

THE INFLUENCE OF TEMPERATURE AND MATRIX CHEMISTRY ON INTERFACIAL SHEAR STRENGTH IN GLASS FIBRE EPOXY COMPOSITES

Ross F, Minty^a, Liu, Yang^a and James L, Thomason^a

a: Department of Mechanical and Aerospace Engineering, University of Strathclyde Glasgow, G1 1XJ, United Kingdom. ross.f.minty@strath.ac.uk

Abstract: *The present work focuses on further investigating the influences of the chemistry of an epoxy system and the testing temperature on the stress-transfer capability of the fibre-matrix interface in a glass fibre-reinforced composite. We discuss how the apparent interfacial shear strength (IFSS) is influenced by the hardener-to-epoxy ratio and testing temperature. The results indicated that the IFSS was strongly dependent on both matrix chemistry and testing temperature. It was observed that the IFSS showed a significant inverse dependence on testing temperature, with IFSS dropping as the temperature was increased for all ratios. Notably it was shown that once the testing temperature was raised above the glass transition temperature (T_g) that ratios possessing excess hardener had larger IFSS values. From the results presented it is hypothesized that residual radial compressive stresses at the interface are influenced by the chemistry of the matrix system and relax away at the higher testing temperatures.*

Keywords: Glass Fibres; Fibre/matrix bond; Interfacial strength; Residual stress.

1. Introduction

With the world's continual growing interest in renewable energy, the designers of wind turbine blades are now under more pressure than ever to produce larger, more powerful wind turbine blades. As such the demand to produce glass fibre-reinforced composites that possess superior mechanical properties has never been higher, with a great level of investment having been placed into research with the goal of broadening our understanding of how to optimize mechanical performance.

If this performance is to be maximised, then it is critical to optimize the stress transfer capability of the interfacial region which exists between the reinforcement fibre and the polymer matrix. If this region is weak, with poor 'adhesion' between the fibre and the matrix, then the composite will fail to reach its true potential in terms of mechanical properties. One accepted mechanically measurable value which can be used to define the strength of the interface is the interfacial shear strength (IFSS) which can be influenced by several factors including the surface chemistry [1], the chemistry of the epoxy system used [2] and the testing temperature [3-4].

Recent work [2-4] has concluded there does seem to be a relationship that exists between stoichiometry, testing temperature and the resulting performance of the interface. However, more work on this subject was warranted in order to fully understand what was occurring at the interface level.

Due to the nature of fibre sizing application, the level of coating applied along the whole length of the fibre is known to vary [5] leading to the potential for localized pockets of epoxy rich or amine rich resin along the entire length of each fibre, threatening overall performance. The influence of these potential small differences in mixture chemistry adhesion with a rubbery

polymer above T_g has never thoroughly been investigated. This paper thus focuses on studying the relationship between testing temperature, the epoxy resin: curing agent ratio (R) and the fibre-matrix interface strength (IFSS) using a microbond technique designed for use within a thermo-mechanical analyser [3].

2. Experimental

2.1 Materials

The experiments were carried out using boron free E-glass fibres, sized with γ -aminopropyltriethoxysilane (APS), taken from larger roving's manufactured by Owens Corning-Vetrotex. The nominal tex was 1200 g/km and the average diameter was 17.5 μm for both. The epoxy resin used was Araldite 506[®] (DGEBA) and the curing agent used was Triethylenetetramine (TETA) with a technical grade of 60%. Both were purchased from Sigma-Aldrich and used as received.

2.2 Sample Preparation

Preparation of the microbond samples began with the application of the glass fibres to sections of 20 mm gauge length card through a combination of double-sided tape and Loctite[®] super glue. Care was taken to ensure that the exposed sections of fibre to be used for the test were protected from contamination, whether through surface or human contact. With the fibres in place, the next task was to apply the droplets of the epoxy resin system.

The mixture of the epoxy system was varied for each batch, with the mass of curing agent applied to the mixture being varied whilst the mass of epoxy resin was maintained at 5 g. This in turn allowed for predefined percentages of TETA to be applied relative to the system. The stoichiometric ratio for the system was calculated as 12.0% TETA, equating to an amine: epoxy group ratio (R) of 1.0. The mass values were monitored to the nearest 0.01 g using a XSE 205 Dual Range analytical balance, manufactured by Mettler Toledo with percentages ranging from as low as 6.8% up to 22.2%, equating to R ratios ranging from 0.55 to 2.08 respectively. The resin mixtures were mixed thoroughly before being degassed for approximately 15 minutes.

The droplet application process involved applying several minute droplets to each fibre, due to the difficulty in producing only a single droplet which would not be too large to test successfully. The application of the minute droplets was completed using a 50 μm piece of steel wire. Once the application process was complete, samples were transferred to a convection oven where they were heated to 60 °C and held isothermally for 1 hour, then further heated to 120 °C and held isothermally for 2 hours. The heating rate was 2 °C/minute for both heating ramps and the samples were left to cool down in the oven overnight.

Prior to testing, all samples were examined under 200x magnification using a Nikon Epiphot inverted microscope to obtain values for the fibre diameter (D_f) and the fibre length (L_E) embedded in the resin droplet. Multiple photos of each fibre were taken to account for all the droplets applied to each sample during the application process. Following testing each sample was re-examined using the Nikon Epiphot inverted microscope to identify the initial primary droplet that had been loaded during the TMA microbond procedure.

2.3 TMA Microbond Procedure

Development of the Thermo-Mechanical Analysis (TMA) microbond technique has been reported previously [3, 6]. The technique uses a TA Q400 thermo-mechanical analyser, in combination with the cooling accessory MCA270 mounted with a film/fibre probe and microbond setup as shown in Figure 1. The droplet applied to the fibre sits on the shearing plate which itself sits on the stationary quartz platform. The movable probe, installed in the centre of the stationary platform, then rests on the paper tab of the sample. It is this probe which applies the load during the test. The entire microbond setup is then enclosed within the TMA temperature controlled, programmable oven. Each sample was initially placed under a very small pre-load of 0.005 N, with the free fibre length between the tab and epoxy droplet maintained at a constant value of 5 mm to match the samples tested in [2].

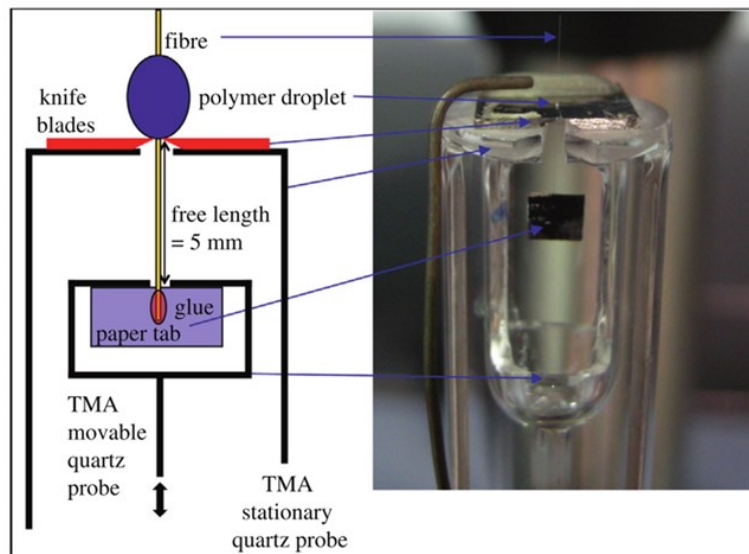


Figure 1. Schematic and close-up photograph of TMA-Microbond test setup.

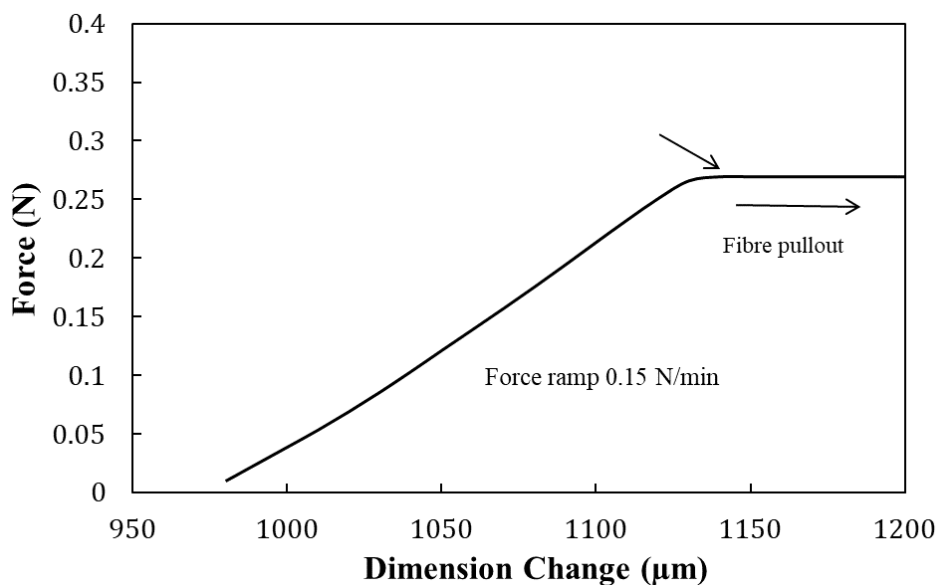


Figure 2. Load/Displacement curve for TMA microbond test.

The notable difference between the TMA and Instron microbond techniques relates to how each technique loads the sample. The Instron technique [2] is carried out by measuring the load generated during the displacement of a droplet at a constant strain rate however the TMA is unable to operate in this mode. Instead, the TMA had to be configured to measure the sample displacement during a linear force ramp of 0.15 N/min [3, 6]. The testing procedure proceeded as follows: the probe displacement was electronically zeroed and the microbond sample loaded into the shearing plate with the paper tab hanging freely below the movable probe. The movable probe was then carefully lowered onto the paper tab before the furnace was closed. The initial sample length and probe position was then recorded, with the furnace then programmed to equilibrate at the desired test temperature (ranging from 20 °C to 120 °C) with an additional three-minute isothermal segment to ensure a constant equilibrium temperature was achieved. The force ramp was then initiated at 0.15 N/min. As the test proceeded the probe displacement would increase and be recorded until a successful de-bond occurred. All tests were conducted under a nitrogen flow of 50 ml/min with approximately 30 samples per ratio tested. A typical result obtained from a TMA-microbond test is plotted as a force–displacement curve in Figure 2. The max force value recorded at de-bond, along with the measured fibre diameter and embedded length, was used to calculate the apparent IFSS value using Eq. (1).

$$\tau_{app} = \frac{F_{max}}{\pi D_f L_e} \quad (1)$$

3. Results & Discussion

Figures 3 to 6 display peak load versus embedded area plots for the samples studied. Figure 3 shows a comparison between the TMA microbond results at 20 °C and the previous published data collected using the Instron microbond technique [2] for R = 1.22.

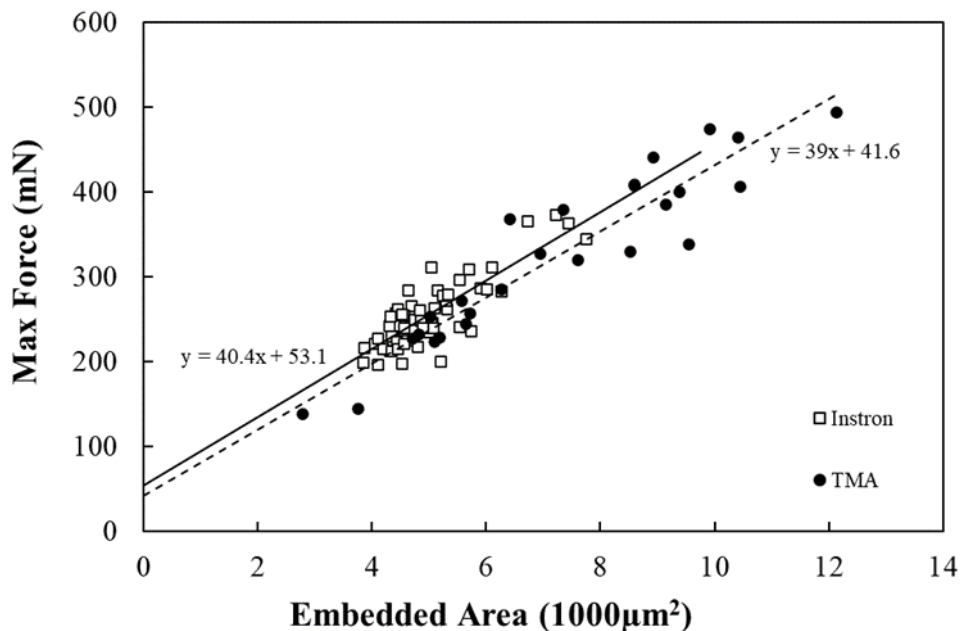


Figure 3. Comparison between force/displacement plots collected using the TMA microbond technique and data collected using the Instron microbond technique, amine: epoxy ratio = 1.22 and testing temperature = 20 °C.

It can be seen that the results collected using the TMA technique correlate well with the results collected using normal microbond testing. Figure 4 shows a comparison between the different testing temperatures for $R = 1.22$. We can see that as the testing temperature was increased, the peak load of the microbond samples decreased, with a notable drop once the temperature was raised above the previous published T_g value of $87.3\text{ }^\circ\text{C}$ [2].

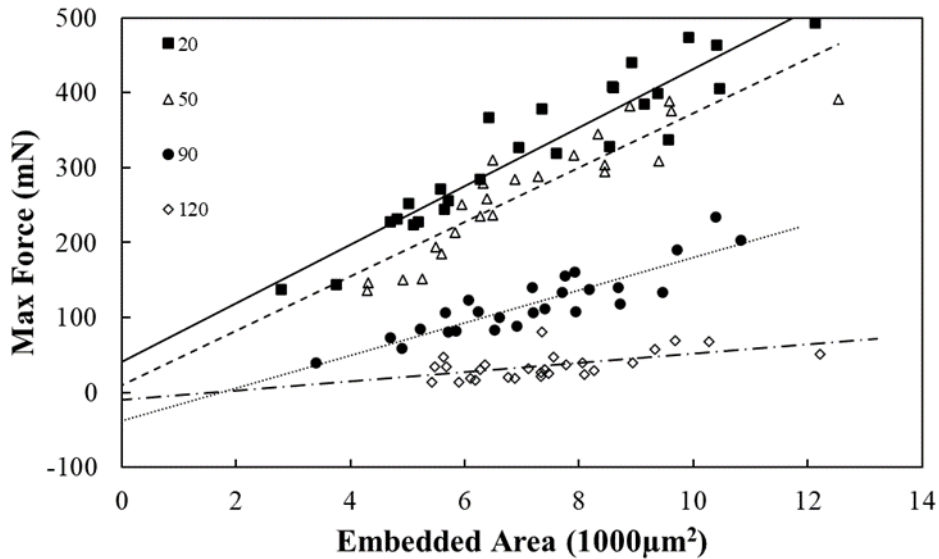


Figure 4. Comparison between force/displacement plots for amine: epoxy ratio = 1.22 at different testing temperatures.

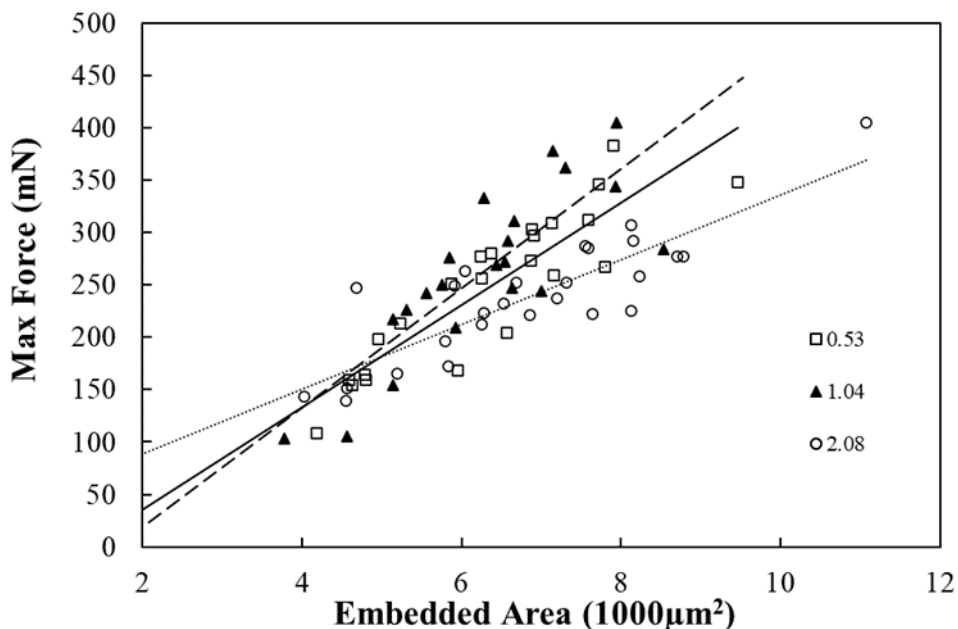


Figure 5. Comparison between force/displacement plots for different amine: epoxy ratios at a testing temperature $50\text{ }^\circ\text{C}$.

Figures 5 and 6 shows plots where the testing temperature was maintained at constant values of $50\text{ }^\circ\text{C}$ and $120\text{ }^\circ\text{C}$ respectively whilst the R ratio of the matrix system was altered. At $120\text{ }^\circ\text{C}$

the effect of changing the matrix chemistry appears greater than at 50 °C. This suggests that the importance of the matrix chemistry to the magnitude of the IFSS may be greater above T_g . It can also be seen that the plot shown in Figure 4 does show some correlation with that shown in Figure 6, with both possessing a notable point of transition.

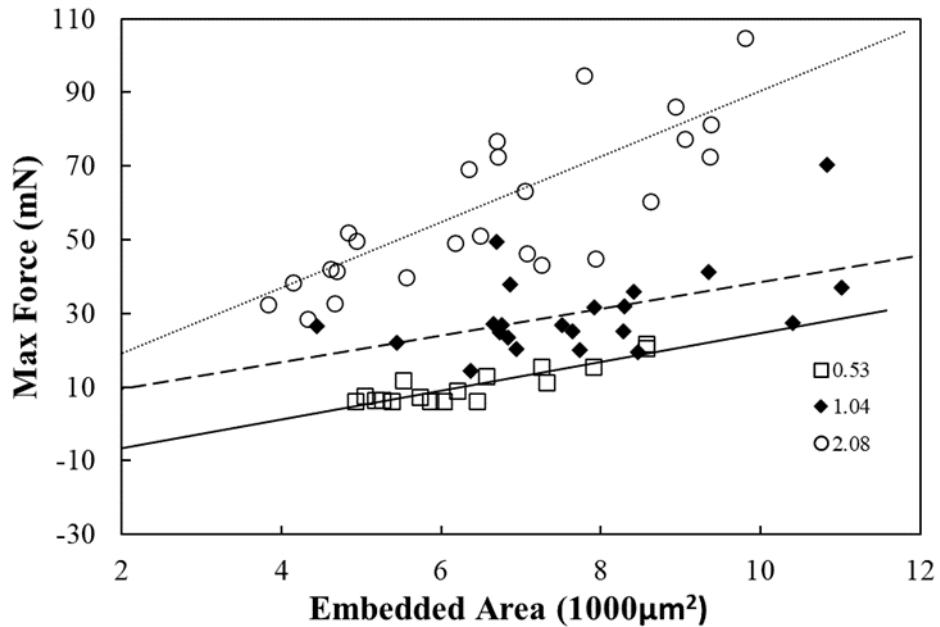


Figure 6. Comparison between force/displacement plots for different amine: epoxy ratios at a testing temperature 120 °C.

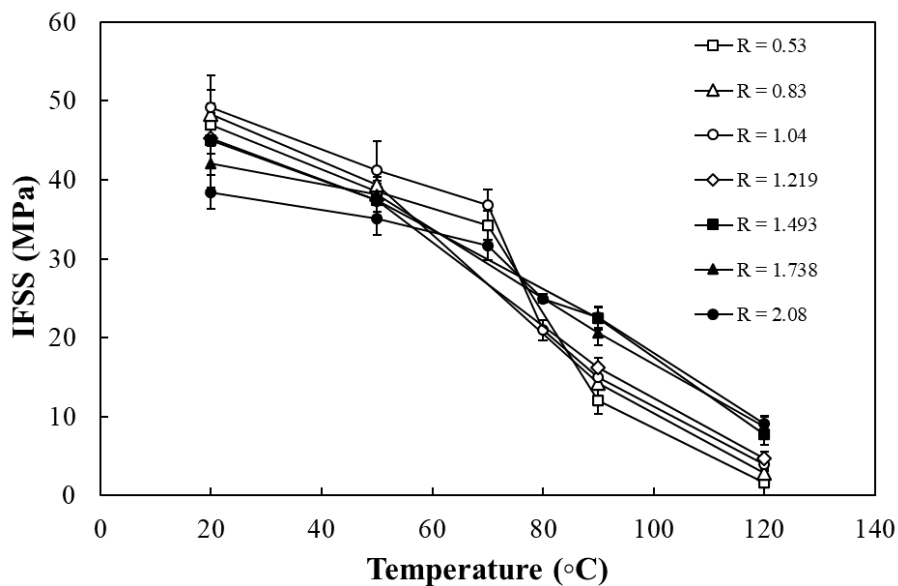


Figure 7. Plot of IFSS versus Testing Temperature.

Figures 7 and 8 present the apparent IFSS values versus the testing temperature and the R ratio of the sample respectively. The data in both figures convey a clear dependence of the IFSS on both the chemistry of the matrix system and the testing temperature. The results in Figure 7 represent the average of individual samples and indicate that the apparent IFSS value decreased

as the testing temperature was increased for all ratios, with R ratios close to the stoichiometric value initially exhibiting the largest IFSS values for temperatures ≤ 70 °C. Interestingly it can be seen in Figure 8 that at temperatures ≤ 70 °C the polymer mixtures containing excess epoxy ($R < 1$) appear to possess higher apparent IFSS values than the polymer mixtures containing excess amine. However, once the testing temperature was increased above T_g the apparent IFSS values appear to decrease less for ratios possessing excess amine ($R > 1$), with this relationship appearing linear at 120 °C. In Figure 7 a notable gap between $R \gg 1$ and $R \approx 1$ can be seen at 120 °C. The observed gradient of transition appears to occur differently depending on the specifics of the matrix chemistry, with ratios where $R \leq 1$ appearing to lose performance sharply once above 70 °C whilst ratios where $R \gg 1$ appear to be less influenced by crossing this temperature. Figure 8 highlights this further by showing that for temperatures below 70 °C, optimized performance occurs around the stoichiometric value but above 70 °C the apparent IFSS value increases as more amine hardener was added to the system. Interestingly, Figure 8 also suggests that there may exist a critical temperature where the IFSS will remain unchanged with changes to the matrix chemistry. This may be the case since the plots for 70 °C and 80 °C appear to be approaching a mid-point where the transition seemingly occurs.

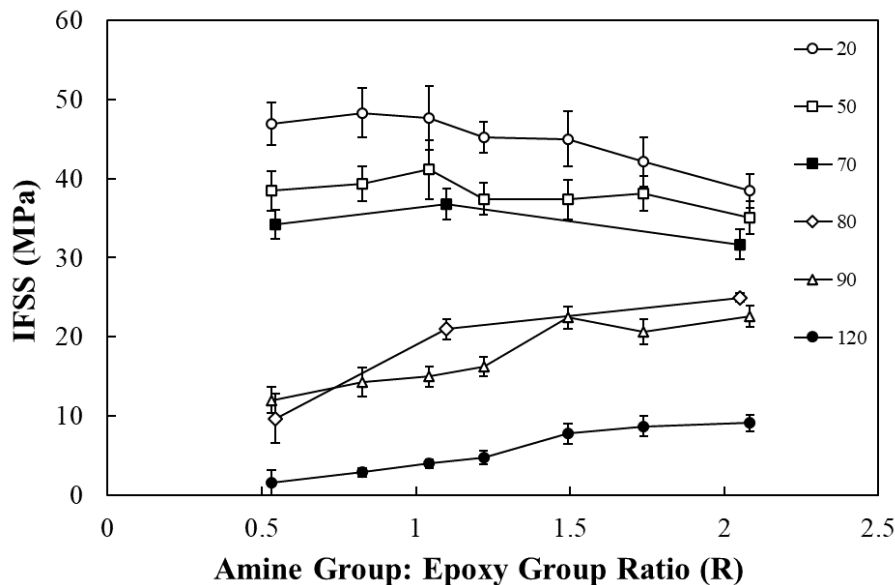


Figure 8. Plot of IFSS versus Amine: Epoxy Ratio (R).

Overall, it appears that the apparent IFSS was clearly influenced by the chemistry of the matrix system as well as the testing temperature, with performance deteriorating consistently as the testing temperature was increased. A potential explanation is that the residual radial compressive stresses (σ_r) formed at the interface during the curing process are being influenced by the properties of the matrix and relaxing away as the test temperature increases [3, 6]. An explanation for the linear apparent IFSS trend shown at 120 °C is that due to the increasing amine content introduced to the system via the extra hardener, there is a combination of an increase in hydrogen bonding as well as an increase in the shear failure behavior of the matrix.

4. Conclusions

The results presented in this paper show that the hardener-to-epoxy ratio and testing temperature both influence the stress transfer capability of the interface in a glass fibre-

reinforced epoxy composite, and in some cases significantly. Each hardener-to-epoxy ratio tested was shown to possess different apparent IFSS values at each testing temperature. Below the epoxy polymer T_g , the highest apparent IFSS value was shown to occur at the stoichiometric value, with apparent IFSS decreasing as the ratio deviated further from this value. However, as the temperature was increased a transition in apparent IFSS was observed when the testing temperature exceeded 70 °C. Whilst interfacial performance continued to decrease overall after this point, the optimum relative apparent IFSS value was shown to improve linearly when more amine was added to the epoxy system. This was the case even at 120 °C.

It was hypothesized that there was some correlation between the deterioration in apparent IFSS observed and the potential relaxation of the “frozen” in residual stresses at the interface as the temperature was increased. It was also observed that at temperatures well above T_g a small value of apparent IFSS still existed, despite the proposed residual stresses having likely relaxed away. It was hypothesized that an increased level of hydrogen bonding, due to the increasing amine content of the matrix system, combined with the variation in shear failure behavior of the matrix due to the differing crosslink densities, was potentially responsible for this.

One practical conclusion from the results presented here is that performance of the interface in thermoset composites is strongly related to the chemistry of the polymer matrix adjacent to that interface as well as the temperature of the surrounding environment. Fibre sizings typically contain chemical reactive groups similar to the polymer matrices in order to promote ‘adhesion’. Such coatings are typically not applied consistently, which may well result in unexpected local variations in the R ratio. Hence it is possible that key interface properties of a glass fibre-reinforced epoxy composite may vary along the entire length of the embedded fibre. Small changes in R may result in small variations in the level of adhesion with minimum impact on performance. However, if the variation from the stoichiometric value is large enough then there may be potential for a significant impact on performance of the final composite material, with the effect of this increasing with rising temperatures.

Acknowledgements

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5. References

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