HIGH THROUGHPUT MECHANICAL MICRO-SCALE CHARACTERIZATION OF COMPOSITES AND THE UTILIZATION OF THE RESULTS IN FINITE ELEMENT ANALYSIS

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Abstract
This study presents preliminary results from the micro-scale behaviour of aged glass fibre composites. The examined composite systems consist of a simple epoxy matrix and glass fibres representing E and E6CR compositions. The micro-scale properties are analysed with single fibre tensile tests and microbond tests to study the properties of the glass fibres and the fibre/matrix interphase, respectively. The ageing environments examined in the study are deionized water and 1 g/dm^3 sulphuric acid at elevated temperatures. The high-throughput testing equipment enables large series of samples: a total of 220 single-fibre tensile tests and 425 microbond tests were performed for this study. Selected samples were subjected to pyrolysis gas chromatography/mass spectrometry analysis for information about the chemical structures present in the systems. The data from the microbond test was utilised in finite element analysis to analyse the effects varying material properties have on the results. This procedure revealed crucial information of the effects of aqueous environment ageing and the viability of the microbond test as an experimental characterization method in glass fibre reinforced composites.

1. Introduction

Understanding the various aspects of composite performance is critical in the design of durable and lightweight products. It is also crucial to understand the change in the performance of polymer composites due to ageing and apply this information in simulations for modern product development and design. However, simulating the behaviour of the material in different environments, requires in-depth understanding of its behaviour and accurate analysis of the validation results.

Micro-scale test methods, such as the microbond method [1], can be used to characterize different behavioural aspects of composites. Recent development has resulted in equipment for both single fibre tensile tests [2] and microbond tests [3] which allow high throughput mechanical testing in a statistically reliable manner. However, the analysis of the micro-scale test results must be done carefully.

For example, the apparent interfacial shear strength (IFSS), calculated from the maximum load during the microbond test, might in some cases fail in representing the actual interfacial strength [4]. Different analysis methods for acquiring more specific properties from microbond data are presented in literature [4-9], although large discrepancy has been noted in the results of interfacial studies by different research groups, caused by differences in devices and procedures [10]. It is also important to consider the different interpretations for the debonding and the importance of interfacial friction and thermal stresses in the behaviour of the system [4,9].

In this study, we investigated the performance of two glass fibre grades and one epoxy resin in different ageing environments, with both available micro-scale test methods [2, 3]. The data from the mechanical tests was analysed with Weibull analysis. Finite element analysis was also used to analyse the significance material property variations in microbond testing. Chemical analysis in the form of pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) was included in the study to explore the viability of the method for detecting differences in interphases of different fibre-matrix systems.

2. Materials and Methods

The changes in composite performance with aqueous environment ageing were studied for two glass fibre grades. The nominal diameters of the fibres were 20 μm and 17 μm for E and E6CR fibres, respectively. Both glass grades were kindly supplied by Ahlstrom-Munksjö. The selected epoxy system was EPIKOTE 828 (Hexion) cured with Jeffamine D-230 (Huntsman). There was a significant age difference between the fibre samples. The E6CR fibres were tested within the recommended period of six months from manufacture, whereas the E-glass fibres were several years old. This was expected to result in significant difference in properties due to the age of the sizing.

For the microbond sample preparation, the resin was mixed with the stoichiometric ratio of 32 parts of curing agent per 100 parts resin. A 2 ml volume of the mixture was held in an oven at 40 °C for 2.5 hours before sample preparation to bring the mixture close to the gel state. The sample preparation was done as previously for six filaments from both roving samples [3]. Approximately 50 droplets were deposited on each filament. Post-curing was done at 50 °C for 20 hours. Two filaments for each fibre-matrix combination were selected for each ageing treatment before the testing and two were left as reference. The selected ageing environments were deionized water and 1 g/dm^3 sulphuric acid solution (pH 1.8 at 24 °C) heated to 60 °C. The microbond samples were immersed in the solutions for 24 hours. The relatively mild ageing procedure was selected based on the previous tests, where most of the samples were badly damaged or lost during the ageing procedure.The ageing environments for bare glass fibres were slightly more aggressive to enable notable changes in the fibres to occur. The selected environments were deionized water and 1.25 g/dm^3 sulphuric acid solution (pH 2 at 95 °C) heated to 95 °C. The fibres were immersed in the solutions for two weeks.

The micro-scale mechanical tests were performed on the automatized Fibrobotics instruments [2,3]. For the microbond test AISI 316L stainless steel specimen holders for the FIBRObond intstrument were used to ensure their stability even during the ageing. The gauge-length for single-fibre tensile tests was 23.5 mm and the crosshead velocity was 0.008 mm/s (0.48 mm/min) for tensile and microbond tests.

Two parameter Weibull analysis was done for the fibre tensile tests. The cumulative failure propability $P_{f,i}$ for each sample was calculated using Equation 1 after ranking the samples from the weakest ($i=1$) to the strongest ($i=N$). The results were plotted in the double logarithimic form (Equation 2). From this graph, the Weibull modulus m (slope), scaling parameter σ_0 (calculated from the intercept) and the coefficient of determination R^2 were determined.

$$P_{f,i} = \frac{i-0.5}{N} \quad (1)$$

$$\ln\left[\ln\left(\frac{1}{1-P_f}\right)\right] = m\,ln(\sigma) - m\,ln(\sigma_0) \quad (2)$$

Pyrolysis gas chromatography/mass spectrometry was done as a double shot pyrolysis procedure with a thermal desoprtion step from 90 to 320 °C at 20 K/min, followed by a 3 min pyrolysis step at 600 °C. The measurement system consisted of a EGA/Py 3030D multi-shot pyrolyzer coupled to a Shimadzu GCMS-QP2010 Plus gas chromatography/mass spectrometer. In an effort to observe any possible signals characteristic to the interphase, the analysis was done to a cured sample of the EPON 828 resin, samples from both E and E6CR glassfibres and selected microbond samples.

3. Finite element model

Finite element (FE) methods were applied to understand the sources of specific types of statistical variation in failure load. The microbond test establishes effects due to the structure and material, e.g., the shear stress (also mean value) distribution can be thought to depend on material variation and geometrical setup such as the fibre diamater-to-droplet size ratio, or the microvice blade contact point. Therefore, it is not clear whether the structural variation or the material variation should be input when analysing microbond test data using finite elements. Here, we target to study the influence of material variation with constant droplet size and microvice blade contact. The droplet, the fibre and the test system (sample holder, microvice blades) were modelled and computed using ABAQUS (2017) standard. The test system was modelled in full 3D (Figure 1) using the sample holder CAD model, an ideal fibre model with a spherical cross-section (Ø 17 μm), and a generic droplet model representative of a typical microscope-imaged resin droplet on a fibre.

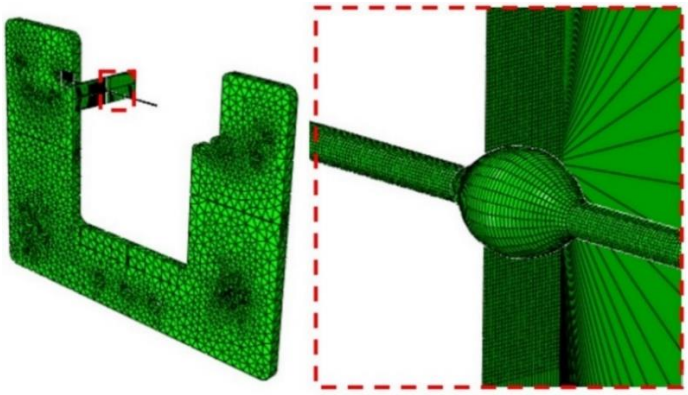

Figure 1. The FE model created to study the effect of modulus deviation in droplet resin.

The fibre was modelled as linear elastic with Young's modulus of 73 GPa and Poisson's ratio 0.3. Ideal, elastic-plastic properties were presumed for the droplet. The droplet Poisson's ratio was set to 0.35 and yield strength to 62.5 MPa [11] but the modulus value was left as variable. The interface between the droplet and the fibre was modelled using cohesive zone modelling (CZM) with zero interface thickness and a cohesive surface. The cohesive surface allows defining interfacial behaviour using a traction-separation law. Here, a bi-linear law was used. The damage initiation was defined using the maximum stress criterion where all the three critical stress values were set to 20.7 MPa. The damage evolution was based on a power law where the exponent was set to unity. The critical limit of the energy release rate per each fracture mode was set to 650 J/m^2. The critical interfacial stresses and energy release rate limits were fitted according to typical test data from the microdroplet tests. This means that the 'interfacial strength' was set constant but the variation in the peak force due to specified droplet's modulus variation was studied.

The FE model was run in an automatised loop by using the simulation engine Isight. For the simulation looping, the droplet's modulus was set as an external variable and was given a specific distribution of values. Here, a normal distribution with average of 3.028 GPa and coefficient of variation 50% was used as input. The calculation space was populated by 100 simulation points, with randomly generated modulus values per analysis case, and the peak force values were collected and automatically analysed in terms of the emerged statistical distribution. An enforced displacement of 100 µm was defined for the sample holder to launch each simulation case.

4. Results and Discussion

The single fibre tensile test results are presented in Table 1. After ageing, some fibres, most propably those corresponding to the lowest initial strength values, were too weak to be tested. This causes the variation of the results to decrease and likely leads to an overestimation of the average tensile strength. From Table 1, one should note the clear decrease in E-glass fibre diameters with ageing. For visualization the results of the Weibull analysis are plotted in Figure 2.

Table 1. Results for the glass fibre tensile tests.

Sample group	No. tested fibres	Avg. diameter [µm]	Tensile strength [MPa]	Tensile modulus [GPa]	Weibull-analysis		
					m	σ(0) [MPa]	R^2
E6CR Ref	45	16.49 ± 1.63	1267 ± 327	70.66 ± 6.79	4.676	1384.4	0.96
E6CR Water	40	17.57 ± 1.92	869 ± 222	54.80 ± 10.02	3.969	961.9	0.95
E6CR Acid	40	17.88 ± 1.97	905 ± 317	58.20 ± 8.66	3.320	1007.3	0.97
E Ref	40	19.25 ± 2.49	794 ± 359	53.61 ± 6.12	2.468	908.1	0.98
E Water	25	18.76 ± 2.59	744 ± 208	57.94 ± 4.02	3.778	825.6	0.97
E Acid	30	16.07 ± 1.97	606 ± 184	50.77 ± 6.62	4.140	667.7	0.88

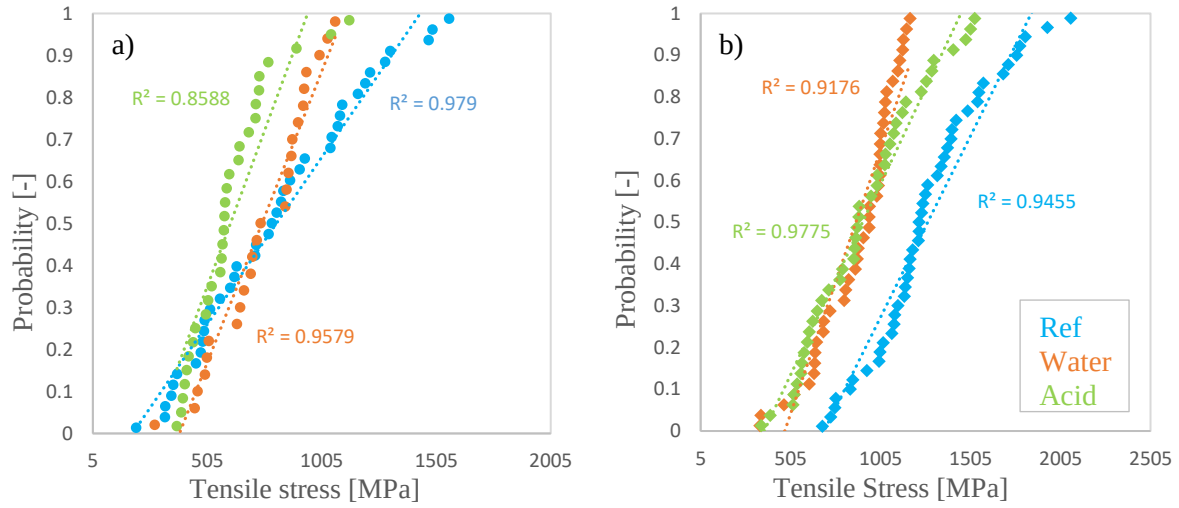

Figure 2. Probability of fibre failure for a) E and b) E6CR single fibres before and after ageing.

The Weibull analysis revealed very different behaviours for the two glass grades (Table 1, Figure 2). The E6CR fibres showed similar results for deionized water and sulphuric acid solution aged samples. Thus, the observed loss of strength is likely caused by removal of the sizing by the hot solution. E-glass

fibres show a significant change in the Weibull modulus, which matches the observation of the difficulties in testing some of the aged fibres. The acidic solution aged samples however appear to exhibit lower strength than the deionized water aged samples.

The microbond test results are presented in Table 2. The IFSS results presented are derived from the linear regression of the peak load vs. the embedded area for the droplet and the variation of the results are represented by the R^2 values [3]. To visualize the results, the maximum force of each microbond test is presented as a function of the adhesion area in Figure 3. The results for individual filaments clearly show a linear dependence on the embedded area, as was also seen by the R^2 values. The variation between separate fibre samples seems to increase significantly with ageing. The results of the reference samples are very similar for both glass grades, but almost identical for the E6CR. For the microbond samples, the Weibull analysis proved mostly inconclusive. However the distributions of the results can be seen from the histograms in Figure 4.

Table 2. Results of the microbond experiments performed with FIBRObond.

Sample group	Fibre	No. droplets/ fibre	Embedded length range [µm]	Fibre diameter [µm]	IFSS [MPa]	Regression R^2
E6CR Ref	1	31	60 - 111	18.1	35.4 ± 1.3	0.97
	2	33	65 - 145	19.2	32.9 ± 1.8	0.92
E6CR Water	1	20	54 - 93	16.8	40.0 ± 4.7	0.81
	2	37	59 - 179	20.2	36.6 ± 1.2	0.97
E6CR Acid	1	26	64 - 135	18.5	45.8 ± 3.8	0.86
	2	39	68 - 142	20.4	30.8 ± 2.6	0.80
E Ref	1	37	72 - 138	22.1	26.8 ± 1.3	0.92
	2	38	66 - 138	20.1	36.5 ± 1.1	0.97
E Water	1	45	57 - 136	17.3	29.7 ± 1.0	0.96
	2	46	53 - 113	16.0	34.6 ± 1.6	0.92
E Acid	1	35	71 - 158	20.6	18.3 ± 1.4	0.85
	2	38	57 - 147	17.6	29.3 ± 1.0	0.96

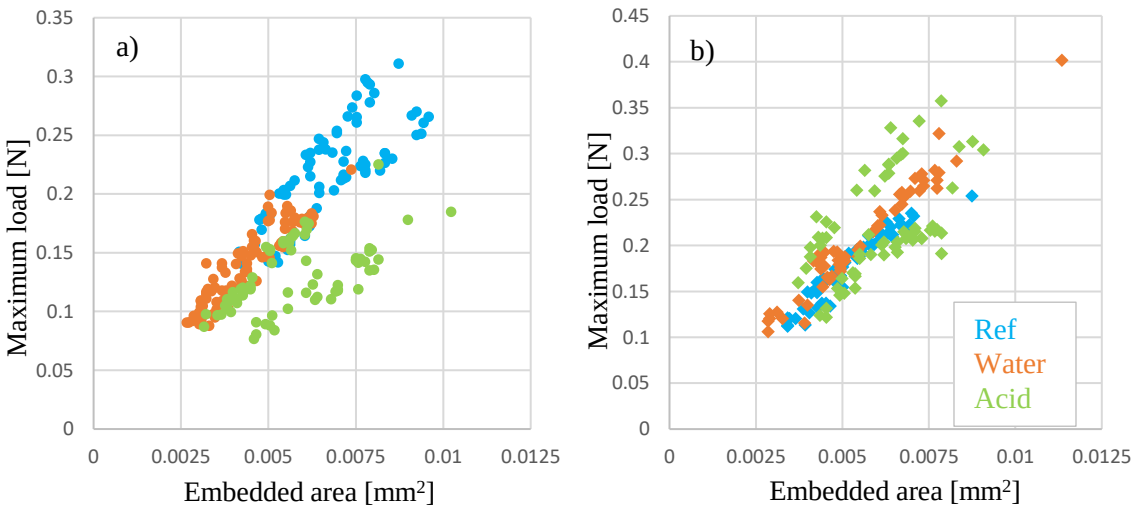

Figure 3. Summary of the microbond experiments for a) E and b) E6CR.

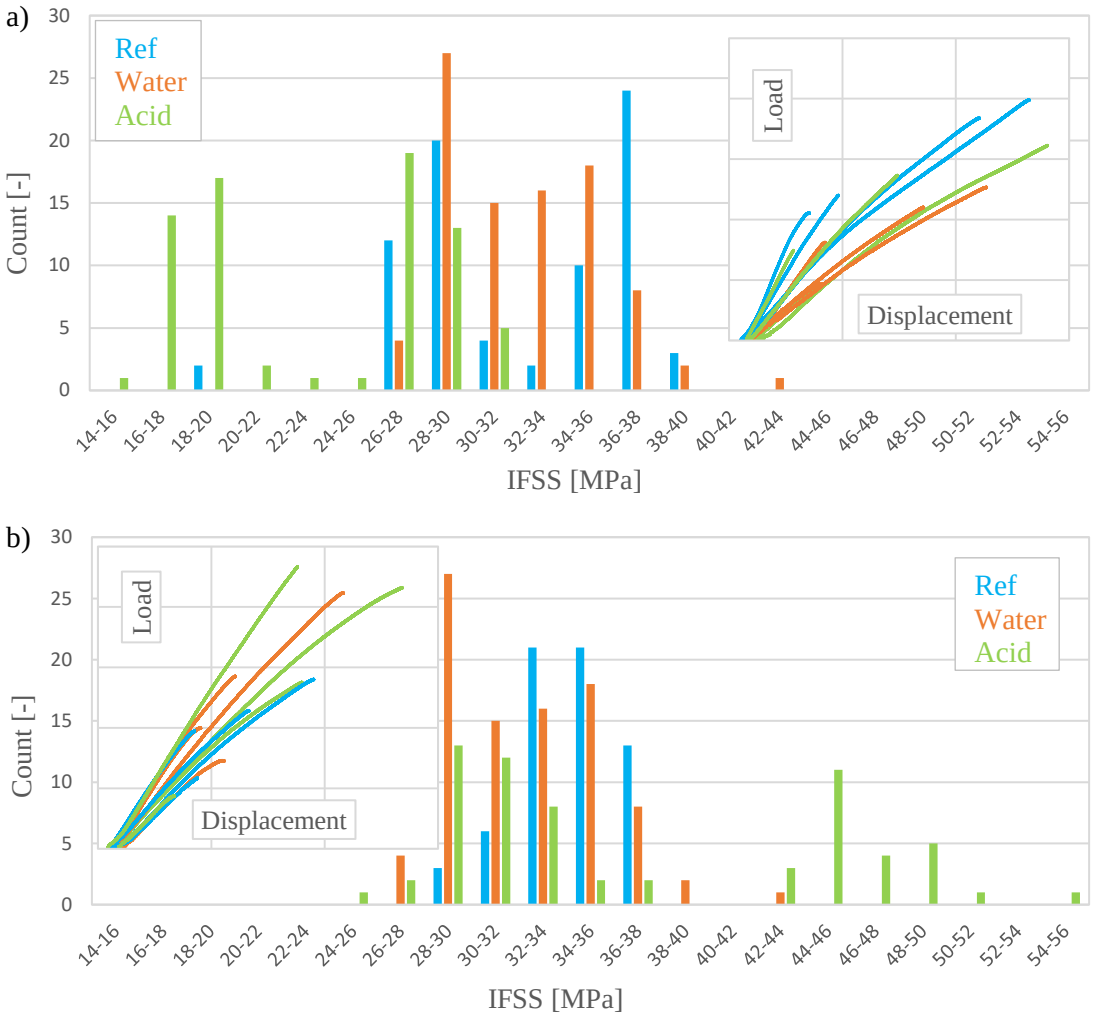

Figure 4. Distribution of the results of microbond testing with examples of the load-displacement curves presented in the overlays for a) E and b) E6CR based samples.

One of the two acid aged E6CR fibre samples represents a significant outlier from the rest of the data. In general one could evaluate that this ageing environment had minimal effect on the E6CR-epoxy system and the outlier probably underwent post-cure during the ageing. The sulphuric acid aged samples show increased variation in the result for E-glass as well.

The Py-GC/MS analysis offers mostly qualitative results. The analysis of the plain glass fibres detects bisphenol-A and long-chain hydrocarbons from the film former/binder used in the sizing. From the E-glass analysis, a bisphenol-A epoxy derivative is detected which indicates an epoxy film former. For the Py-GC/MS test of the cured EPON 828 resin, the major signals include bisphenol-A and polyoxypropylene chains as expected. Other signals of phenol based structures are likely from further degradation of DGEBA structures in the material.

Interestingly, for the microbond samples the Py-GC/MS signals for the thermal desorption and pyrolysis steps mosly correspond to the signals detected for the resins and fibre samples, respectively. This means significant degradation of the resin in the thermal desorption and only residues and the sizing are left for the pyrolysis step. For comparison, an incompletely cured sample of the resin showed huge emissions in the thermal desorption step compared to the properly cured resin sample. This would then indicate

that the degree of cure for the droplets is notably lower than for a bulk sample with the same curing procedure and thus support also our hypothesis for the observed post-curing effect of ageing.

The FE analysis results (Figure 5) show that the normal-distributed modulus of the droplet leads to a modified distribution of maximum, peak force values. The formation of maximum force-modulus pairs leads to a series with the mean trend following initially a parabolic increase. The increase of force with modulus tend to cease and finally form a plateau. In terms of statistical distribution, the median tends to move towards the plateau force level when the range is divided into even steps. In general, the effect of droplet's modulus seems low, even when noting that the interfacial strength was set constant. For a future analysis, several different statistics of the modulus distribution must be considered to form quantitative conclusions.

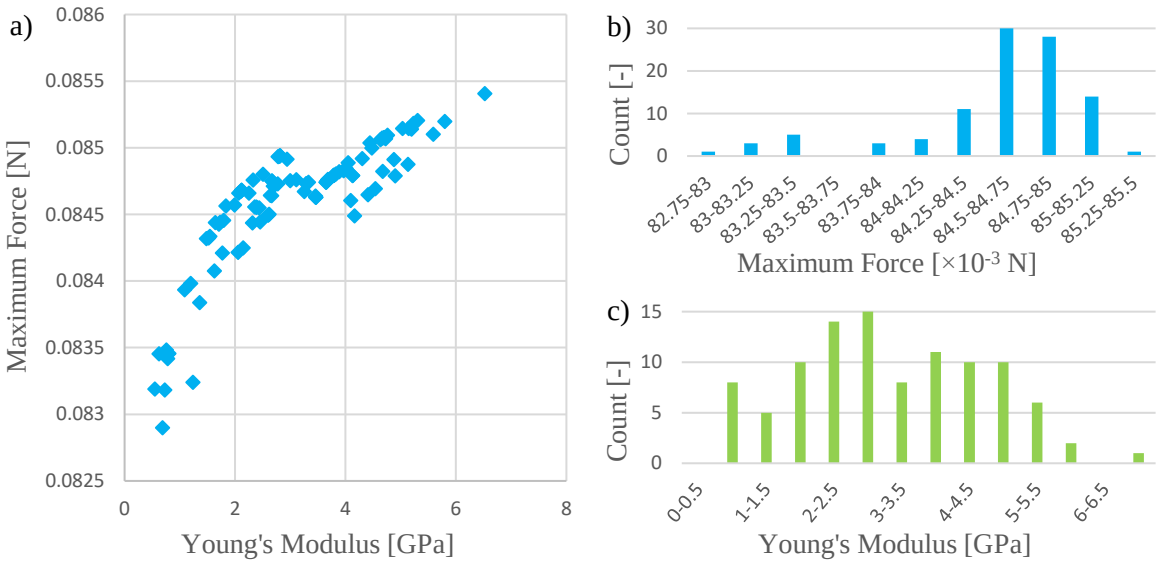

Figure 5. FE simulation results: a) peak force as a function of the droplet's Young's modulus; b) the statistical distribution of maximum force values c) distribution of input modulus values (random sets from normal distribution).

5. Conclusions

In this study, we utilized recently developed micro-scale testing methods to observe the ageing behaviour of glass fibre composites, mainly in terms of the fibre reinforcements and the interphase. High throughput testing methods enabled a large number of individual tests to create statistically relevant data. Based on the analysis, the significant ageing effects of aqueous environments for glass fibre composites include degradation of the sizing layer and the mechanical properties of the glass. However, the decreased mechanical performance of E6CR-glass is mainly due to the sizing layer and likely therefore mitigated in a composite structure. In our tests the tensile modulus of glass fibres, from which the sizing was removed either by age or by aqueous environment ageing was 10–20 GPa lower than the reference, assuming similar mechanical properties for freshly sized E and E6CR fibres. The tensile strength also decreased significantly.

The curing of the microbond test droplets was shown to be incomplete both by the post-curing observed when the samples were aged in elevated temperatures and by the Py-GC/MS analysis. The significance of this phenomena in microbond testing warrants further study.

However, according to the finite element analysis, even a wide range of droplet Young's modulus values does not significantly affect the maximum force during a test presuming the interface strength is constant. The statistical analysis, however suggests that a specific distribution of moduli does not directly get reflected by the maximum force value distribution. In general, the microbond test performed with FIBRObond can be adequately modelled by the created FE model and further analysis of the mechanics of the test will be conducted.

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