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TESTING TEMPERATURE ON INTERFACIAL SHEAR STRENGTH MEASUREMENTS OF EPOXY RESINS AT DIFFERENT MIXING RATIOS

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ABSTRACT

The interfacial properties as Interfacial Shear Stress (IFSS) in fibre reinforced polymers are essential for further understanding of the mechanical properties of the composite. In this work a single fibre testing method is used in combination with an epoxy matrix made from Araldite 506 epoxy resin and triethylenetetramine (TETA) hardener. The IFSS was measured by a microbond test developed for a Thermal Mechanical Analyzer. The preliminary results indicate that IFSS has an inverse dependency of both testing temperature and the mixing ratio of hardener and epoxy resin. Especially interesting was the decreasing dependency of mixing ratio at higher temperature.

1 INTRODUCTION

Glass fibres are by far the most common reinforcement used in the composite industry. For many years the focus has been on improving design, structure and processing. With an increasing interest in building larger and stronger constructions a need for understanding composites on a microscale level has arisen [1]. The performance of glass fibre reinforced polymers is affected by the adhesion between fibre and matrix. The interface chemistry and the compatibility with the matrix are believed closely related to the adhesion while the matrix composition is another important factor [2]. The effect on the composite properties by small changes in glass fibre, matrix or sizing composition can be very complicated and expensive to evaluate using full-scale composites. Measuring the interfacial shear strength (IFSS) by single fibre testing can be a valuable indicator of the nature of the adhesion between glass fibre and polymer matrix. However, IFSS can be measured by several different experimental methods, and thus it is difficult to compare the values found in literature. The most used methods for measuring IFSS are fragmentation test, indentation test, pull-out test and microbond test [3-5]. The simplest way to calculate IFSS is by equation 1 assuming a constant shear along the interface:

$$\tau = \frac{F_{max}}{D \cdot L_e \cdot \pi} \quad (1)$$

Where F_{max} is the maximum force, D is fibre diameter, and L_e is the length of embedded fibre.

The laboratory developed microbond technique for thermal mechanical analyzer (TMA) proposed by Thomason and Yang [6] presents the option of temperature control during testing. They have shown a correlation between the measured IFSS and the testing temperature, which depends on the glass transition temperature (T_g) of the matrix used. The present work investigates the temperature correlation with an addition of varying the mixing ratio of epoxy matrix (given as weight percentage of hardener of the total weight), since it is known to influence the T_g of the matrix [7].

From literature it is expected that the IFSS will be higher with lower testing temperature for epoxy matrix based composites. The inverse relation between IFSS and testing temperature is explained by a decrease in the strength of the matrix and not of the fibre-matrix interface [8].

The effect of changing the mixing ratio of epoxy resin and hardener relates to the chemical structure and properties of the matrix. Cure shrinkage, gelation and crosslinking will possibly play a role in how IFSS is affected by the mixing ratio. Together with testing temperature it is attempted to get an indication of how IFSS is affected.

2 MATERIALS AND METHODS

The analysed fibres are E-glass fibres (17 μm diameter of monofilament) coated with γ-aminopropyltrimethoxysilane supplied by Owens Corning-Vetrotex. IFSS was measured by a microbond test technique developed for TMA (a Q400 from TA instruments) by the Advanced Composites Group at University of Strathclyde [6,9]. The samples were produced with approximately 80 mm single fibres from roving bundles mounted on cardboard frames ensuring a length of 5mm between the frame edge and the droplet.

Droplets of epoxy matrix made from Araldite 506 resin and triethylenetetramine (TETA) hardener both purchased from Sigma-Aldrich were applied to the single fibre with a thin steel wire. Epoxy resin and hardener were mixed in different ratios around the stoichiometric value and subsequently degassed for approximately 15 minutes. The samples were placed in a convection oven which was heated to 60 °C and kept there for one hour then further heated to 120 °C for two hours. The samples were left in the oven to cool down over night.

The dimensions e.g. fibre diameter, embedded fibre length and maximum droplet diameter of each sample where determined before testing by image analysis using a Nikon Epiphot inverted microscope with 200× magnification and the image processing program ImageJ.

The microbond test for TMA is described in detail by Thomason and Yang [6]. The setup is basically retaining a droplet embedding a fibre while loading the fibre in tension until the droplet debonds and releases the fibre. The maximum force was determined for each sample from the load-displacement curve obtained during testing. Retaining the droplet was done with a two knife blade wedge and the loading by the movable quartz probe in the TMA and a paper tab glued to the fibre. The probe was pulled with a speed of 0.1 mm/min.

3 RESULTS

The pulling force was measured until the droplet debonded off the fibre and paired with the embedded area of the tested droplet. Three batches of epoxy matrix for droplet samples were made, each with different mixing ratio between epoxy resin and hardener given as a weight percentage of the hardener, TETA. The droplet samples were visually analysed before testing to obtain the dimensions of the embedded area and after testing to confirm the debonding.

The glass transition temperature of the epoxy matrix system depends on the mixing ratio. The highest T_g value is located around the stoichiometric ratio between epoxy resin and hardener [7]. Three mixing ratios were chosen: below, around and above the stoichiometric value listed in table 1.

Thomason and Yang [9] have showed a correlation between testing temperature and the measured

IFSS value with a clear separation of the results into groups: above, around and below T_g of the matrix. The highest values of IFSS were found at testing temperatures below T_g and the lowest IFSS values at temperatures above T_g. The testing temperatures for the three different mixing ratio batches were based on these results yielding four different testing temperatures since the mixing ratio below (batch 1) and above (batch 3) the stoichiometric value resulted in approximately the same T_g.

	Batch 1	Batch 2	Batch 3
Mixing ratio (wt.%)	7.7	14.7	20.4
Approximate T_g (°C)	50	80	50
Testing temperatures (°C)	20, 50, 80	50, 80, 110	20, 50, 80

Table 1: Schematic overview of the varying parameters of the three batches. The mixing ratio given as weight percentage of hardener against the total weight of hardener and epoxy resin.

The IFSS values are calculated as in equation 1 from the individual measurements of F_{max} and embedded area. The average values of IFSS of the three different mixing ratio batches are displayed in relation to both mixing ratio and testing temperature in the interaction plot in figure 1. Each point covers around 20 individual measurements.

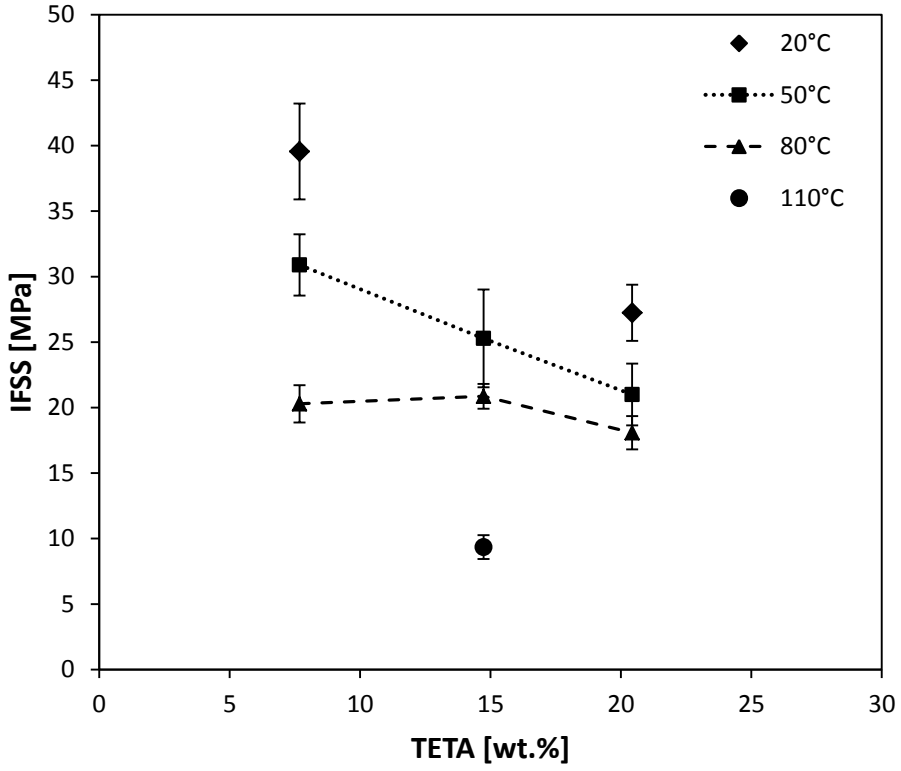

Figure 1: Interaction plot of Interfacial Shear Stress (IFSS) as a function of both testing temperature and mixing ratio, given as the weight percentage of hardener (TETA) against the total weight of hardener and epoxy resin. The 95% confidence intervals are displayed for each data point.

Within the same mixing ratio the results exhibits the same correlation as described in literature [9-10]: the higher the testing temperature the lower the IFSS value. Comparison of the tendency with varying mixing ratio gives the indication that the correlation is most pronounced at lower mixing ratios but more data points will be needed to support or dismiss this. Another possible correlation is that high testing temperatures will yield similar values of IFSS not affected by the mixing ratio.

4 DISCUSSION

The experimental dataset covers three mixing ratios: below, around, and above the stoichiometric value and for each mixing ratio three testing temperatures were chosen: below, around, and above T_g. This leaves the dataset incomplete when focusing on testing temperature as there is only two data points for tests performed at 20 °C and only one at 110 °C. These data points are pending but a suggestion of how the data will be distributed is displayed in figure 2 based on the data obtained at testing temperatures of 50 and 80 °C.

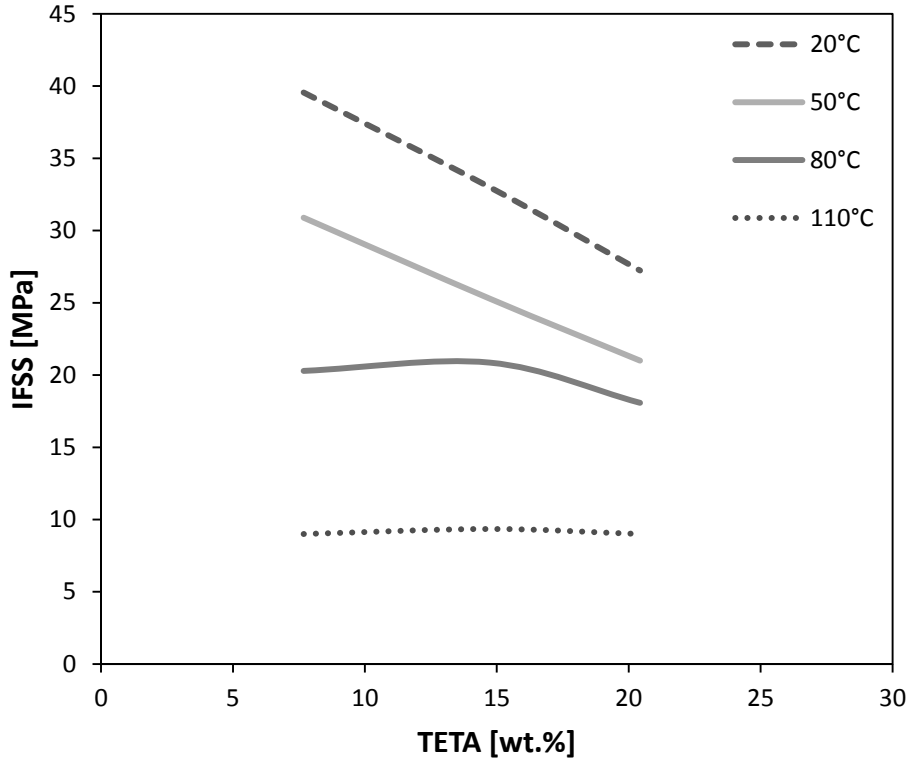

Figure 2: Plot of Interfacial Shear Stress (IFSS) as a function of both testing temperature and mixing ratio, given as the weight percentage of hardener (TETA) against the total weight of hardener and epoxy resin. The plot covers the missing data points at 20 and 110 °C based on the experimental data obtained at 50 and 80 °C yielding a linear correlation.

Measurements of IFSS are mostly used qualitative to compare samples tested with the same method and parameters. IFSS is very sensitive to variation e.g. in sizing, moist content, fibre surface roughness causing difficulties when a quantitative comparison is desired [3-4]. When comparing samples with an epoxy matrix it is necessary to be aware of the conditions at which the matrix was prepared regarding curing temperature and mixing ratio of resin and hardener as both influence the glass transition temperature of the matrix.

The results presented in figure 2 indicate that the change in IFSS is most distinct measured at room temperature where IFSS decrease with increasing concentration of hardener or at low mixing ratio below the stoichiometric value where IFSS decrease with increasing temperature. IFSS is often measured at room temperature which leaves the results obtained more vulnerable to small differences in the mixing ratio. All the IFSS test use very small amounts of matrix especially the microbond test. High accuracy is crucial when preparing the epoxy matrix both in measuring the amounts and in the mixing to ensure homogeneity. If the temperature in the lab changes significantly during the day or season it might be necessary to use a temperature chamber to stabilize the temperature in order to be able to compare the results obtained at different times.

The increase in IFSS with decreasing temperature has been explained by thermal and residual stresses as a result of cure shrinkage, the latter being the main source. Cure shrinkage occurs during the entire cure but induces most stress after gelation as the structure becomes more rigid and less able to relax [9-13]. As with temperature, the invers relation between IFSS and mixing ratio can also be explained by shrinkage caused stresses through cross linking density. The cross linking density is highly related to the structural behavior and therefore the stresses caused by shrinkage. High cross linking density yields better physical properties and can be obtained by mixing epoxy resin and hardener at stoichiometric ratio [14-15]. The mixing ratio affects T_g of the matrix, a maximum can be found with ratios around the stoichiometric ratio where the cross linking density also is at its maximum [16-17].

From this it would be expected that the maximum IFSS is found at the stoichiometric ratio. The results indicate on the contrary a maximum IFSS at mixing ratios below the stoichiometric ratio and that the mixing ratio becomes less influential at temperatures well above T_g. When using mixing ratios below and above the stoichiometric ratio the physical properties deteriorate with decreasing cross linking density but it also yields lower shrinkage and thereby the concomitant residual stresses [14-15]. This explains why the IFSS values measured at mixing ratios below the stoichiometric ratio are higher, but not why the values obtained at mixing ratios above the stoichiometric ratio are lower. When using a large excess amount of hardener it is possible that the polymerization reaction between epoxy resin and hardener starts yielding linear polymers instead of the desired cross linked polymer affecting the physical properties of the matrix in a way that decreases the IFSS [14].

5 CONCLUSIONS

- The IFSS was found to be depended on the testing temperature yielding a higher value at lower temperatures. This inverse dependency has also been described in literature were it was related to residual stresses at the interface due to cure shrinkage.
- The dependency of testing temperature appears greater at low concentrations of hardener in the epoxy matrix. The incomplete dataset indicates that the effect of mixing ratio is most distinct at low testing temperatures e.g. room conditions.

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