COMPOSITE INTERFACES
2023, VOL. 30, NO. 4, 377–391
https://doi.org/10.1080/09276440.2022.2116842

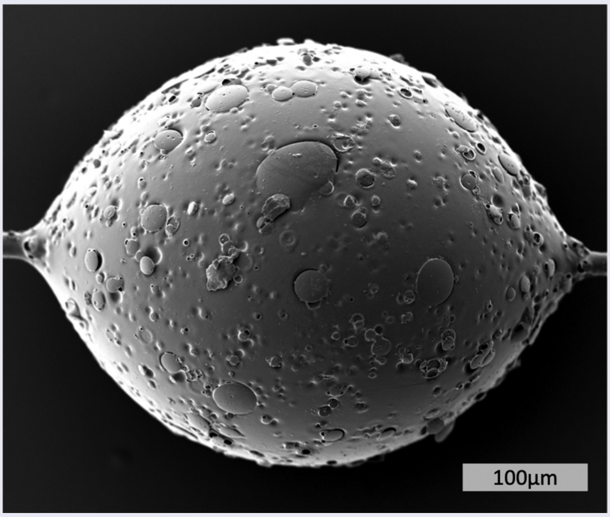
Taylor & Francis
Taylor & Francis Group

The effect of environmental ageing on the interphase in glass fibre – vinyl ester composites

James L Thomason and Georgios Xypolias

Advanced Composites Group, Department of Mechanical and Aerospace Engineering, University of Strathclyde, Glasgow, UK

ABSTRACT
The results of a study of environmental ageing on the apparent interfacial shear strength of glass fibre–vinyl ester microbond samples are presented. The scale related issues of estimating water absorption levels in microbond samples are reviewed and discussed and a solution based on Fickian diffusion is given. Interphase strength of microdroplets aged in water at 23°C was relatively stable up to 6 days exposure after which strength degradation was fairly rapid. Immersion in water at 50°C resulted in an immediate 20–30% irreversible loss of strength. Further exposure beyond 2 days led to total loss of integrity of the microbond samples. Electron microscope images of aged microdroplets appeared to show the development of a bi-phasic microstructure. The presence of two phases in small scale vinyl ester polymer samples was confirmed by DMA on thin films.



ARTICLE HISTORY
Received 9 July 2022
Accepted 21 August 2022

KEYWORDS
Interphase; adhesion; ageing; durability; glass fibre; vinyl ester

CONTACT James L Thomason james.thomason@strath.ac.uk Advanced Composites Group, Department of Mechanical and Aerospace Engineering, University of Strathclyde 75 Montrose Street, Glasgow, Scotland

1. Introduction

The use of glass fibre reinforced polymer (GRP) composites in the renewable energy sector has significantly increased over the last decade. Such GRP composites can undergo significant changes in performance as a consequence of long-term environmental exposure. The work reported here forms part of the larger EU Horizon 2020 funded DACOMAT (Damage Controlled Composite Materials) project whose objective is the development of more damage tolerant and damage predictable low-cost composite materials for use in large load carrying constructions such as bridges, buildings, wind-turbine blades, and offshore structures [1]. It is known that this may reduce durability of the materials and eventually trigger irreversible degradation mechanisms which will affect their properties. The state of the fibre/matrix interphase is a crucial region in defining the reliability, and therefore the durability, of composite materials or structures during their service life [2–5]. Micromechanical single fibre composite testing is one of the few available experimental routes to directly probe the stress transfer capability of the interphase. It has been shown that improvements registered at the microscale do often correlate with improvements in composite macroscale properties [4,5]. Furthermore, moisture ingress at and along the region between the fibre and the matrix is often proposed as a potential route for moisture penetrating into polymer composites. Moisture ingression is known to cause the hydrolysis of the bonds at the composite interphase, resulting in reduced load transfer capability between the matrix and the fibre [2,4].

The scope of the present work is the assessment of the durability of composite laminates and structures through understanding of the changes in the micromechanical performance of the glass fibre vinyl ester (GF-VE) fibre-matrix interphase as a function of the environmental history. Interphase performance, in the initial dry state term and after longer term environmental ageing, has been characterised by measuring the Interfacial Shear Strength (IFSS) using microbond testing [6–9]. This report is about establishing the conditions for ageing of the microbond samples on a baseline GF-VE system which could be used to rapidly screen development combinations much faster than the process of producing full scale composite laminates, long term ageing and then mechanical testing. A challenging aspect of micromechanical testing is the preparation, conditioning and testing of appropriate small-scale samples which still reflect the properties and performance of the same materials in a macroscopic composite. Notwithstanding the name ‘microbond’ test, it should be noted that the mass of these polymer ‘microdroplets’ extends down into the nanogram range [7,8]. Microscale curing issues of thermosetting resin systems have been reported in the literature prior to the development of the microbond test [10] and have been identified as areas for improvement in some of the critical reviews of microbond and micromechanical testing methods [6–8]. However, there has been little significant effort to address this phenomenon directly, despite the growing usage of the microbond test. A number of scale-related issues in the conditioning and testing of samples for this investigation were identified and are discussed.

2. Materials and methods

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 h, 80°C for 3 h and 100°C for 1 h. SE 3030 boron-free E-glass fibres with a vinyl ester compatible sizing were provided by 3B Fibreglass as a 2400 tex direct roving.

2.2. Vinyl ester polymer sample ageing

The thick VE polymer specimens (80 x 80 × 4 mm)were manufactured by using open silicone moulds. VE polymer thin films were prepared by means of a seam roller by applying several resin layers on a silicone rubber substrate. The resin was left at ambient laboratory conditions for 30 min to become more viscous and facilitate rolling before use. All cured film sheets were removed from the substrate were cut into 25 × 25 mm specimens, which were dried under vacuum for 48 h before use. The thin films used for the moisture uptake measurements were 130 ± 20 μm thick and were aged by immersion in deionized water at either 23°C or 50°C.

2.3. Microbond testing

The microbond test was used to assess the GF-VE interfacial shear strength (IFSS) as a function of immersion time in deionized water at 23°C and 50°C. The microbond test used was built in house and has previously been described in detail [6,7]. The general procedure for microbond sample preparation procedure has also been previously described [6,7]. However, for water immersion the microbond test samples could not be mounted on the standard card windows which are often used. Instead microbond samples were prepared by fixing the single fibre specimens to a stainless steel washer by the means of araldite glue [8,11].

A stainless steel rig was manufactured to accommodate microbond specimens, adhered onto stainless steel washers. A high-grade stainless steel was selected for the fabrication of the rig to allow long-term conditioning in wet environments without rusting. Each microbond rig measure 130 × 70 x 2.5 mm with a central window (100 x 20 mm) and contained ten circular incisions – five on each side of the window (see Figure 1). The role of the incisions was to enable the exact positioning of the washers to accommodate the single fibre micro-composites. Each pair of washers opposing each other produced two microbond samples, as fibres were positioned along the length of the inner window, aligned along the vertical axis. The washers were adhered to the circular incisions of the rig by double sided tape and double sided tape was also placed on the top end of each washer for the initial mounting of the single fibres. Each single fibre sample was carefully selected from a fibre roving sample approximately 20 cm long which had been removed from the inside the roving package. One placed in position the fibres were secured with araldite epoxy placed on the inner end of the washer closer to the gap of the

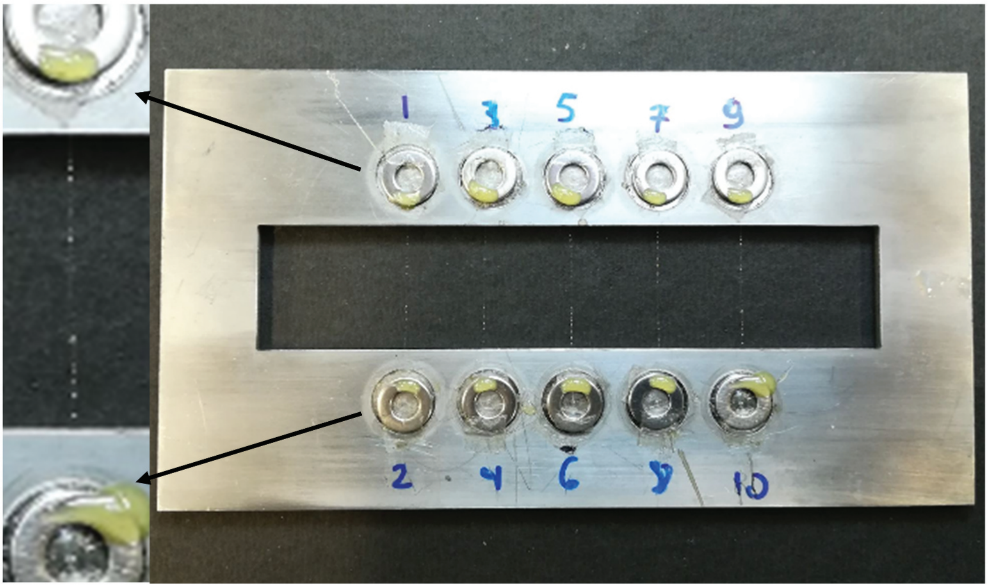


Figure 1. Microbond sample preparation rig with magnified view showing microdroplets on fibre.

rig. The glue was left to cure for a minimum of 2 h prior to micro-droplet application. Extensive care was taken in the application of araldite epoxy to the inner end of the fibre to prevent spreading on the fibre and thus avoid discrepancies in the gauge length value.

Prior to use the vinyl ester resin was stored in a fridge at a temperature of 8°C. It was removed from the resin container by the use of a pipette, was transferred into air-tight containers preventing styrene vaporisation, and was left for 24 h to reach room temperature before use. The liquid resin was placed into a small plastic container by the use of a pipette and curing agent was gradually introduced to the pre-polymer mix by the means of a syringe with a fine needle. Approximately 2 g of resin were used per application. The mixture was weighed using a microbalance and was stirred thoroughly for at least 30 seconds. Several micro-droplets were applied onto each fibre by the means of a short steel wire of 0.125 mm in diameter. The resin application involved the ‘tapping’ of the end of the wire, including a minute volume of resin onto each fibre to form a micro-droplet. Several droplets were applied on each fibre and a dry area was left in the mid-section to define each pair of specimens. Micro-droplet application was followed by the curing of the specimens for 24 h at room temperature under a nitrogen environment followed by post-curing for 24 h at 60°C, 3 h at 80°C, 1 h at 100°C in an air circulating oven.

After curing the microbond samples were examined using a Leitz Ergolux optical microscope, at 200x magnification. The most suitable, axisymmetric droplets were identified for each specimen and droplet diameter, fibre diameter (d), and fibre embedded length (L_e) were measured. Prior to testing, the fibres were cut at the mid-point to producing two microbond samples. Specimens were aged by full immersion in deionized water at 23°C and 50°C using two separate water baths. Once withdrawn from the water baths excess water was removed carefully without any direct contact with the microdroplets. Exposure to the laboratory environment was unavoidable for these aged samples; ten specimens were extracted at a time for testing. This meant that the latter of the ten specimens to be tested remained exposed to ambient conditions longer than the first of the samples and that consequently the exposure time to ambient conditions after ageing varied for almost every specimen. However, this did not appear to have a significant effect on the measured average value of IFSS as no major data scatter was observed between the first and last test specimen in a series. For most of the exposure times a second set of conditioned microbond samples was redried (24 h at 10% RH) prior to testing. The debonding force (F_{max}) for each sample was determined in the microbond test rig operating at 0.1 mm/min and the apparent IFSS calculated using:

$$IFSS = \frac{F_{max}}{\pi d L_e} \tag{1}$$

2.4. Dynamic mechanical analysis

DMA analysis was carried out using a Q800 Dynamic Mechanical Analyser (TA Instruments). Measurements were in tension mode according to ASTM D5026–1 [12] using a 10 µm amplitude with a preload force on 0.1 N and 105% force track. Samples were equilibrated at 25°C for 5 min then ramped at 2 °C/min up to 150 °C.

2.5. Fickian diffusion

The theoretical treatment of moisture absorption in polymers due to Fickian diffusion is well established and the background equations will not be derived here. In terms of what may be happening in the polymer and polymer microdroplet samples we refer to Equation 2 for the time dependent water uptake M(t), as a fraction of the final equilibrium of Me, in an infinite parallel sided slab of thickness (a) made of a polymer with diffusion coefficient (D) [13].

$$\frac{M(t)}{M_e} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2} exp\left[-(2n+1)^2(D\pi^2 t/a^2\right] \tag{2}$$

Similarly Equation (3) describes diffusion into a spherical particle radius (a) [11]

$$\frac{M(t)}{M_e} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2} exp\left[-Dn^2\pi^2 t/a^2\right] \tag{3}$$

3. Results and discussion

3.1 Estimation of water absorption in microbond samples

The standard water absorption investigation method in polymers of measuring sample weight change over increasing exposure time is not applicable to microbond samples. The challenge in applying this method is illustrated in Figure 2. This Figure show results for the dimension determination (length and diameter) of a large number of test microdroplets of VE on the glass fibres used in this investigation. The droplet length and diameter can be used to estimate the droplet volume by approximating the droplet

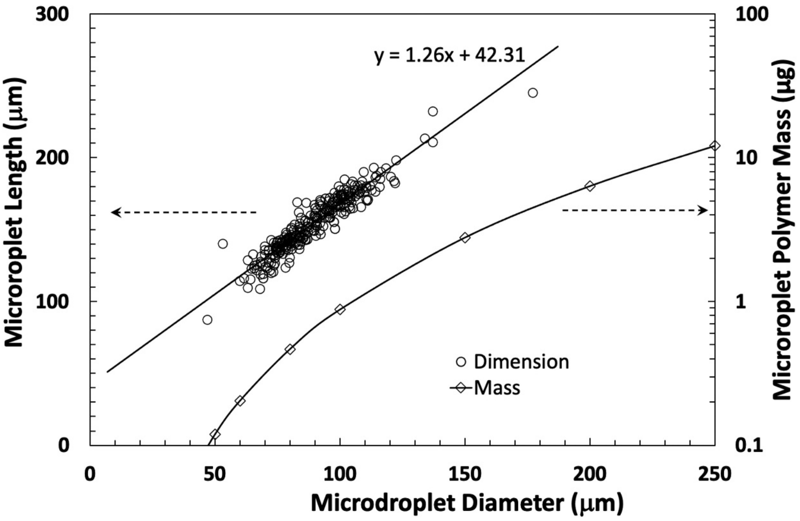


Figure 2. Typical range of microbond sample dimensions and polymer mass.

shape to that of an ellipsoid. After subtracting the small contribution of the fibre embedded in the droplet, the weight of polymer in the droplet can be estimated using the bulk polymer density value of 1.13 g/cc (we assume here that there is no scaling issue changes in the polymer density when going from bulk to microscale). The resulting approximate mass range of polymer in these droplets is illustrated on the right side of Figure 2 (where the droplet dimension have simply be calculated using the best fit line shown from the experimental data on droplet dimensions).

It can be seen that the mass of many of these droplets is less than 1 μg. Standard absorption experiments would therefore require the measurement of the droplet mass with an accuracy better than 1 ng. While this in itself is challenging, the bigger issue is the problems of, removal of excess surface water from the sample before weighing, and the mass of water evaporating from the sample during the measurement process, which result in weight variations much greater than the accuracy of the measurement required. Consequently, it is necessary to design some model of the system to estimate the time scale required in the immersion exposure of microbond samples.

3.2 Vinyl ester polymer water absorption

The weight changes recorded for bulk polymer specimens (4 mm thick plaques) immersed in water at 23°C and 50°C are shown in Figure 3. The specimens exposed at 23°C followed a Fickian-like behaviour and reached equilibrium after approximately 3 months (51 √h) reaching a saturation level of approximately 0.9%. The specimen immersed at 50°C also exhibited Fickian-like behaviour with a saturation level of approximately 1.3% achieved after 24 days (24 √h). Both data sets were fitted to Equation (2)to obtain diffusion coefficients of 0.65×10^{-6} and 2.2×10^{-6} mm^2/s for water absorption at 23°C and 50°C respectively.

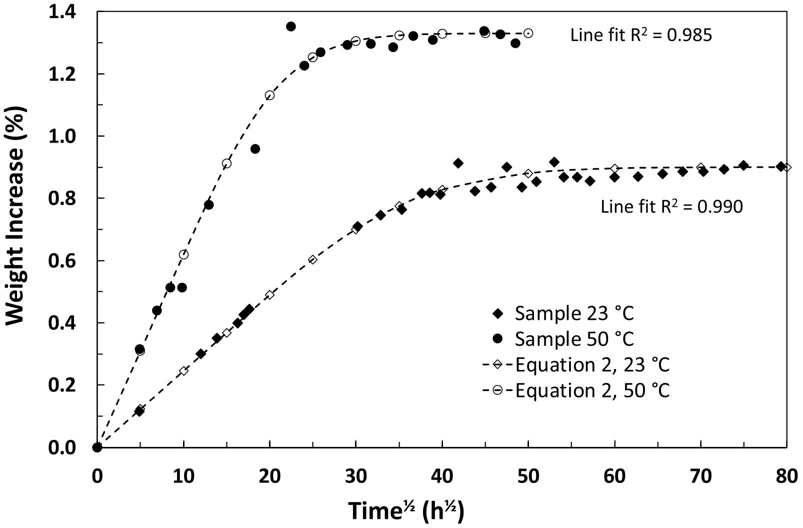


Figure 3. Time dependent water absorption of 4mm thick VE polymer at 23°C and 50 °C.

It is possible to use these values of the diffusion coefficients and saturation levels of the bulk specimens in Equation (2)and Equation (3) to make predictions of weight changes over time of microscale samples immersed in water under the same conditions (assuming that these values are transferable across the length scales involved). Figure 4 shows the predicted relative weight increase for various polymer sample configurations under different conditions.

It can be seen that at 23°C a 100 μm thick film would reach 95% saturation after approximately 70 min immersion in water which is only 1/1600th of the time require for the 4 mm thick sample shown in Figure 3. However, Figure 5 shows an enlarged image of

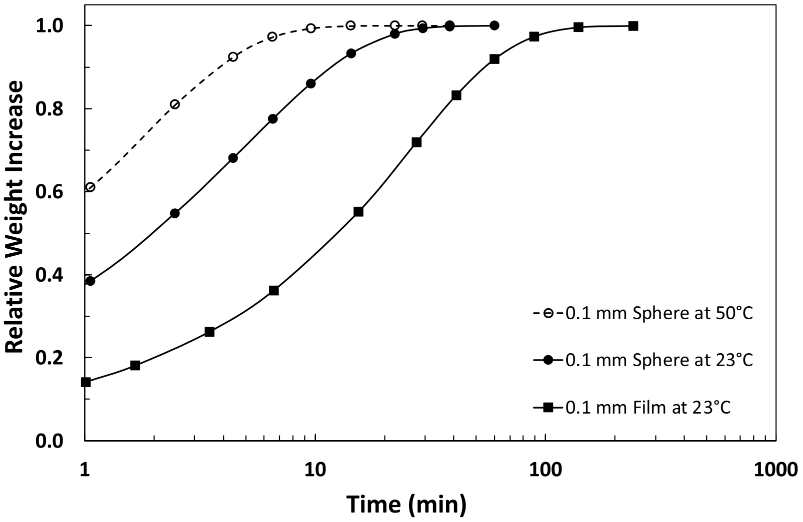


Figure 4. Fickian diffusion into VE polymer sample configurations under different conditions.

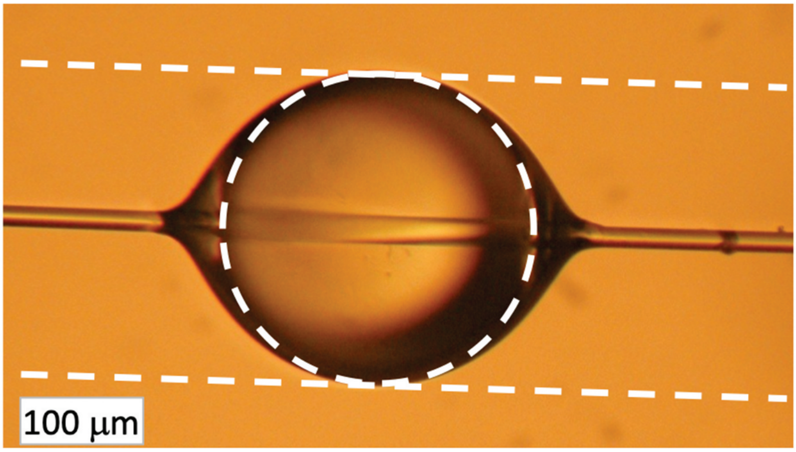


Figure 5. Comparison of thin film and sphere as model for microdroplet diffusion.

a microbond sample from this study. The parallel dotted lines show how an equivalent thickness film would appear compared to an equivalent diameter sphere. It is clear that a sphere is a better model of a microdroplet when considering the available analytical solutions to the 1-D Fickian diffusion equation.

The predicted relative weight change of a 100 μm diameter polymer sphere in water at 23°C is also shown in Figure 4. It can be seen that such a sphere would reach 95% saturation in only 15 min which is only 20% of the time required for the 100 μm thin film. Assuming from Figure 4 that the results for an actual droplet shape are much closer to the theoretical values for a sphere than a film then the estimated time to saturation of such a droplet is approximately 20–30 min at 23°C. Figure 4 also shows results for the weight increase of a polymer sphere in water at 50°C. It can be seen that after only one minute the sphere has already reached 60% of the saturation level and reaches 95% saturation after only 5 min. It can therefore be assumed that a 100 μm diameter microdroplet sample will reach saturation in 50°C water in less than 10 min.

The effect of sample thickness was examined experimentally by measuring the weight changes of thin polymer films (130 μm thick) immersed in water at 23°C and 50°C. Results are shown in Figure 6 along with the predictions of 1-D Fickian diffusion (Equation (2)) using the same diffusion coefficients and saturation levels obtained from the 4 mm thick samples presented above. The film samples immersed at 23°C do initially track the Fickian predictions, reaching the predicted saturation level at approximately 24 h exposure. However, with longer exposure the film samples exhibited small weight fluctuations with a possible trend for weight increase above the original saturation level.

This may be an indication of further moisture-induced effects, including moisture induced plasticisation or even irreversible degradation, such as hydrolysis and leaching [14]. The films treated at 50°C exhibited a rapid weight increase reaching a maximum value at, or before, 5 h exposure, followed by small weight fluctuations typical of experimental variability with continued immersion.

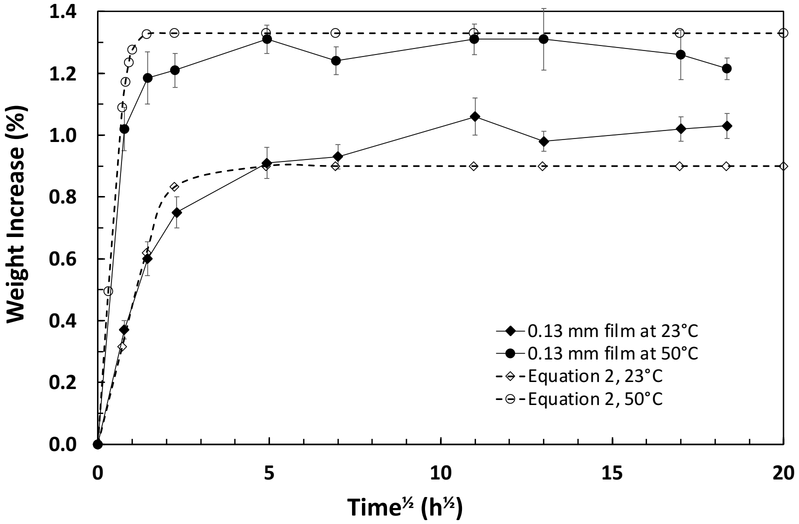


Figure 6. Time dependent water absorption of a thin film of VE polymer at 23°C and 50 °C.

3.3 Microbond results

Figure 7 shows peak force against embedded area results for the dry GF-VE system. This gave a baseline apparent IFSS value of 35.3 MPa for comparison with the hydrothermally aged samples. The results of the microbond testing after sample immersion in water at 23°C are shown in Figure 8. The error bars represent 95% confidence limits of the average values. From the previous discussion and calculations presented in Section 3.2 it can be assumed that all of the data points (with the exception of zero time) were obtained on

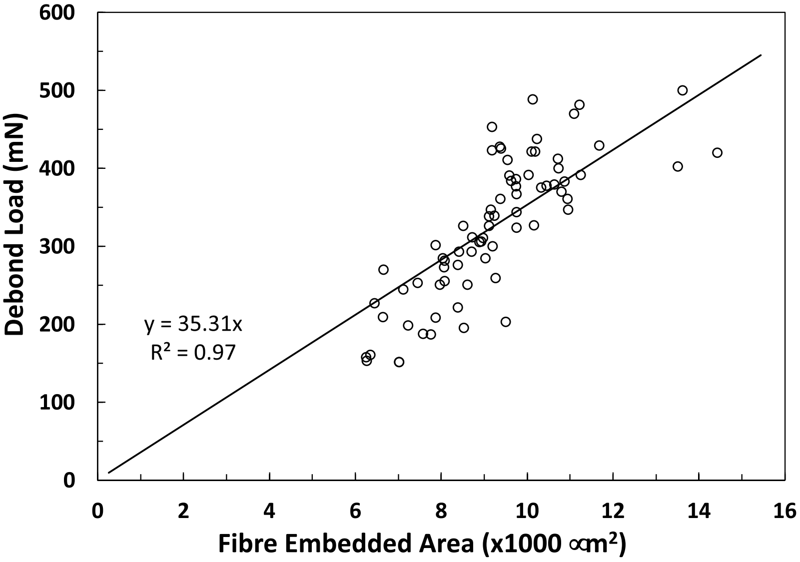


Figure 7. Baseline GF-VE microbond results for debonding load versus embedded area.

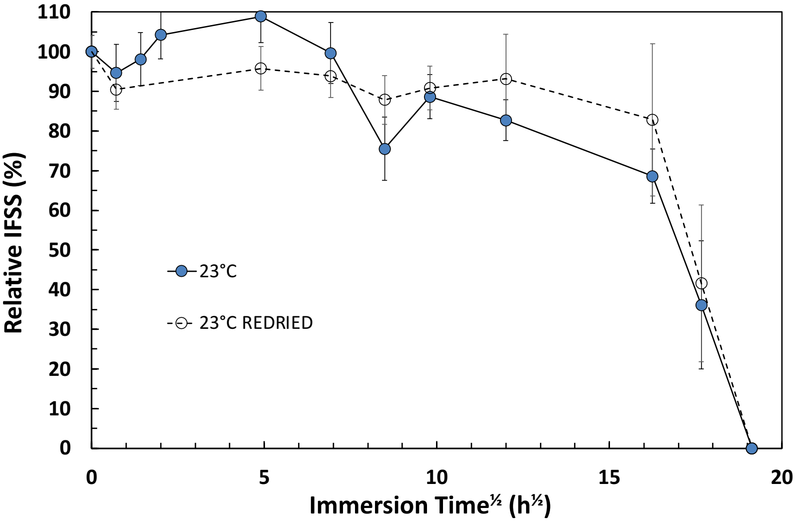


Figure 8. Development of GF-VE IFSS with immersion time in water at 23 °C.

microdroplets which had exceeded the time required by the 1-D Fickian diffusion into a sphere model (Equation 3) to reach saturation.

There appears to be a trend of slightly increasing IFSS in the first 24 h of water exposure. Although none of the average apparent IFSS values up to 24 h are significantly different (*t*-test at 95% confidence level) from the baseline dry values, the value at 24 h (approx. 5 ∏h) has a p value in the t-test of 0.06 when compared to the baseline value and so would be significant at 94% confidence level. Further exposure above 24 h leads to a steady decline in IFSS up to 260 h (approx. 16 ∏h) above which the IFSS drops rapidly. Samples which were redried before testing basically exhibited a uniform 10% reduction in IFSS compared to the initial baseline value up to 144 h immersion. At longer exposures the redried samples tracked the wet samples with a gradual and then steep decline in IFSS. A return to the original IFSS value was not observed with any of the conditioned and redried samples indicating the permanent nature of the change in the interphase caused by the ageing process.

The results of the microbond testing after sample immersion in water at 50°C are shown in Figure 9. Unlike the results at 23°C, the apparent IFSS of the samples dropped by 20–30% almost immediately on immersion in water at 50°C. This level of apparent IFSS was maintained up to 48 h exposure above which the value fell steeply and became unmeasurable after 144 h exposure. Interestingly, the values for the redried samples more or less tracked those of the wet samples and showed little evidence for recovery of interfacial strength upon redrying. This would appear be further evidence of irreversible changes in the samples occurring during immersion at 50 °C.

Figures 10-14 show a series scanning electron micrographs revealing changes in morphology of microdroplet samples which were aged under different conditions. Significant changes in the droplets can be observed when compared with the unaged droplet in Figure 10 which shows a fairly featureless droplet surface. It can be noted that all aged droplets exhibit a diagonal crack across the droplet meniscus, independent of

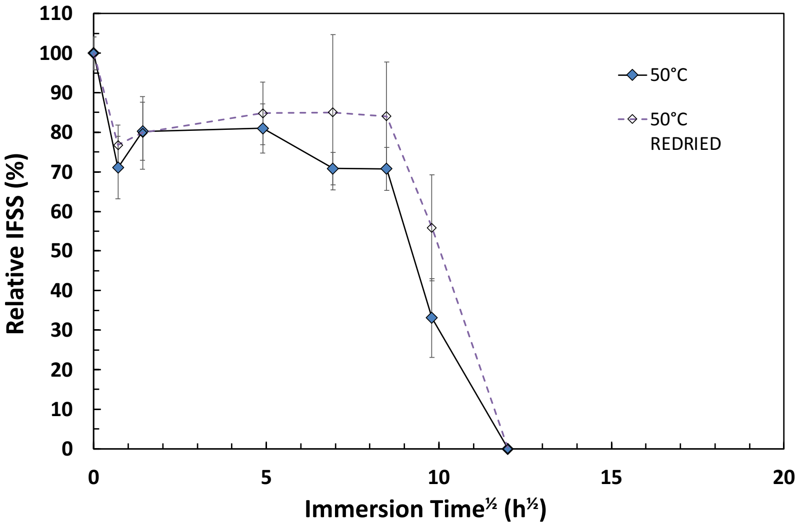


Figure 9. Development of GF-VE IFSS with immersion time in water at 50 °C.

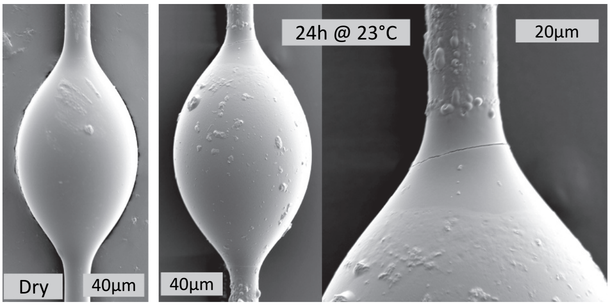


Figure 10. SEM images of VE microdroplet, dry and after 24 h immersion at 23 °C.

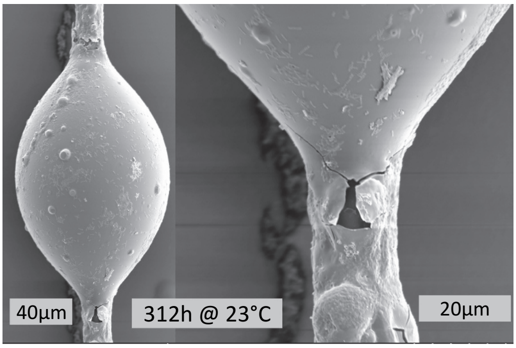


Figure 11. SEM images of VE microdroplet after 312 h immersion at 24 °C.

immersion time or temperature. It can be suggested that such cracks may act as initiators of the debonding process when tested and reduce the required debonding force. Moreover, such cracks may introduce an easier route for water to penetrate directly to

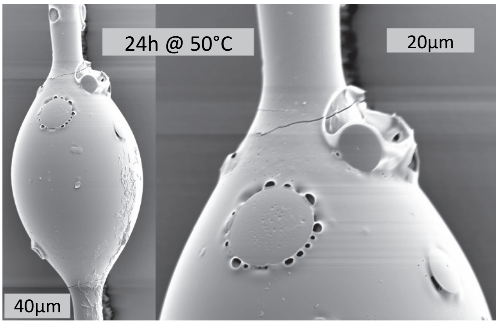


Figure 12. SEM images of VE microdroplet after 24 h immersion at 50 °C.

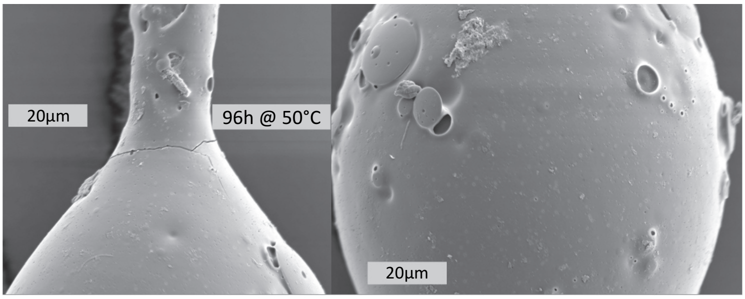


Figure 13. SEM images of VE microdroplet after 96 h immersion at 50 °C.

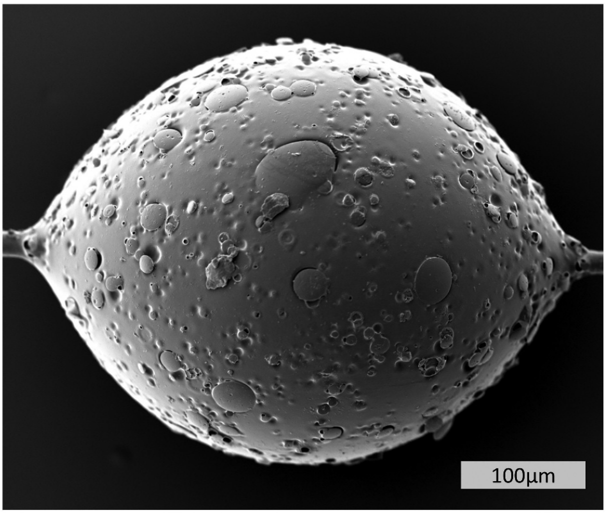


Figure 14. SEM image of a large VE microdroplet after 96 h immersion at 50 °C.

the fibre-matrix interface and consequently may also affect the resultant debonding load-displacement curve during a microbond test. It was further noted that these meniscus cracks appeared to develop into more serious areas of degradation when the droplets had been aged for longer times (see Figures 11-14).

A major form of degradation identified for these aged microdroplets aged was the appearance of surface blistering. In the early stages of ageing this manifested as raised discs on the microdroplet surface. In the later stages of ageing these micrographs clearly show some of the discs in the process of peeling away from the droplet surface. The surface craters where these discs have been removed by the ageing are also clearly visible in a number of the micrographs in Figures 12-13.

Figure 14 shows extensive development of these discs and craters on a large VE microdroplet after hydrothermal ageing for 96 h at 50°C. Ageing has resulted in the formation of disk-shaped blisters throughout the surface of the droplet. There is also clear evidence of cratering on the droplet surface where discs have been removed during ageing, while other discs appear at various stages during the process of being removed. Preferential swelling of one phase may have caused sufficient stress to remove these discs. Alternatively water penetration at the phase boundary may be the catalyst which drives the discs debonding process. In any case the use of water immersion to reveal this interesting microstructure in VE microdroplets invites further investigation.

3.4 Dynamic mechanical analysis of vinyl ester microstructure

Cured vinyl ester polymers have been reported as having a bi-phasic structure resulting from the formation of densely cross-linked microgel structures. More specifically, cured vinyl ester polymers may consist of highly cross-linked methacrylate epoxy compounds surrounded by a lightly cross-linked, styrene-rich region. Vinyl ester curing has been associated with the formation of microgel structures, which have been found to significantly affect the cure kinetics of the polymer. These microgels have been characterized as small clusters, gel particles or tightly packed spheres (high cross-link density) which exhibit a diameter of 0.3 and 1 mm and have the ability to dissolve in some solvents. They are reported to occur mainly in the early stages of the cure and at low temperatures and, are produced by the synergistic reactions of the vinyl ester and styrene monomers. Furthermore, microgels can be generated through styrene swelling of the polymer; microgels contain some styrene monomer but the majority of the styrene is present in the surrounding regions [15–17].

It can be suggested that the discs visible on the microdroplet images in Figures 10-14 may well be evidence for a two-phase structure in the polymer of the microdroplet which has been made visible by the water ageing process. Further evidence for the possible bi-phasic microstructure of VE samples prepared on the microscale was obtained by thermal analysis. As mentioned previously the mass the individual microdroplets is so small as to preclude standard polymer thermal analysis techniques such as differential scanning calorimetry. However DMA was conducted on the VE thin film prepared for the water absorption study. Figure 15 shows the storage and loss modulus curves for film thickness of 165 μm, hence a film with at least one dimension of the same order of magnitude as microdroplet dimensions. The loss modulus curve appears to exhibit a pair of overlapping peaks with well-defined maxima at 88°C and 110°C. Such multiple peaks in DMA loss modulus curves are often assigned to the glass transition temperatures of different phases in the polymer sample. Hence it appears that a bi-phasic microstructure is present in these small-scale VE polymer samples. How this bi-phasic VE polymer microstructure affects the formation and properties of the fibre-matrix interphase will require further investigation.

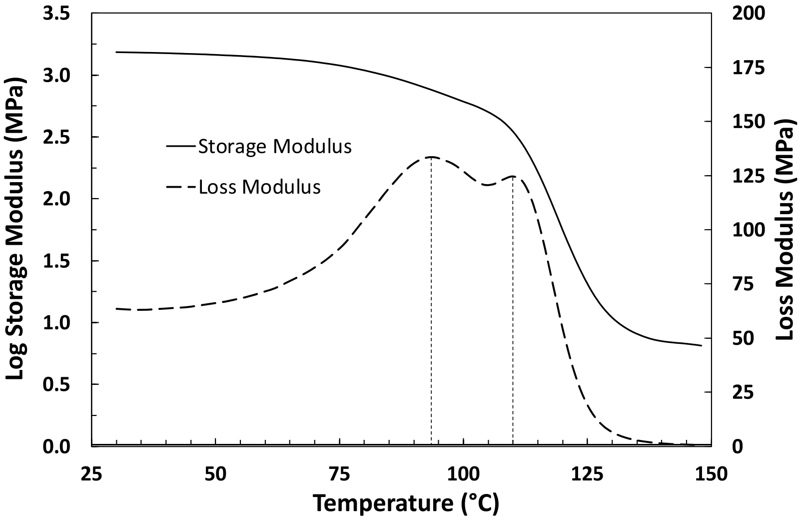


Figure 15. DMA results from a 165 μm thick ve film.

4. Conclusions

The changes in the stress transfer capability of the fibre-matrix interphase is glass fibre – vinyl ester composites upon exposure to water can have important consequences to composite performance. Micromechanical test methods, such as the microbond method, are one of the only methods of directly assessing the state of the fibre-matrix interphase. However, standard gravimetric analysis of sample weight change on water exposure is not feasible given the nanogram scale of the amount of polymer in a microbond sample. The water uptake profile for microbond samples has been estimated through the use of water uptake measurements on polymer samples at different scales and translation to the microdroplet scale through the use of various forms of the Fickian 1-D diffusion equation. It was shown that microdroplets could reach saturation in 50°C water in as little time as 5 min whereas a standard bulk sample required 24 days. The IFSS for microdroplet aged in water at 23°C was relatively stable up to 6 days exposure after which degradation of the IFSS was fairly rapid. Immersion in water at 50°C resulted in an almost immediate irreversible loss of IFSS of 20–30%. Further exposure beyond 2 days led to total loss of integrity of the microbond samples.

The results of a scanning electron microscopy study showed that as VE polymer microdroplets aged small micron sized discs of materials became visible on the droplet surface. These discs eventually peeled away from the surface leaving craters on the droplet surface. It was concluded that the ageing process appeared to expose a biphasic microstructure in the VE polymer microdroplets. Results from DMA on thin VE film samples supported the suggestion of a bi-phasic microstructure in small scale VE polymer samples.

Acknowledgements

This work was supported by the DACOMAT project from the European Union's Horizon 2020 research and innovation programme 5 under GA No. 761072.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

The work was supported by the Horizon 2020 [761072].

ORCID

James L Thomason http://orcid.org/0000-0003-0868-3793

References

[1] www.dacomat.eu

[2] Maxwell AS, Broughton WR Survey of long-term durability testing of composites adhesives and polymers, Report MAT 85. Teddington, UK: NPL Laboratory; 2017.

[3] Thomason JL The interface region in glass fibre-reinforced epoxy resin composites: 2. water absorption, voids and the interface. Composites. 1995;26(7):477–485.

[4] Sethi S, Ray BC Environmental effects on fibre reinforced polymeric composites adv. Colloid Interface Sci. 2015;217:43–67.

[5] Gibhardt D, Doblies A, Meyer L, et al. Effects of hygrothermal ageing on the interphase, fatigue, and mechanical properties of glass fibre reinforced epoxy. Fibers. 2020;7(6):55.

[6] Yang L, Thomason JL Development and application of micromechanical techniques for characterising interface strength in composites. Polym Test. 2012;31(7):895–903.

[7] Thomason JL, Jenkins PG, Xypolias G. Microbond testing of the interface in glass fibre vinylester composites composite interfaces 2021. DOI: 10.1080/09276440.2021.2011593

[8] Thomason JL An overview of some scaling issues in the sample preparation and data interpretation of the microbond test for fibre-matrix interface characterisation. Polym Test. 2022;111:107591.

[9] Haaksma RA, Cehelnik MJ A critical evaluation of the use of the microbond method for determination of composite interfacial properties. Mrs Proc. 1989;170:71–76.

[10] Järvelä P, Laitinen KW, Purola J, et al. The three-fibre method for measuring glass fibre to resin bond strength. Int J Adhes Adhes. 1983;3(3):141–147.

[11] Nagel U, Yang L, Kao CC, et al. Effects of thermal recycling temperatures on the reinforcement potential of glass fibers. Polym Composites. 2018;39(4):1032–1040.

[12] ASTM-D5026-15. Standard test method for plastics : dynamic mechanical properties : in tension. West Conshohocken, PA, United States: ASTM International; 2015.

[13] Crank J The Mathematics of Diffusion. Oxford: Clarendon Press; 1975.

[14] Ghorbel I, Valentin D Hydrothermal effects in the physico-chemical properties of pure and glass fiber reinforced polyester and vinylester resins. Polym Compos. 1993;14(4):324–334.

[15] Stone MA, Fink BK, Bogetti TA, et al. Thermo-Chemical response of vinyl-ester resin. Polym Eng Sci. 2000;40(12):2489–2497.

[16] Ziaee S, Palmese GR Effects of temperature on cure kinetics and mechanical properties of vinyl–ester resins. J Polym Sci, Part B: Polym Phys. 1999;37(7):725–744.

[17] Li P, Yu Y, Yang X Effects of initiators on the cure kinetics and mechanical properties of vinyl ester resins. J Appl Polym Sci. 2008;109(4):2539–2545.