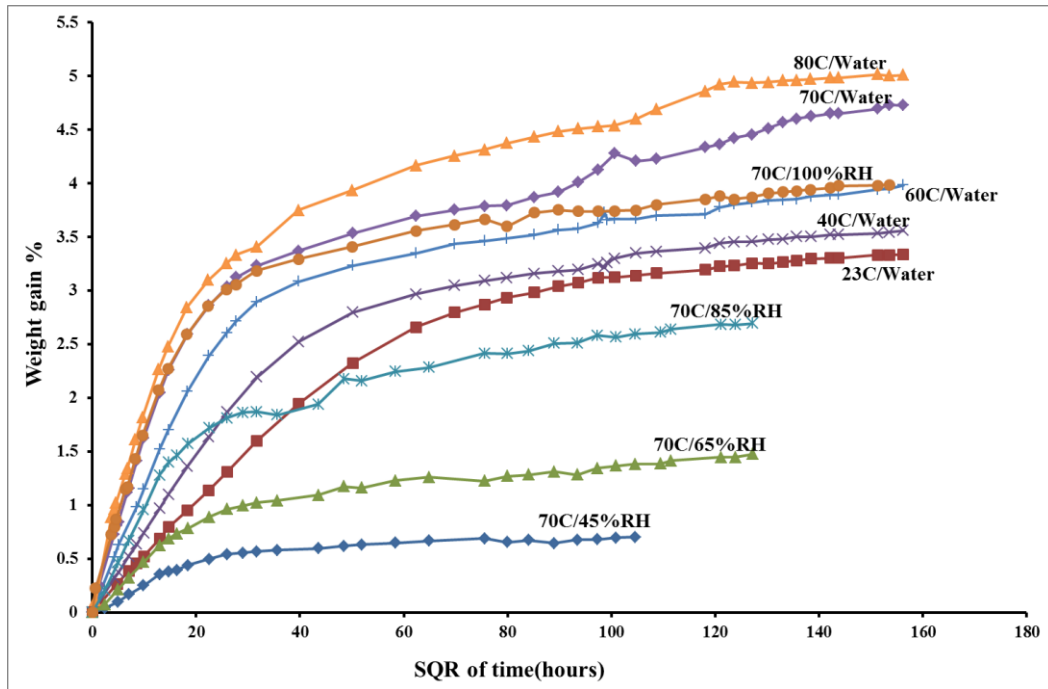
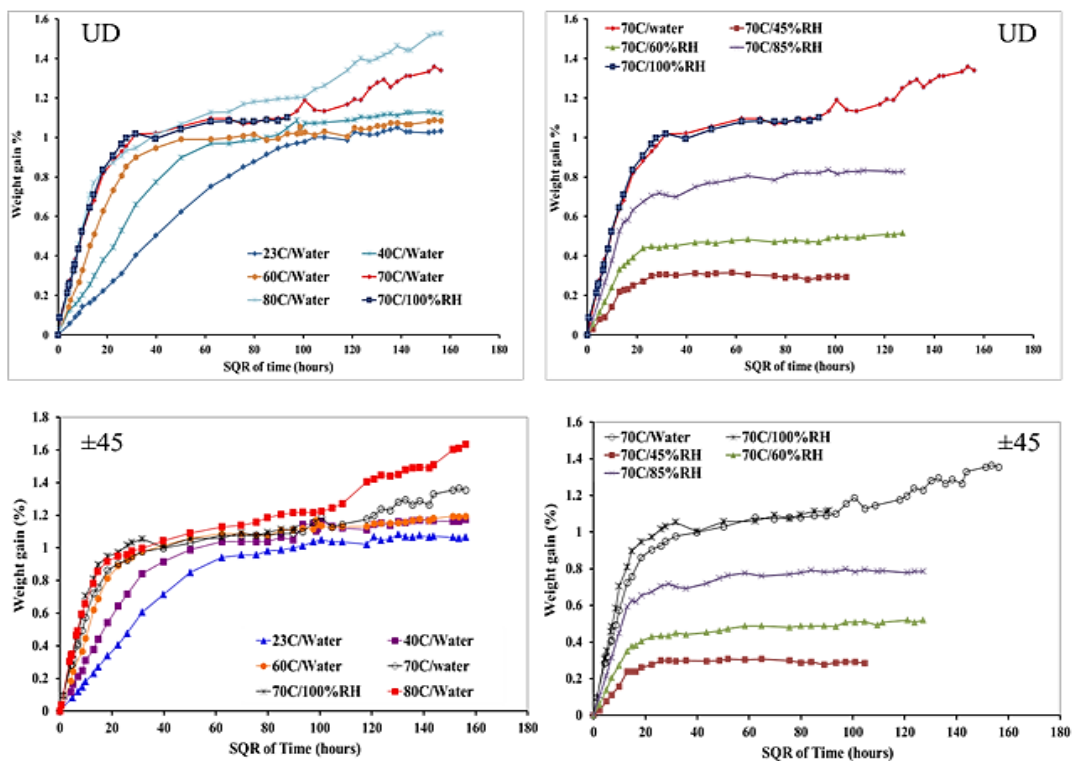**Figure 1.** Absorption behaviour of 977-2 epoxy resin.

Figure 2. Absorption behaviour of UD CF/977-2 epoxy resin (Top) and ±45˚ CF/977-2 epoxy resin (Bottom) at various temperatures (Left) and various relative humidities (Right).

The diffusion in UD and ±45° composites is mainly through the thickness. Evidently, typical Fickian diffusion is observed for all materials in the initial stage followed by slow increase at longer times even after 3 years of exposure. This two-stage diffusion behaviour was also noticed in several previous studies [9-10]. This linear relationship between weight gain and square root of time means that water uptake in the initial stage is diffusion controlled which has been reported by other researchers [11-12].

The values of maximum moisture content M_m of UD and ±45° composites were lower than that of the pure resin. For example, M_∞ for UD, ±45° and pure resin in water at 70°C was 0.92%, 0.93% and 3.0%, respectively. This can be attributed to the fibres' presence which drastically reduces the resin mass and restrict the water absorption, or it may be that there are more water-attractive sites in the unreinforced resin than in the composite. Since fibre volume fraction of these composites is usually between 57-63%, equating to a resin weight fraction of about 37%, and as the fibres do not absorb water [13], the water content in the resin fraction of the composites is given by 0.92/0.37 or 2.5%, close to the value in the unreinforced resin. This suggests that the main difference is simply due to the lower resin volume fraction in the composites, with possibly slightly more (rather than less) attractive sites for water.

4. Saturation Values

The maximum moisture contents in the specimens exposed to water uptake for between 2 and 4 years at various temperatures and humidity are given in Figure (3). These values confirm that the moisture content is a function of the resin content. Therefore, the total saturation values of 977-2 an epoxy resin were examined in order to better understand the composite materials. Figure (3) shows the saturation values versus the temperatures and relative humidity, and confirms that the maximum moisture content is dependent on both the temperature and the relative humidity of the environment.
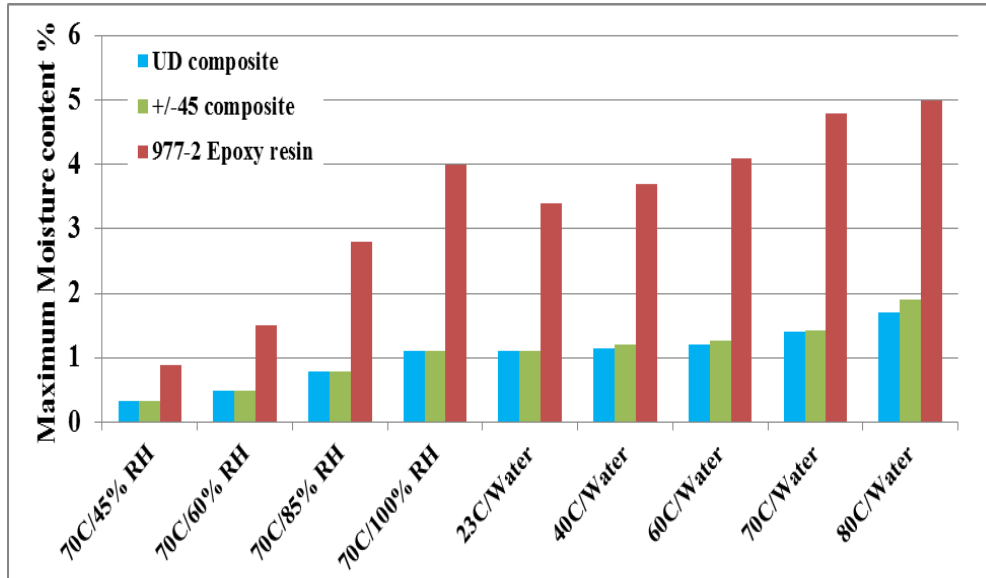
Figure 3. The maximum moisture contents.

The water solubility into epoxy resins and their composites might be expected to increase with temperature because of the free volume of the epoxy resin increases with temperature allowing more water to diffuse into this additional volume [14]. The same effect was noticed by other researchers [15-17]. This may be because increasing the temperature of exposure increases the thermal energy and mobility of the water and the segmental motions of the polymer chains allowing more water to penetrate into the higher density regions of the resin [18]. Moreover, exposure to elevated temperature, for instance 80℃, can lead to cracking, chalking and flaking of polymers allowing more water to diffuse in [19].

The results shown in Figure (3) show a moderate increase in solubility as the temperature increases; however, Figure (5 A) shows a somewhat different picture. Since most of the samples haven't reached saturation, and since equilibrium moisture content is necessary for the calculation of the diffusion coefficients, it was important to determine the Fickian moisture level at which the best curve fit for the Fickian part can be obtained. Therefore, the long term behaviour for the resin and composites under all conditions was subtracted, giving a value of the Fickian saturation for each sample, as illustrated in Figure (4). Once the long-term behaviour has been removed, there is much less dependency on temperature, Figure (5 A), and the composite samples show very little variation. This suggests that the

initial Fickian saturation is not that dependent on temperature but that the long-term increase in solubility does increase with temperature.
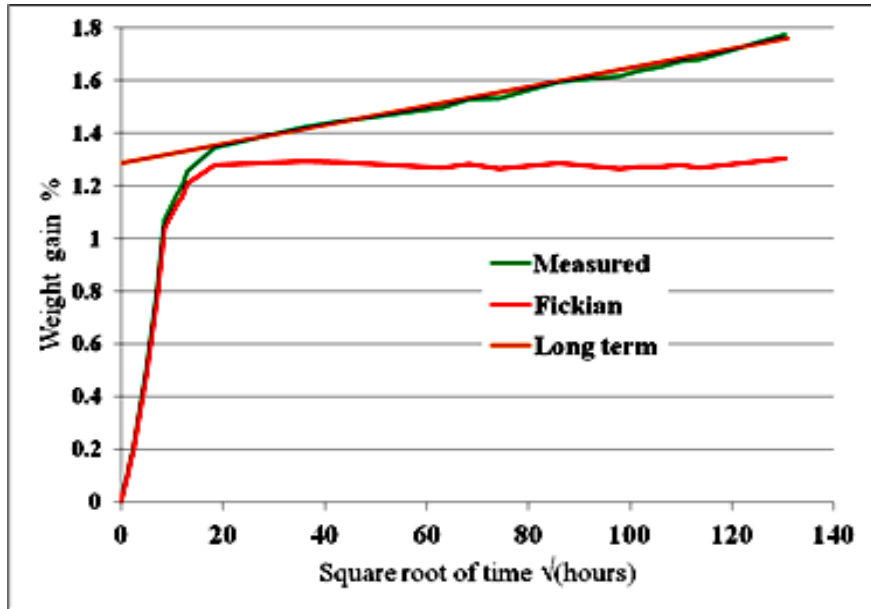

Figure 4. Extraction of Fickian behaviour from long term water uptake measurements.
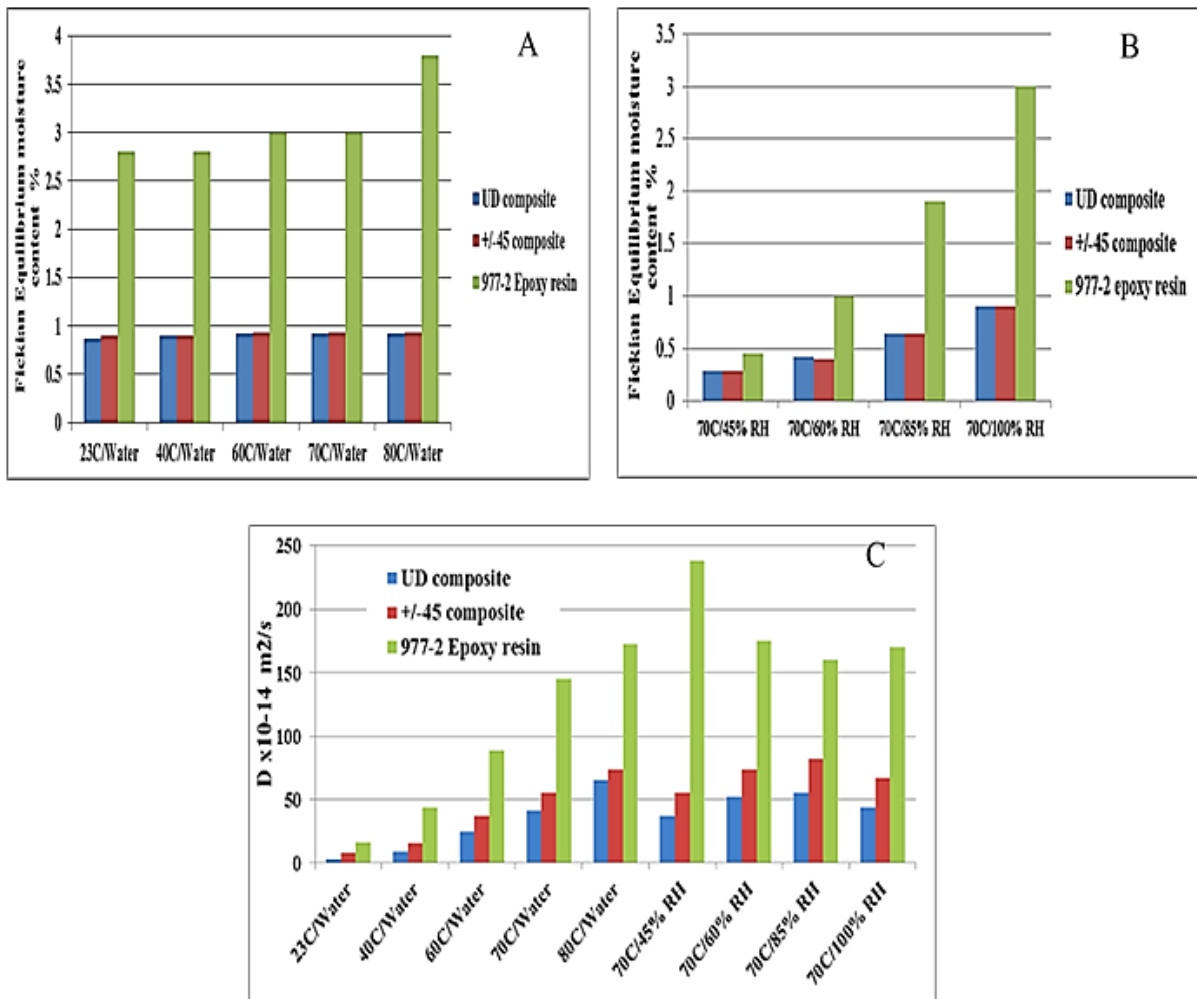
Figure 5. Fickian equilibrium moisture contents at various temperatures (A) and various relative humidity (B). Diffusion coefficient at various temperatures and humidity (C).

The equilibrium moisture content is much more dependent on the relative humidity, where the maximum moisture content increased with humidity, both for the total saturation and Fickian component, Figures (3) and (5 B). Those figures show that with increasing humidity the maximum moisture content increases significantly, this is in accordance with findings of [5, 20-21]. The humidity will affect the water activity and this will have a direct effect on the solubility, though in a non-linear way. The maximum moisture content for most of the specimens is seen to approach a constant value for the specimens fully immersed in water. At 70°C, the 100% humidity produces a slightly lower level of saturation than complete immersion.

5. Diffusion Coefficients

Using the Fickian saturation values obtained by the technique mentioned before, the initial Fickian diffusivity was calculated. To compensate for edge effect, the edge correction factor used in this study was derived by Starink, Starink and Chamber [5-6], equation (1).

$$f_{ssc} = 1 + 0.54\frac{h}{l}\sqrt{\frac{D_y}{D_x}} + 0.54\frac{h}{w}\sqrt{\frac{D_z}{D_x}} + 0.33\frac{h^2}{l.w}\sqrt{\frac{D_z D_y}{D_x^2}} \qquad ; D_x{\neq}D_y{\neq}D_z \qquad \text{Eq(1)}$$

where *h, l and w* are the thickness, length and width of the sample.

It was assumed here that the geometrical effects of the *UD* and ±45˚ composites is neglected, and the diffusion coefficient in the composites is the same in all directions, as it is in the resin; i.e. $D_x{=}D_y{=}D_z$. Therefore, the edge correction factor used becomes equation (2):

$$f_{ssc} = 1 + 0.54\frac{h}{l} + 0.54\frac{h}{w} + 0.33\frac{h^2}{l.w} \qquad\qquad \text{Eq (2)}$$

The initial Fickian diffusivity D_F was calculated using equation (3).

$$D_F = \frac{g_{meas}^2 h^2}{M_F^2 16\pi(1 + 0.54\frac{h}{l} + 0.54\frac{h}{w} + 0.33\frac{h^2}{l.w})} \qquad\qquad \text{Eq (3)}$$

It can be seen from Figure (5 C) that the Fickian diffusion coefficients of epoxy resins are higher than those of the composites at all temperatures and relative humidities. This can be attributed to the presence of the fibres which don't absorb water and thus hinder the diffusion by increasing the diffusion path, and it also suggests that the diffusion coefficient increases with the matrix volume fraction [9]. Moreover, the ±45˚ specimens have higher diffusion rates than the UD specimens, presumably as there are easier diffusion pathways between the layers where more fibre-ends are exposed to give a shorter diffusion path [9].

6. Rate of Long Term Increase in Water Concentration

Diffusion in general is a thermoactived process and the diffusion coefficient is very sensitive to temperature of immersion. This temperature dependency can be expressed by the Arrhenius equation,

where diffusion coefficient shows a linear relation when plotted in terms of *ln(D)* versus *1/T* as shown in

Figure (6 Top). Figure show that increasing the temperature accelerates short-term diffusion and increases

the diffusion coefficient. Similar behaviour was observed by researchers which attributed it either to the

degree of swelling which resulted in micro cracks [15], or to the increase in the volume occupied by the

molecules because of their thermally dependent vibrational movement [22].   Figure (5 C) shows the

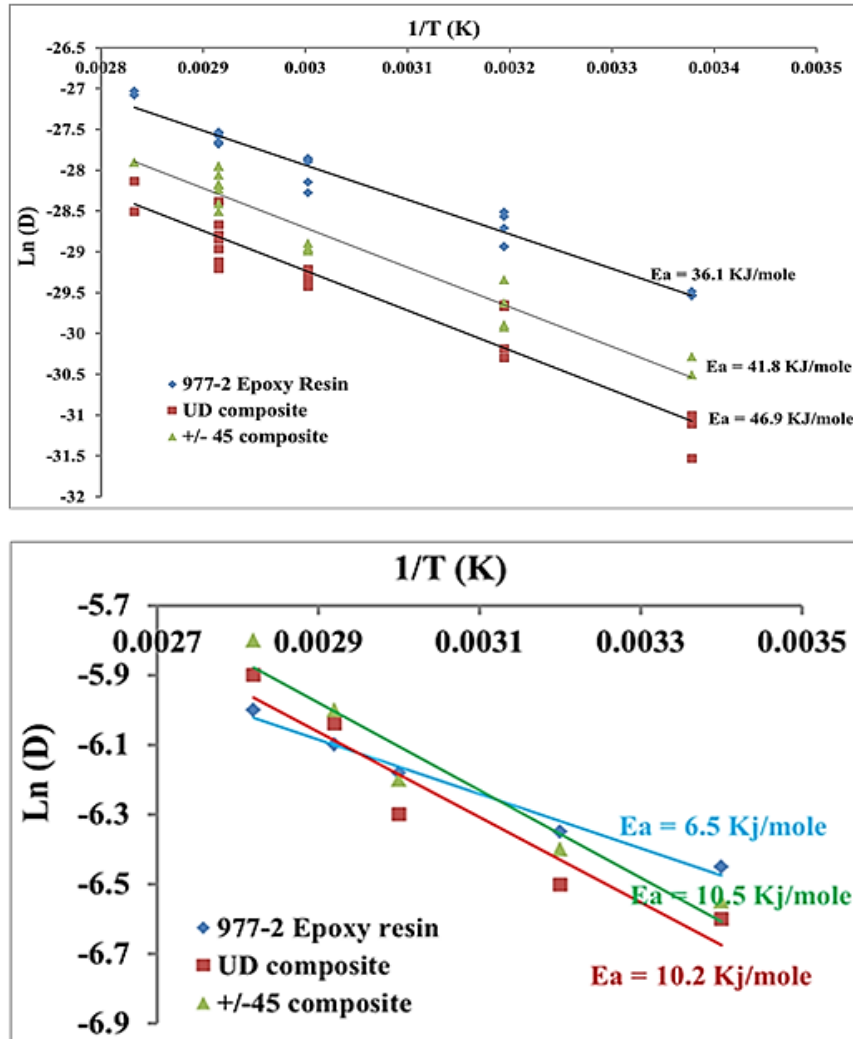dependency of diffusion coeffiecents on both temerature and relative humitiy.

Figure 6. Arrhenius plots for the Fickian diffusion values(Top) and for the long-term pseudo-diffusion

values (Bottom).

According to Arrhenius equation, the diffusion coefficient is dependent on the activation energy,

which is expected to be the same for composites with impermeable fibres and pure resin. Generally, the

activation energies of the resin and its composites should be the same if water diffusion through the matrix was the only mechanism of water penetration. The activation energy can be calculated from the slopes in Figure (6 Top) and this shows that there are some differences in activation energy between materials. The values for the neat resin seem to be slightly lower than for the composites, suggesting that the presence of the fibres may hinder water movement through the resin, possibly by providing additional constraints to polymer chain movement [23]. The differences are not particularly large and may be due to experimental variations. The values of activation energy are similar to those found for secondary chain relaxation in epoxy resins of around 50 kJ/mol [24].

From the long-term behaviour, the rate at which the saturation increases can be determined by deriving a 'pseudo-diffusion' (D_L) rate by taking the gradient of the weight uptake vs √(time) graph for the second stage and then dividing by the Fickian saturation. This rate assumes that sample geometry has no effect, and so no account was made of edge effects. These values again vary a little with humidity for the 70°C samples, but with no significant trend. They do increase significantly with temperature so again can be plotted using an Arrhenius equation, as shown in Figure (6 Bottom). The graph shows that there is a very clear difference between the resin and the composites, with again the resin having a lower value, again indicating that the fibre provide additional constraint which isn't present in the resin. The E_a values of the composite samples are quite similar, confirming that the long-term behaviour is not affected by composite structure. The activation energy for this second stage behaviour is considerably lower at about 10 kJ/mol.

7. Reasons for the two-stage water uptake

It can clearly be seen that all samples display the two stage behaviour which is shown in both resins and the composites of the 977-2 resin at all temperatures and at all humidity levels. It is also evident in drying and re-absorption tests. The possible reasons or mechanisms for this gradual increase in moisture absorption are:

1- Water molecules binding to active sites such as functional groups on curing agents

For the first of these mechanisms, slower diffusion of water molecules to bound sites may occur. Functional groups remaining from the curing reaction are a good example of these bound sites. Polymer/water interactions, in which water establishes strong hydrogen bonds with the polar groups in

epoxy resin allowing more water to diffuse in, have been suggested to govern the two-stage water uptake process. Therefore, drying tests were performed on some conditioned specimens at low temperature 23°C and high temperature 70 C to investigate this.

The results, displayed in Figures (7), show that a small amount of water is not desorbed but is retained in the composite after drying at both temperatures suggesting that water molecules may interact with specific sites (hydrophilic groups). It has been found in many studies that the nature of water in epoxy resin can be presented in two forms (hydrogen bonded molecules or clusters in the free volume or voids) that might be the responsible for the non-Fickian behaviour [25-27]. The presence of residual moisture in epoxy resin was also reported by [28-29]. This small residual moisture content left from desorption process from high moisture-saturation could only be removed by drying the specimens at relative high temperature. Therefore, it can be concluded that the absorbed water in epoxy system exists in two types of bound water, type I in which water can be removed easily at low temperature, and type II where absorbed water can be removed only at high temperature [25].
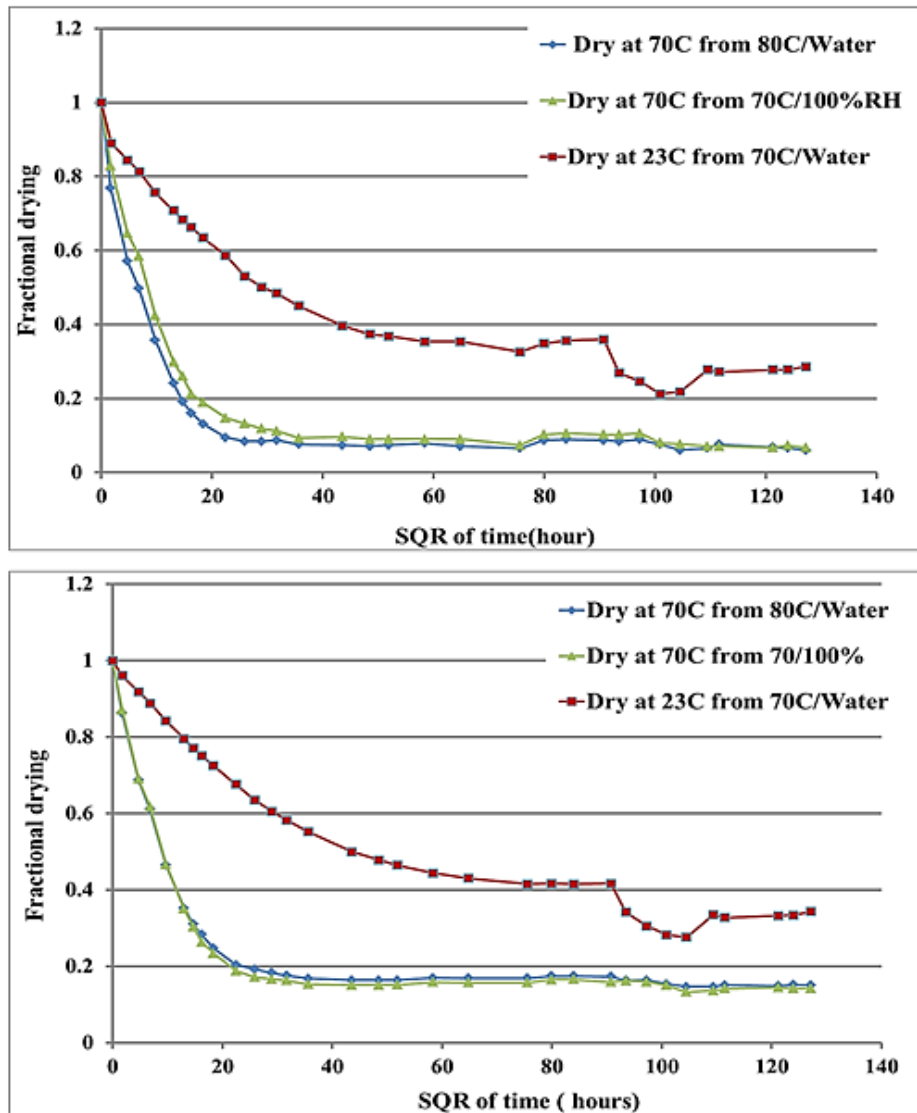
Figure 7. Desorption behaviour of UD CF/977-2 epoxy resin (Top) and pure 977-2 epoxy resin (Bottom).

To investigate this further, immersion and drying of 977-2 epoxy resin was also carried out using hexane at 23°C and 45°C to determine whether the same effects are seen in a non-polar liquid which is not 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 (8 A) and Figure (8 B), respectively. The same type of two-stage behaviour is shown, with strong indications of an incomplete drying with about 10% of the absorbed hexane still remaining in the specimens. This would suggest that the role of hydrogen bonding is not that significant. Although water molecules binding to certain sites in the epoxy resin may be a reason and would explain the incomplete drying, it is hard to picture how this mechanism

would increase the diffusivity on drying and re-immersion. It would also not be expected with a non-polar liquid such as hexane.
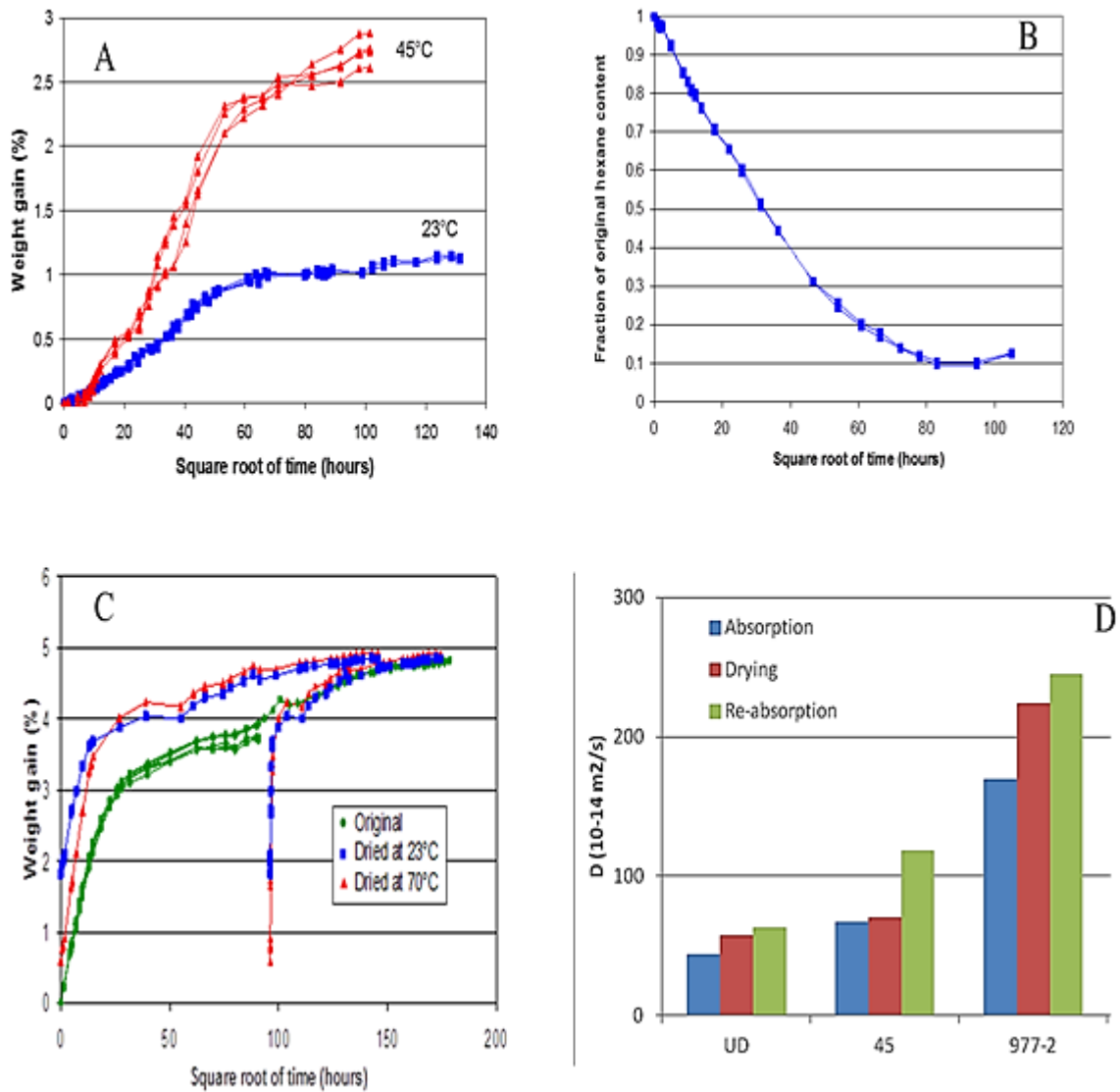
Figure 8. A) Weight gain for samples of 977-2 resin in hexane. B) Fractional drying for samples of 977-2 resin in hexane. C) Re-immersion behaviour of 977-2 epoxy resin and D) Fickian diffusivities for samples immersed, dried and re-immersed at 100%/70°C.

2- Polymer chain relaxation

Moisture diffusion is usually associated with the relaxation process in glassy polymers, and both moisture diffusion and relaxation are sensitive to temperature [23]. Therefore, the mechanism of slow molecular relaxation could reasonably explain the long-term behaviour. Since water is known as a good plasticizer of the resin, the absorbed water in all hygrothermally-aged specimens is believed to induce

structural relaxation in the resin, which allows additional pockets of free volume for the water (or hexane) molecules to occupy. This mechanism can reasonably explain the slow increase in the second stage of the uptake curves. Other studies [7, 15, 18] also attributed the two-stage water uptake to resin relaxation phenomena. The relaxation process is usually slow and is one in which the polymer chains slowly re-arrange in the presence of absorbed water molecules, resulting in additional absorption. The structural relaxation is generally much slower than the diffusion process. Therefore, the first and second stages can be treated as diffusion controlled and relaxation controlled, respectively. The activation energy of the long-term behaviour is about 10 kJ/mol which is lower than that recognised for secondary chain relaxation which is about 50 kJ/mol and similar to the Fickian activation energy. It may well be that the presence of water plasticised the polymer and reduced the activation energy for secondary bond relaxation.

The long-term weight gain is seen to continue for all samples for more than 3 years with little indication of the final equilibrium uptake. This would require the time scale of the relaxation process to be very much longer than that of the diffusion. There is some evidence that the neat resin samples immersed in water at 80°C may have reached a final equilibrium value, though the equivalent composite samples are still increasing , Figures (1-2). The relaxation of the network to a more open structure would lead to increased diffusivity on drying and re-immersion. The re-immersion of specimens was carried out after drying to investigate that. Figure (8 C) shows the re-absorption curves against original absorption of 977-2 resin. Plotting the re-immersion data with time starting from zero shows that the diffusivity is higher than the original weight gain data. On the other hand, if 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. This structural relaxation in the second stage indicates that a drying step does not reverse the structural change of the network that occurred in the first absorption process. Generally, specimens immersed in water for long periods will be subject to structural relaxation accumulating from segmental movement of the swollen resin. Because of this, the network structures of hygrothermally-aged specimens are different from the original materials. On the other hand, during the desorption stage the water is removed and T_g increases but the polymer network cannot relax to the original dry state because the relaxation process is suppressed. Therefore, the structural change of the network is irreversible [31]. For the same specimens subject to absorption, drying and then resorption,

Figure (8 D) shows that the diffusion rates seen during re-absorption are higher than those noticed during initial absorption. This clearly indicates the irreversibility of the structural change of polymer network and the history-dependency of diffusion properties.

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-sized holes. This purely physical mechanism of bound water could be explained if most water has been removed from the polymer, reducing the degree of plasticisation, and decreasing chain segment movement, then the only way to remove the trapped water molecules would be to significantly increase the temperature, as was referred to above.

3- Chemical degradation

A further mechanism may be that during moisture absorption water attacks the epoxy resins chemically causing hydrolysis, leading to dissolution, and leaching of water-soluble polymer molecules followed by depolymerisation chain scission. This chain scission, in the early stage, may lead to the chemical addition of the water and thus to weight increase in the second stage [18, 27, 31, 32].

The neat epoxy resin samples showed some discolouration on the surface after long-term immersion at the higher temperatures that is probably due to some chemical degradation. This discolouration was observed near to the surface and did not penetrate into the centre of samples, even after 3.6 years of water exposure. Moreover, it was seen that the FTIR spectroscopy did not show any significant signs of degradation. In one or two samples, a slightly larger carbonyl peak at about 1740 cm-1 was seen, as shown in Figure (9), but this was not seen consistently. The fact that the two-stage behaviour is seen at all temperatures also suggests that chemical degradation is not the main cause of the two-stage behaviour. The activation energy of epoxy hydrolysis has been reported to be much higher at about 120 kJ/mol [33], which does not match the value of about 10 kJ/mol obtained for the long-term uptake. The slight chemical degradation from the surface can be probably put down to the reaction with oxygen dissolved in the water, but this is unlikely to be the main cause of the long-term behaviour.
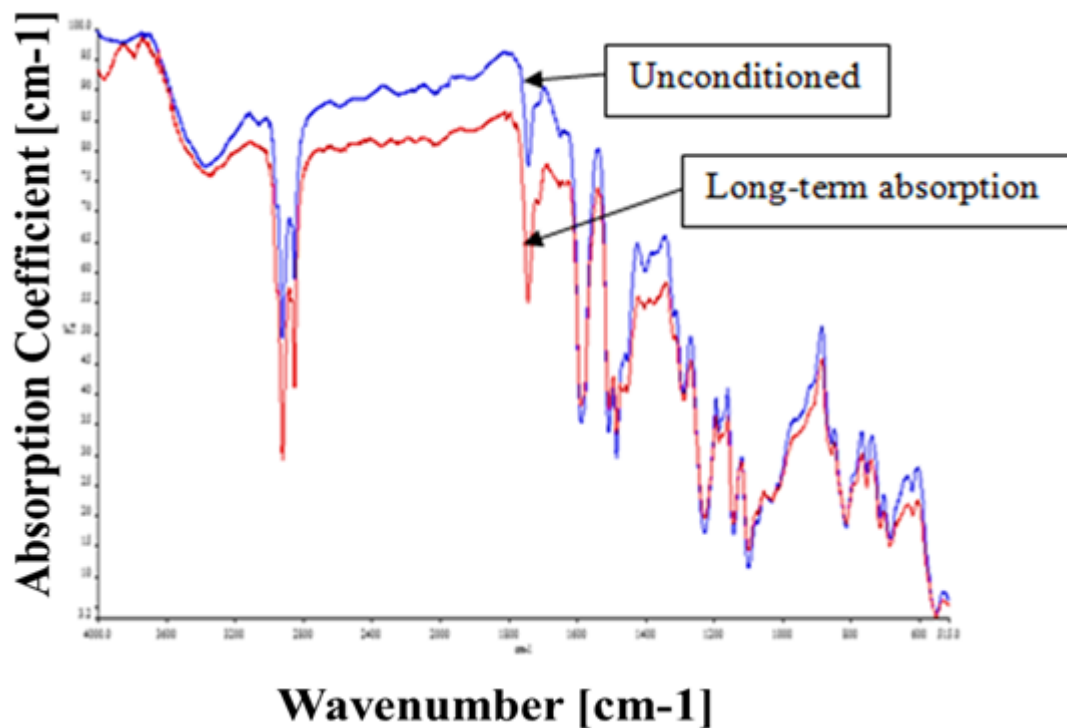
Figure 9. FTIR Spectroscopy results of sections through 977-2 in the unconditioned state (blue) and after long term water exposure at 80°C (red).

4- Development of microcracks which open to allow increased absorption

Figure 20 shows microscopy images of samples sectioned after long term immersion. The formation of microcracks cannot be considered as a reason since no microcracks were seen microscopically, Figure (10), and there is no reasonable mechanism, which can relate incomplete drying to microcracks. An increase in desorption rates could be due to the increase of the area/volume ratio in the cracked materials [34]. It has also been suggested that the hygrothermal ageing causes irreversible degradation in the form of fibre-matrix interfacial debonding and formation of voids and micro-cracks into macro-cracks, which in turn produce new paths for diffusion, and wicking of water. Consequently, they enhance the level of moisture absorption, and considerably affect the values of diffusivities [15, 35].
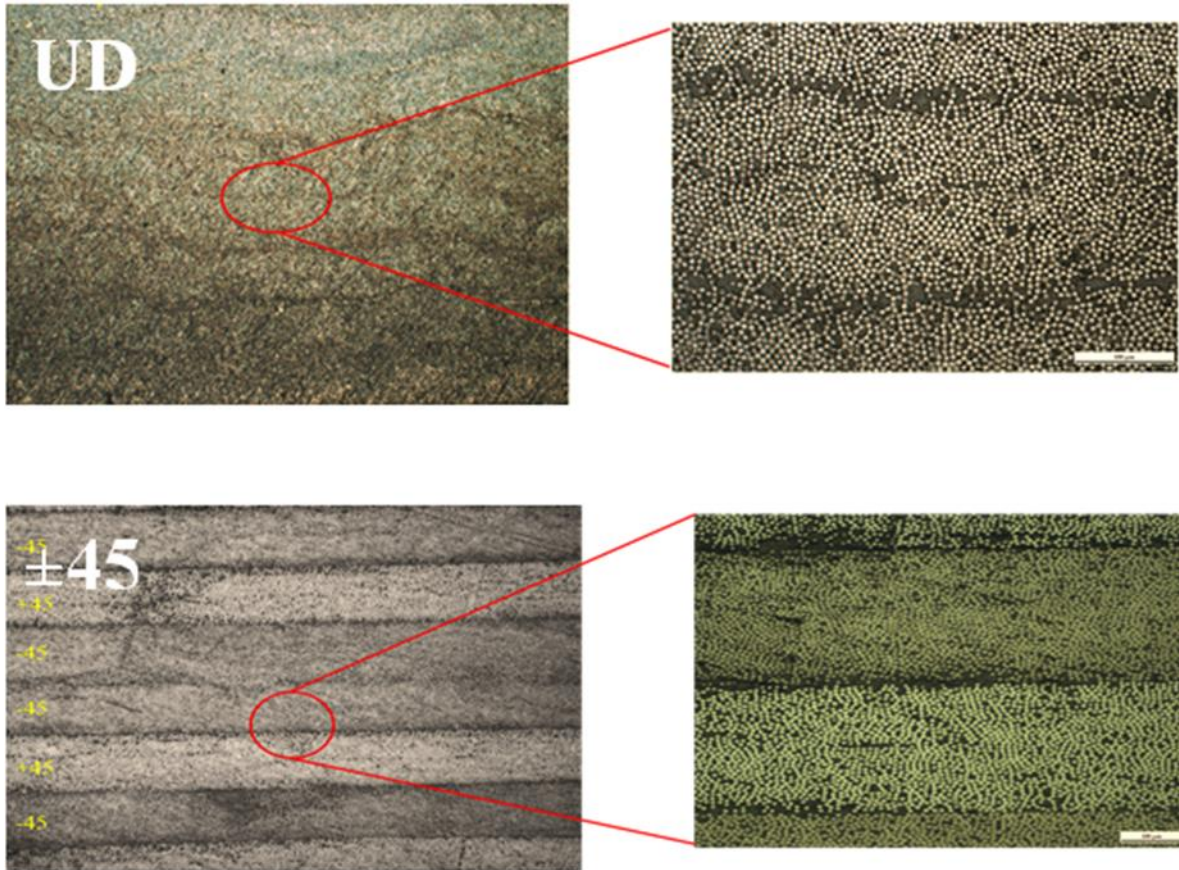
Figure 10. Microscopy images of UD and ±45 CF/977-2 epoxy composites.

5- Slow absorption of water into toughening particles

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 [36]. Water wicking along the fibre-matrix interface, voids, and microcracks has also been suggested to play a significant role in increasing the diffusivity in polymer composites [23, 37].

From the discussion above, some of the mechanisms suggested above can be reasonably easily rejected and it would seem that the long-term behaviour is primarily due to molecular relaxation. This would explain the long-term nature, the variation with temperature and the fact that it has a similar rate for all materials. It would also explain the higher rates of desorption and re-absorption and the fact that similar behaviour was seen with hexane. The remaining water that is not removed on drying would seem to indicate more a chemical binding mechanism, but this would not be expected with hexane and a molecular relaxation process could explain this for both liquids. There is no evidence of cracking or other forms of damage and little evidence of major chemical degradation. There are a few signs of the other

mechanisms having a minor role. For instance, there are some signs of surface chemical degradation at the higher temperatures, possibly more due to reaction with oxygen. The fact that the resin samples immersed at 80°C seem to have reached an equilibrium but the composite samples are still increasing in weight may point to some cracking or debonding in the composites at the highest temperatures.

8.   Conclusion

The water absorption behaviour of carbon fibre / epoxy composite and the constituent unreinforced resin has been found to follow a Fickian model initially followed by a slight and continuing increase in saturation with time, a behaviour that continues for at least 3.7 years. The initial saturation levels increase slightly with temperature for water immersion, while these levels increased more considerably with increasing relative humidity. The equilibrium moisture contents, normalised for resin content are rather higher for the neat epoxy resin than for the composites. This can be due either to the constraining role of the fibres or a variation in curing level in the interphase region. Since the diffusion coefficient is dependent on the activation energy, the analysis for both initial stage and long term stage of absorption showed that there is a very clear difference between the resin and the composites. The resin exhibited lower values in both stages than composites indicating that the fibre provide additional constraint to polymer chains movement which isn't present in the resin. Moreover, the activation energy for this second stage behaviour was considerably lower compared to the initial stage behaviour.

The slow continued weight gain in the long-term absorption experiments has been found to be coupled with an incomplete drying and a higher diffusion rate on drying and subsequent re-conditioning. These consequences are more noticed with the epoxy resins than for the composites and are observable at higher temperatures. The possible reasons behind this can either be the binding of water molecules at active sites, molecular relaxation, or chemical degradation. Further tests with hexane showed that molecular relaxation is the most likely dominant mechanism.

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