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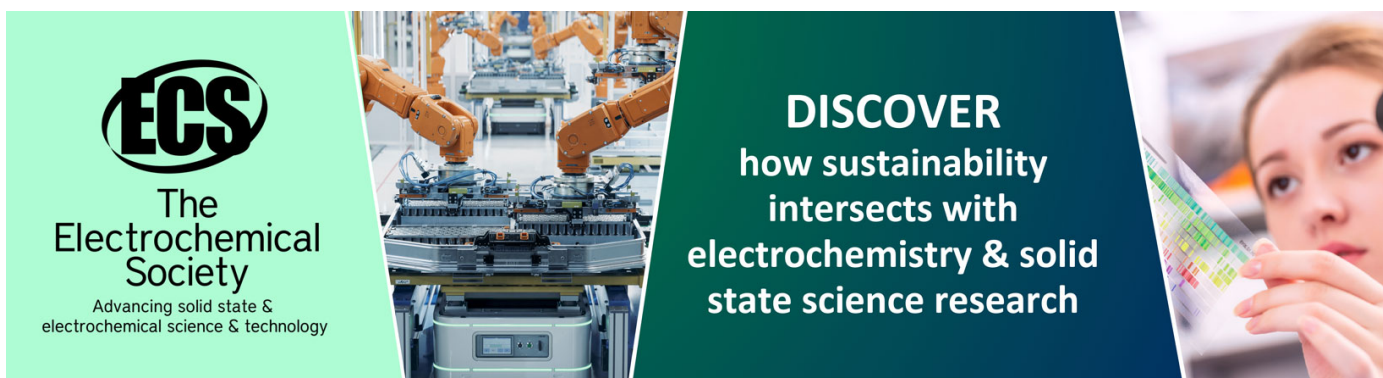
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The effect of environmental ageing in the interphase of a glass fibre/vinyl ester composite designed for wind turbine applications

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Abstract. The use of advanced fibre reinforced polymer (FRP) composites in the renewable energy sector has significantly increased over the last decade. However, the durability and damage tolerance of such materials when exposed to environmental conditions still remains under investigation. This creates some uncertainty for their introduction and development in the sector. The scope of the present work is the assessment of the durability of composite laminates and structures through providing a fundamental understanding of the micromechanical performance of the glass fibre/vinyl ester fibre-matrix interphase as a function of the environmental history. An accelerated ageing study has been conducted in order to create a correlation between the moisture sorption at the interphase and its effect in the micromechanical performance of the composite system. The composite interphase performance has been assessed by measuring the Interfacial Shear Strength (IFSS) using the microbond test. An estimation of the moisture sorption of each microbond sample has been obtained by the gravimetric analysis of thin film neat resins specimens of similar thickness to the microbond sample diameter. These results have also been coupled to results obtained by Fourier-transform Infrared Spectroscopy (FTIR). Additionally, moisture induced degradation has been characterised by recording the change in the T_g of the vinyl ester resin as a function of environmental ageing by a number of thermal analysis techniques.

1. Introduction

The popularity of FRPs in wind turbine applications has significantly increased over the last decade. During their service life their contact with environmental degradation agents, such as moisture and thermal cycling is inevitable. Regardless of the close attention to details and the employment of optimum design methods, the long-term exposure of FRPs to the use-environment will likely shorten the durability of the materials and eventually trigger irreversible degradation mechanisms which will affect their properties. Moisture uptake is known to cause a series of degradation phenomena in thermoset polymers and FRPs, such as swelling and plasticization of the matrix, hydrolysis and loss of adhesion at the fibre/matrix interphase [1]. A method of accurately determining the effect of the in-service environmental conditions to the exposed material is yet to be established. This creates a level of uncertainty about the durability of composites for infrastructure applications, where clients and stakeholders need to "know" how the material will perform in over timescales of many decades.

A real-time assessment of in-service composite structures is a time-consuming process involving high costs. These parameters can be lowered by employing in-lab accelerated ageing conditions. The



basic concept of accelerated ageing is to increase the severity of the degradation conditions, such as temperature or humidity, to a higher level than that achieved in real-life operating environments [1].

It has been suggested in previous studies that the fibre/matrix interphase is a crucial region of FRPs [2, 3]. In fact, the condition of the interphase can define the reliability and therefore the durability of composite materials or structures during their service life. The hydrothermal conditioning of the interphase directly can significantly accelerate ageing times. Even though the transferability of the properties of the fibre/matrix interphase to the bulk laminate is complex, it has been established that a strong interphase can potentially contribute to an FRP with high mechanical and chemical properties, and an interphase failure is likely to compromise the performance of the bulk material and even lead to its failure [1, 2, 3]. Studies have also shown that whenever there is any improvement in the macroscopic properties of the composite, there was a corresponding improvement in the micromechanical properties of the composite as well [3, 4]. The integrity and properties of the interphase are particularly sensitive to hygrothermal ageing. In fact, moisture exhibits the ability to force itself between the fibre and the matrix and therefore the interphase is a potential passageway for the permeation of moisture into polymer composites. Moisture ingress is known to cause hydrolysis of the bonds at the composite interphase, resulting in reduced load transfer capability between the matrix and the fibre [1, 3].

The objective of this study was to create a correlation between the moisture uptake of a glass fibre/vinyl ester interphase and its translation into the micromechanical properties of the system. This work is an initial approach in predicting the hydrothermal response of the GFRP intended for wind turbine blade applications and is a part of a greater study aiming to develop more durable composites for use in large infrastructures. Thin film specimens have been used as model for the moisture uptake in the interphase, while bulk resin specimens have been conditioned hydrothermally too to allow a comparison between the micro and macro scales. A great part of this work is focused on the change of neat resin properties, which in turn can have a great effect in the glass fibre vinyl ester interphase.

2. Experimental

2.1. Materials

The experiments were conducted using a low viscosity bisphenol epoxy based vinyl ester resin (DION® VE-1260), with a styrene content of 48 – 52%. The resin was supplied by Polynt Composites Ltd. The resin was mixed with a UN 3103 Organic peroxide type C initiator (1.95%) and was initially cured under a nitrogen environment for 24 h at room temperature and post-cured at 60 °C for 24 hours, 80 °C for 3 hours and 100 °C for 1 hour. The nitrogen environment was chosen due to the susceptibility of microdroplets (high surface area to volume ratio) to oxygen, which can act as a copolymer and result in incomplete matrix cure. The glass fibre used was a Boron-free Advantex® ECR glass fibre a commercial glass vinyl ester compatible sizing (se3030). The fibre was provided by 3B Fibreglass in the form of a direct roving.

2.2. Ageing Parameters

The ageing conditions were selected as a starting/reference point in order to produce initial results and examine the durability of a glass fibre/vinyl ester interphase in a wet environment. A water temperature within the range of room temperature (23 °C) was selected, as well as a temperature of 50 °C as a means of accelerating the ageing process. Specimens were aged by full immersion in deionized water using two different water baths.

2.3. Sample Preparation

2.3.1. Microbond Sample Preparation. A high grade stainless steel rig was designed and manufactured in order to accommodate microbond specimens and allow their exposure in humid environments. The single fibre specimens were adhered on a stainless steel washer by the means of araldite glue. The microbond sample preparation procedure has been previously described by Yang and Thomason [5].

Acceptable droplet dimensions were considered: 90-180 μm in embedded length and 40-80 μm in diameter.

2.3.2. Neat resin sample preparation. Thin films were used as a model of prediction of moisture uptake in microbond droplets. Film thickness was kept as close as possible to the embedded length of the microbond droplets. The fabrication of films was carried out with the means of a seam roller by applying several resin layers on a silicone rubber substrate of 170 x 100 mm and a thickness of 5 mm. The resin was left at ambient laboratory conditions for 30 minutes to become more viscous and facilitate rolling before use. All cured film sheets were removed from the substrate were cut into 25 x 25 mm specimens, which were dried under vacuum for 48 h before use.

Generally, the manufacturing of thin neat resin film was a challenging task, due to the nature and the physical properties of the thermoset (i.e. low viscosity), as well as the difficulty to produce specimens of such thickness. Several techniques and various substrates were used until the optimum result was achieved. The films used for the moisture uptake measurements were $150\pm30\ \mu\text{m}$ and $220\pm30\ \mu\text{m}$ for the 50 °C and 23 °C hydrothermal exposure, respectively. The bulk neat resin specimens were manufactured by using open silicone moulds providing specimen dimensions of 80x80 mm and a thickness of around 3.9 mm.

A semi-sphere droplet-like specimen with a flat bottom was also manufactured for thermal analysis by piping resin (mixed with initiator) onto a non-porous release film. The thickness of the droplet was around 2 mm. Cured semi-sphere specimens are illustrated in Figure 1. The purpose of these specimens was to allow accurate Tg measurements (DSC) according to ASTM 1356-08.

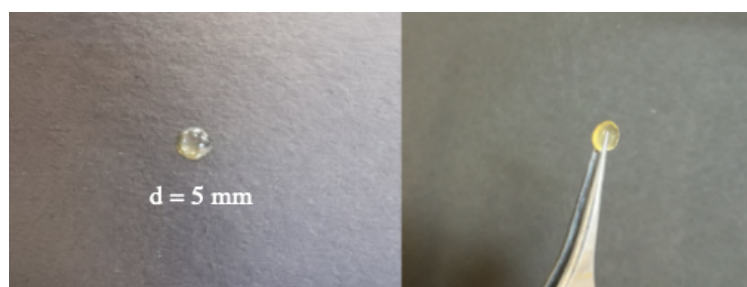


Figure 1. Neat resin semi-sphere droplet-like specimens used for thermal analysis.

2.4. Microbond Test

The microbond test was used to assess the change of IFSS of a single fibre glass fibre/vinyl ester system as a function of short-term, full immersion exposure in deionized water at 23 °C and 50 °C. The microbond test used was built in house and is described in detail by Yang and Thomason [5]. Upon ageing specimens remained in a desiccator of 10% RH at room temperature for 0.5 h prior to testing.

2.5. Gravimetric Analysis and Fourier-transform Infrared Spectroscopy (FTIR)

The gravimetric analysis on neat resin specimens was carried out by removing the specimens from the exposure medium, drying them with paper and weighing them at the nearest analytical balance. Assuming Fickian diffusion, diffusion coefficients were determined for the bulk resin specimens. According to those, equilibrium times were calculated for the film specimens and were compared to experimental data obtained. All equations used were taken from ASTM D5229/D5229M - 20.

An FTIR analysis was carried out for the coupling of the gravimetric measurements. Preliminary results have been included only for the film specimens exposed at 23 °C. A total of 9 specimens were analysed. All measurements were taken using an Agilent Technologies 4100 Exo Scan FTIR. A 45° specular reflectance interface was used for the collection of the spectra. This is a non-destructive interface and allowed multiple measurements of the same specimens at different ageing intervals. A thin

and light-weight stainless steel plate was placed on top of the thin film specimen producing a transfectance effect. This was required due to the partial transparency of the specimen, which can cause the light exerted the interface to dissipate. Spectra were run with background scans between each run at 64 scans and 8 cm^{-1} resolution resulting in a spectral acquisition time of under 30 seconds. All measurements were taken from the centre point of the films and all spectra were averaged and normalized used Origin software per batch. Spectragryph software was used in order to calculate the difference in areas between signals and therefore moisture gain. The integration with baseline tool was used.

2.6. Thermal Analysis

A DSC analysis was carried out to provide insight on the T_g of the matrix at different thicknesses. All results included in this paper are representative of the dry state of the matrix material prior to ageing. A Q20 differential scanning calorimeter with a cooling unit was used for all DSC tests. The instrument was manufactured by TA instruments. The following heating programme was used for each specimen:

- Equilibrate at -10°C and held isothermally for 10 min (cycle 1)
- Temperature ramp at $10^\circ\text{C}/\text{min}$ up to 180°C and held isothermally for 10 min (cycle 1)
- Temperature ramp at $20^\circ\text{C}/\text{min}$ to -10°C and held isothermally for 10 min (cycle 2)
- Temperature ramp at $10^\circ\text{C}/\text{min}$ up to 180°C (cycle 2)

A cool air environment supplied at 50 ml/min was used for all tests. The glass transition temperature could then be assigned from a clear step change visible on the resultant thermal curve of heat flow plotted against temperature.

3. Results

3.1. Gravimetric Analysis and FTIR

The gravimetric measurements for the bulk resin specimens exposed at 23°C and 50°C in deionized water are shown in Figure 2.

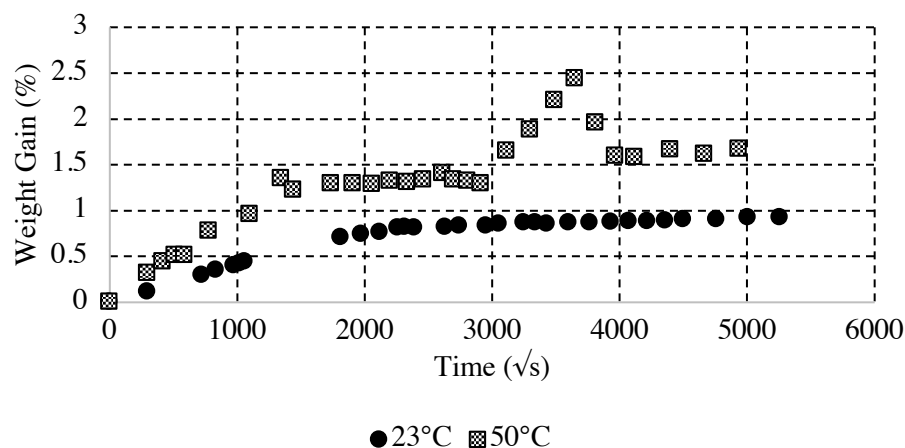


Figure 2. Gravimetric measurements of bulk resin specimens at 23°C and 50°C .

The specimen exposed at 23°C followed a Fickian-like behaviour and reached equilibrium after approximately 2 months ($\approx 2300 \sqrt{s}$) absorbing approximately 0.87% of water. The specimen exposed at 50°C exhibited a different response to hydrothermal ageing. Even though a stabilisation in the weight gain of the matrix was observed after 1 month ($\approx 1800 \sqrt{s}$) of exposure at around 1.3% gain, indicating equilibrium, an abrupt increase in weight was observed after around 3.3 months ($3300 \sqrt{s}$). This was attributed to hydrolytic degradation mechanisms starting to take place within the polymer network of the specimens. Both specimens were re-dried after exposure. It was observed that the specimen exposed

at 50°C experienced a weight loss of 0.6% from its original weight, while the specimen exposed at 23°C experienced no weight change. Assuming Fickian diffusion for both specimens (until initial equilibrium for the specimen at 50°C), the diffusion coefficients were determined and are shown in Table 1. Using the diffusion coefficients of the bulk specimens, a prediction of time to equilibrium for the thin film specimens was carried out and all resulting values are contained in Table 1.

Table 1. Diffusivity values of bulk resin specimens and estimation of equilibrium times for thin films

	Diffusivity (mm ² /s)	Time to equilibrium (√s)	Time to equilibrium (days)	Thickness (mm)
23°C	4.9E-07	275	0.9	0.2
		344	1.4	0.25
50°C	1.37E-06	123	0.2	0.15
		165	0.3	0.2

The gravimetric measurements for the film specimens aged at 23°C and 50°C are shown in Figure 3. Confidence limits of 95% have been included for all gravimetric measurements. The moisture gain measured by the FTIR analysis for the films exposed at 23°C has also been plotted in Figure 3. As shown, the equilibrium time obtained through gravimetric measurements for the film exposed at 23°C was between 2 and 4 days ($\approx 416 - 588 \sqrt{s}$) experiencing a moisture gain of 1.28%. Most values measured by FTIR are within the error bars of the gravimetric data, except for the values recorded the first 24 h ($\approx 293 \sqrt{s}$) of exposure. The films treated at 50°C reached equilibrium almost immediately after they were exposed in the aqueous medium. Strong fluctuations in the moisture gain of the films were observed throughout their exposure. These changes could be attributed to a combination of moisture induced degradation phenomena, such as plasticization, hydrolysis and leaching.

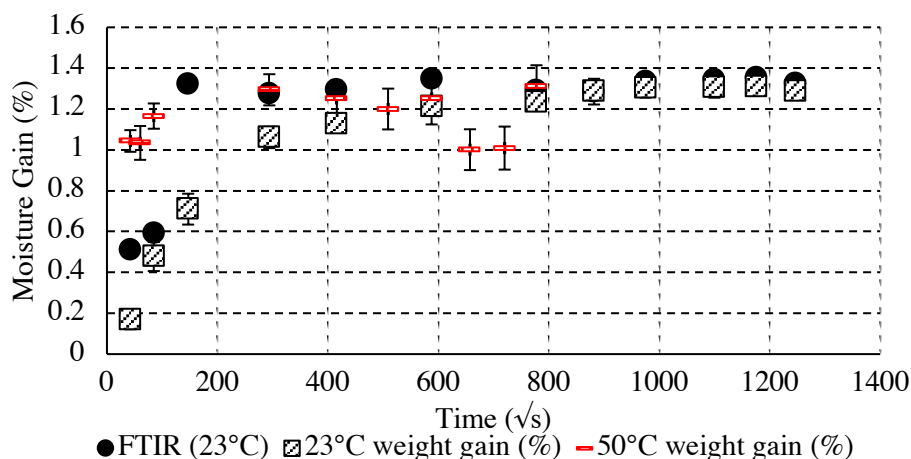


Figure 3. Gravimetric measurements of aged films and FTIR quantitative measurements for film at 23°C.

Hydrolytic degradation and leaching were confirmed by an apparent weight loss of re-dried film specimens. More specifically, a 0.8% reduction from the weight of the virgin specimen was observed after 72 and 96 h of hydrothermal ageing at 50°C and 1.1% after 168 h. This is a clear indication of chemical changes in the polymer structure.

3.2. Thermal Analysis

The Tg values obtained for the bulk resin and films of different thicknesses are contained in Table 2. Both DSC cycles employed are shown in the Table. It was evident that the Tg of the thin films shown from the 1st DSC cycle was within the 59 – 69°C range, depending on the thickness of the film. However, re-heating the film (after heated isothermally at 180°C) resulted to a step change in temperature and therefore a possible Tg at around 107°C. This value was found to be close to the Tg value of the bulk resin specimen.

Table 2. Tg change vs thickness of dry matrix. Tg 1 represents the step change in temperature in cycle 1 and Tg (2) in cycle 2

Thickness (mm)	Tg (1) (°C)	Tg (2) (°C)
0.15 ± 0.2	59	109
0.2 ± 0.2	69	108
0.25 ± 0.2	64	108
2 ± 0.2 ^a	100	107
3.9 ± 0.2	107	110

^asemi-sphere shaped droplet - flat bottom

3.3. Microbond Test

The IFSS of the glass fibre/vinyl ester microcomposites are presented graphically in Figure 4. Confidence limits of 95% are included for each experimental value shown. It was evident that a reduction in the IFSS of the system ($\approx 25\%$) was not present until 72 h of ageing. All the IFSS values recorded prior to 72 h are the same within the range of the 95% confidence limits. On the other hand, an immediate decrease of approximately 28% was observed in the IFSS of the microcomposites conditioned at 50°C. A further drop of 37 - 40% from the dry value started taking place after 48 h. A comparison between a dry and aged (24 h at 50°C) microbond droplet is shown in Figure 5 and is indicative of the moisture induced degradation at 50°C. “Flaked-off” resin components are apparent in the surface of the aged droplet, which may be indicative of leaching, which in turn can contribute to reduced adhesion.

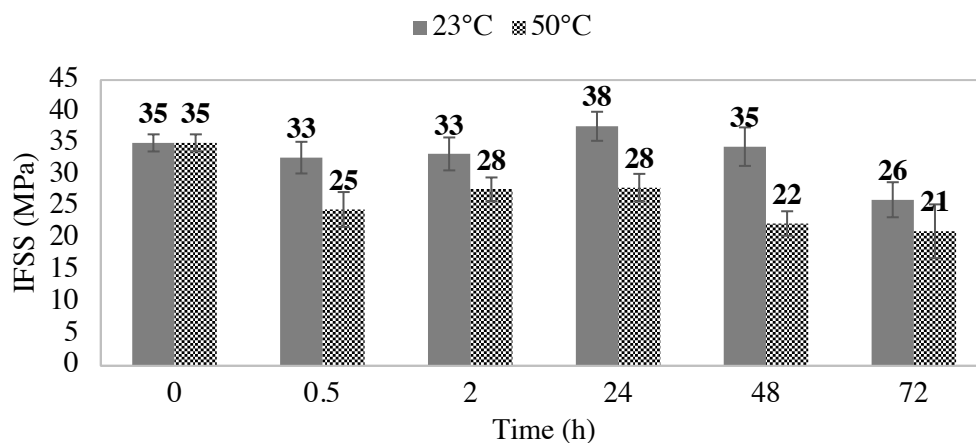


Figure 4: Interfacial Shear Strength as a function of ageing.

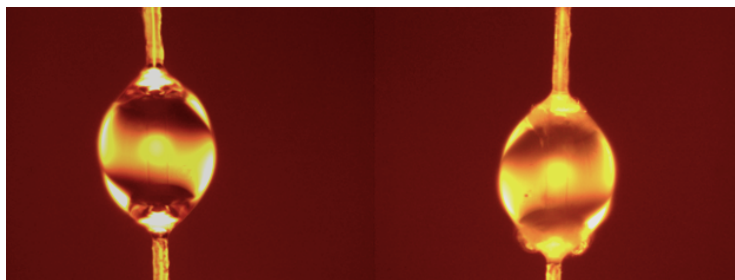


Figure 5. Morphology comparison of dry (LHS) and aged microbond droplet (RHS) on glass fibre at 50°C in deionized water. Images obtained by the means of an optical microscope at 200x magnification.

4. Discussion

Moisture induced degradation was evident from the presented results for both specimens immersed at deionized water of 23°C and 50°C. An unexpected increase in the moisture gain of the bulk specimen aged at 50°C was observed after initial equilibrium. The effect was attributed to probable swelling and plasticization, which are moisture induced degradation phenomena commonly present in thermoset resins [1]. Leaching, which is usually induced by hydrolysis was also confirmed, since the specimen experienced a weight loss of 0.6% from its dry state. A difficulty in extracting all moisture from the specimen was present. A decaying weight loss was observed while the specimen was dried under vacuum for around 2 weeks and after it was firstly induced to a temperature of 50°C for 72 hours, until the weight was stabilised. On the other hand, the specimen at 23°C was fully dried within 72 h under vacuum and no further weight changes took place. The difficulty of drying the specimen was an indication of water molecules trapped within microcavities and capillaries, found in the polymer network of the thermoset making it susceptible to hydrolysis. This effect has been previously studied by S.O. Han [6] and is an indication of chemical ageing. A Fickian-like behaviour was observed for the bulk resin specimen conditioned at 23°C. Physical ageing (reversible degradation) was observed since the specimen was dried out to its original weight after 72 h under vacuum.

Even though the estimation of equilibrium times of the film specimens by using the bulk specimen diffusion coefficients was close to the experimental values recorded, the weight gain behaviour of the films was found to vary from that of the bulk specimens. More specifically, the total averaged weight gain of the film specimens exposed at 23°C was found to be higher than that of the bulk specimen. Nevertheless, the film exhibited a Fickian-like behaviour, similar to the one of the bulk specimen. This was attributed to potential incomplete cure and a variation in the properties of the material, which was justified by the thermal analysis. It was apparent that the Tg of the resin varied significantly with a change in the thickness of the material – the Tg of the films exposed at 23°C was notably lower than that of bulk resin. A similar effect has been presented by P. Zinck and J. Gérard on polyepoxide films [7].

The 50°C aqueous environment was found to be aggressive for the vinyl ester film even after short-term exposure. Saturation was reached by the polymer almost immediately after being exposed to water and strong fluctuations in moisture gain were observed. Similar to the bulk specimen, irreversible ageing took place with the polymer losing approximately 0.8% of its weight after 72 and 96 h of ageing and around 1.1% after 168 h of ageing. Due to the continuous fluctuation in weights and the large error bars it was difficult for an average, maximum weight gain to be identified. However, a relatively stable weight gain plateau was observed between 24 h ($\approx 293 \sqrt{s}$) and 96 h ($\approx 587 \sqrt{s}$) of ageing and a weight gain of around 1.2%, which is close to the 1.3% weight gain value exhibited by the bulk resin specimen at its initial equilibrium. The chemical attack induced by the elevated temperature of the aqueous medium can be justified considering that the film specimens were actually exposed to a temperature close to their Tg (60°C).

Incomplete polymerization is often apparent in thermosets such as vinyl ester resins cured in low or moderate temperature regimes. Incomplete polymerization may potentially increase the susceptibility of the polymer to hydrolysis, plasticization and further deterioration, such as leaching when exposed to hydrothermal environments [8–10]. Thermal analysis carried out on vinyl ester films (≤ 250 μm) was an indicator of incomplete cure of the resin. The T_g obtained in the 1st heating cycle (DSC) ranged from 59 to 69°C depending on the film thickness. However, re-heating the film to a value above its initial T_g increased the T_g of the resin to the same magnitude as the T_g of the bulk specimens.

The link between the moisture level in the composite interphase and its effect on the micromechanical performance of the microcomposite was established through the microbond test. A significant reduction in the IFSS of the specimens aged at 23°C was present after 72 h of ageing, which is the stage when moisture gain equilibrium was achieved in the interphase according to the thin film model. However, no significant changes were identified during the initial stages of moisture uptake. A probable indication is that water is penetrated through the sample thickness and not the interphase. The sharp weight increase of the film treated at 50°C was translated into an immediate compromise in the micromechanical performance of the system. In addition, degradation increased with time and a further decrease of around 40% was apparent after 48 and 72 h. The leaching effect confirmed by the weight loss of the film model and the changes in the microbond sample morphology are indicators that chemical changes are induced in the fibre/matrix interphase. However, microscopy images of a higher resolution as well as a screening of re-dried IFSS values would contribute to the understanding of the degradation effects in more depth.

5. Conclusion

The effect of hydrothermal ageing was found to be severe for the glass fibre/vinyl ester interphase. The increase in temperature not only resulted in accelerated moisture gain but also led to degradation effects for the system. Chemical changes in the polymer were induced regardless of its scale and a reduction in the adhesion between the fibre and matrix was evident after short-term exposure. A reduction in the IFSS at 23°C was observed upon moisture equilibrium. The ageing environment of 50°C was found to be aggressive for the microbond specimens and a sharp moisture gain of the model films correlated with a sharp decrease in the IFSS. There is significant doubt about the transferability of material properties from the microscale to macroscale when it comes to mechanical performance. Moreover, the chemical structure and the moisture uptake kinetics of vinyl ester films were found to be significantly different from those of the bulk matrix. FTIR was found to be a useful tool for quantifying moisture gain in films – nevertheless – a more thorough study to fully quantify moisture uptake in the material would be beneficial. The recording of the films T_g change as a function of hydrothermal ageing will also be useful to provide more insight into the moisture induced degradation in vinyl esters.

Acknowledgements

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