TEMPERATURE DEPENDENCE OF THE INTERFACIAL SHEAR STRENGTH IN GLASS REINFORCED POLYPROPYLENE AND EPOXY COMPOSITES

J.L. Thomason[1], L. Yang[1]
[1] Department of Mechanical and Aerospace Engineering, University of Strathclyde, 75 Montrose Street, Glasgow, G1 1XJ, UK
* Corresponding author (james.thomason@strath.ac.uk)

Keywords: *Interface, Interphase, Glass fibre, Polypropylene, Epoxy*

1 Introduction

It is well known that optimization of the stress transfer capability of the fibre-matrix interface region is critical to achieving the desired mechanical performance in composites [1]. The ability to transfer stress across the interface in composites is often reduced to a discussion of 'adhesion' which is a simple term to describe a combination of complex phenomena on which there is still significant debate as to what it means and how to measure it. One generally accepted method for characterisation of composite interface stress transfer capability is the mechanically measured value of interfacial shear strength (IFSS). Despite the high level of attention commonly focused on the chemical influences, such as coupling agents, on the level of IFSS in composites, a number of authors have commented on the role of thermo-physical contributions to the stress transfer capability at the fibre-matrix interface [2-6]. A detailed examination of background to this hypothesis indicates that this should result in a significant inverse temperature dependence of the apparent IFSS. However, the accurate and reproducible measurement of IFSS by direct micro-mechanical methods is a challenge to experimental researchers. Consequently most reported work on IFSS is restricted to room temperature characterization. Nevertheless, many composite applications require performance to be maintained across a wide temperature range and although fibre and polymer matrix properties as a function of temperature are often available there is very little data in the literature on the effects of temperature on interfacial stress transfer capability.

We have recently reported the development of a method which allows the measurement of IFSS over a wide temperature range [6,7]. In this paper we present data obtained using the microbond test in the temperature controlled environment of a thermo-mechanical analyser (TMA). IFSS in glass fibre–polypropylene and glass fibre-epoxy systems in the temperature range -40°C to 150°C are presented and discussed.

2 Experimental

Boron free uncoated and γ-aminopropyltrimethoxysilane coated E-glass fibre (average diameter = 17.5µm) were supplied by Owens Corning - Vetrotex and commercial isotactic homopolymer polypropylene PP 579S with melt flow index = 47 g/10 min at 230°C was supplied by SABIC-Europe. The epoxy was Araldite 506 (DGEBA) cured with a triethylenetetramine (TETA), both obtained from Sigma-Aldrich UK. The uncoated glass fibre and unmodified homompolymer PP (GF-PP) were selected to represent glass fibre-thermoplastic composites with little probability of chemical bonding at the fibre-matrix interface. The APS-sized glass fibre and epoxy (GF-EP) were selected to represent glass fibre-thermosetting composites with high potential for chemical bonding to exist across the resulting fibre-matrix interface.

The reproducible preparation of microbond samples is critical to the outcome of the measurement and the avoidance of erroneous interpretation of sample preparation induced effects in terms of interface related phenomena [6-7]. The specific procedure to form a PP microdroplet on a glass fibre and details for the room temperature ("normal") microbond test have been reported previously [7-9]. In the present work, the formation of PP microdroplets for the

microbond test was initially carried out in air. However, after the discovery that this led to significant oxidative-thermal degradation of the PP which significantly affects the value obtained for IFSS, subsequent sample preparation was carried out under the nitrogen [9]. However, this led to a very low yield rate for the axisymmetric droplets with respect to the fibre. In order to solve these problems, a PP fibre was tied around the glass fibre prior to heating so that the PP distributed symmetrically around the fibre during melting. A different method was used to form the microbond samples with epoxy. The resin and hardener were thoroughly mixed in stoichiometric proportions recommended by the manufacturer and degassed under a vacuum for 12 minutes. Epoxy droplets were then deposited on a single fibre using a thin wire, which had a small resin bead on its tip. Approximately 40 droplets were placed on the fibres before these samples were transferred into a convection oven, where they were heated first up to 60°C and held isothermally for 1 hour followed by another 2 hours heating at 120°C. The heating rate was set to be 2°C/min. After heating, the samples were left in the oven to cool down. The full cure was examined using a DSC, which indicated that there was no further exothermic event detectable in a temperature range from 20°C up to 200°C for the cured epoxy and that the polymer glass transition temperature (Tg) occurred in the range 60°C<Tg<80°C.

Prior to testing the microbond samples were examined using a Nikon Epiphot inverted microscope (x200 magnification) in order to determine the fibre diameter (D_f), embedded fibre length (L_e), and the maximum droplet diameter (D_m). Development of the TMA-Microbond test (TMA-MBT) has also been previously reported [6]. Figure 1 shows the experimental setup for the TMA-MBT. The droplet sits on a shearing plate, which rests on a stationary quartz probe. The movable probe, concentrically installed with the stationary probe, rests on the paper tab attached to the glass fibre as shown in Figure 1. This assembly is enclosed in the TMA temperature controlled programmable oven. The interfacial shear stress can be generated at the desired isothermal temperature by pulling down the paper tab using the movable probe. The free fibre length above the polymer droplet matrix was set at a constant value of 5 mm and the rate of fibre displacement was 0.1 mm/min. The load-displacement curve from each test was recorded (typical example is shown in Figure 1) to obtain the maximum force (F_{max}). This was used with the corresponding fibre diameter and embedded length to calculate the IFSS using to Equation 1.

$$\tau_{ult} = \frac{F_{\max}}{\pi D_f L_e} \qquad (1)$$

In order to fully understand and interpret the temperature dependence of the IFSS measured using the TMA-MBT test it was also necessary to carry out a full thermo-mechanical characterisation of the properties of PP and cured epoxy matrices and single glass fibres using dynamical mechanical analysis, differential scanning calorimetry and thermo-mechanical analysis. Dynamic mechanical analysis was carried out using a TA Q800 DMA configured for a three-point bending test with support span length of 50 mm and a heating rate 3°C/min at frequency 1 Hz, oscillating amplitude 100 µm, static pre-load 0.1 N, and force track: 150%. The coefficient of linear thermal expansion of fibre [10] and matrix was measured using a TA Q400 TMA with heating rate 3°C/min with a 0.1 N static force. Differential scanning calorimetry studies were carried out using a TA Q2000 DSC with a heating/cooling rate of 10°C/min and a 5-6 mg sample size.

3 Results

3.1 Temperature dependence of IFSS in GF-PP

Results of F_{max} versus embedded area obtained for GF-PP samples, prepared under nitrogen, using the "normal" and the TMA microbond test at room temperature are shown in Figure 2. It can be seen that the comparison of the two test configurations indicate an excellent level of reproducibility of the apparent IFSS of PP with bare glass fibre. The TMA-microbond results for F_{max} versus embedded area obtained for this system at five different test temperatures in the range -40°C to 100°C are shown in Figure 3. Once again the data for each test temperature exhibit a strong linear relationship with a low level of scatter, high values of R^2, and all extrapolated lines pass through the origin as predicted from Equation 1.

The results for IFSS obtained for GF-PP at five different test temperatures in the range -40°C to 100°C are summarised in Figure 4 which shows the average values with 95% confidence limits (between 25-45 individual measurements per temperature) of apparent IFSS plotted versus the testing temperature. It is clear from Figure 4 that the IFSS of GF-PP is significantly dependent on testing temperature. It is worth noting that the rate of change of IFSS with temperature is highest around room temperature (approximately 0.22 MPa/°C at 20°C) which is in the region of the glass transition temperature (Tg) of the PP matrix (-10 < Tg < 10°C depending on the preferred method for defining Tg). It is well known that the scatter in the measurement of IFSS using the microbond test can often be quite high. The results in Figure 4 indicate that variations of the sample test temperature, for instance over the length of a day or more extremely summer to winter comparisons, could contribute significantly to observed scatter in the results for IFSS measured in polypropylene matrices.

3.2 Temperature dependence of IFSS in GF-Epoxy

The TMA-microbond results for F_{max} versus embedded area obtained for the GF-EP system at seven different test temperatures in the range 20°C to 150°C are shown in Figure 5. It can be seen that nearly all data sets exhibit a strong linear relationship with a low level of scatter, high values of R^2. In particular, the data sets obtained well above or below the matrix Tg show low levels of scatter with high levels of slope below Tg and low levels of slpe above Tg. However, the data set obtained at 80°C shows a very much higher level of scatter. Clearly there is a large change in the magnitude of the IFSS around the matrix Tg and consequently it is not surprising that the data obtained at 80°C show large levels of scatter. Further examination of Figure 5 reveals that for data sets obtained above Tg the extrapolated lines pass through (or close to) the origin as predicted from Equation 1. However, the data sets obtained below Tg all show extrapolated lines which clearly do not pass through the origin. We have previous observed that data sets which do not extrapolate through the origin are a strong indication of some unknown experimental parameter which is unaccounted for [6,7]. In this case of GF-PP, SEM examination of post-debond samples led us to understand the need to avoid thermal-oxidative degradation of the PP during sample preparation was critical to obtaining reproducible results from the microbond test. For this reason we also undertook a series of SEM analyses of post-debond GF-EP samples tested at different temperatures.

The key result from this SEM analysis is illustrated in Figure 6. It was found that all GF-EP samples tested above Tg revealed a fully debonded, relatively undamaged, epoxy droplet still remaining on the fibre. However, virtually all samples debonded below Tg were found to be very similar in appearance to the sample shown in Figure 6. It can be seen that a substantial fraction of the droplet which was close to the knife edges has not been debonded at the fibre-matrix interface. Instead it appears that the fracture has propagated into the matrix from the knife edges until reaching the fibre and then the crack has proceeded further along the fibre-matrix interface. Consequently, it was necessary to corrected the values of the embedded length used in Equation 1 (or to calculate embedded area in Figure 5) to account for the reduction in the actual debonded interfacial area in these samples. Figure 7 shows the TMA-microbond results for F_{max} versus corrected embedded area obtained for the GF-EP system at seven different test temperatures. It can be seen that all extrapolated lines now pass through (or close to) the origin as predicted in Equation 1

The results for average IFSS obtained for GF-EP at test temperatures are summarized in Figure 3 which shows the average values with 95% confidence limits (between 10-20 individual measurements per temperature). It can be clearly seen that there also exists a significant temperature dependence of measured IFSS in this thermosetting system. The IFSS drops from 54 MPa at 20°C to just 2 MPa at 150°C. It is noticeable that the highest rate of change of IFSS with temperature is also in the region of the glass transition temperature of the epoxy matrix with 1.1MPa/°C at 70°C. This value is almost five times higher than that in GF-PP at 20°C and this clearly plays a role in the high degree of scatter observed in Figure 7 for the data obtained at 80°C.

4 Discussion

Those familiar with DMA of polymers will recognise the similarity between the IFSS data in Figures 4 and 8 and the typical DMA results for the storage modulus of many polymers across temperature range which includes the polymer Tg. This similarity is clearly visible in Figure 9 which shows the results for the IFSS results from GF-PP and GF-EP normalised to the highest value obtained for each system compared to the normalised DMA storage modulus data obtained for each matrix system. The similarity in the shape of the data curves is striking. Indeed it is possible to explain some of the apparent shift in temperature between the IFSS and modulus data being due to the IFSS measurements being made isothermally in one instrument and the modulus data being obtain from a dynamic heating scan in a different instrument. Consequently the overlap of the two types of measurement may be even closer than presented in Figure 9. This correlation is further examined in Figure 10 where the normalised IFSS data is plotted directly against the appropriate normalised matrix modulus.

It is relatively simple to show that an increase in apparent IFSS with decreasing temperature is a phenomenon which would be expected if compressive residual stresses and interfacial static friction play a significant role in the interfacial stress transfer capability in these composites [6]. If the temperature dependence of the fibre and matrix modulus and expansion coefficients is known then the residual compressive stress (σ_R) at the interface can be calculated from available models [2,3,11]. Raghava [11] proposed that the radial stresses due to thermal shrinkage can be calculated from

$$\sigma_R = \frac{(\alpha_m - \alpha_f)(T_s - T_t) E_f E_m}{(1 + \nu_f + 2V_f) E_f + (1 + \nu_m) E_m} \qquad (2)$$

where α is the thermal expansion coefficient, T_s is the stress free temperature, T_t is the testing temperature, ν is the Poisson ratio, V_f is the fibre volume fraction, E is the modulus and f and m are subscripts for the fibre and matrix respectively [11]. For many composite systems $E_f >> E_m$, in which case Equation 2 approximates that σ_R scales with the magnitude of $\Delta\alpha.\Delta T.E_m$. This could already be a good explanation of the general form of the temperature dependence of IFSS appearing to be remarkably similar to the temperature dependence of E_m as seen in Figure 9.

Nairn developed a more complex model [2] which accounted for the effects of differences in the axial and transverse fibre properties and Wagner and Nairn later expanded that model to allow for the presence of an intermediate interphase in the system [3]. The results of these models for residual stress are of similar magnitude when isotropic fibres such as glass are being considered. These models also predict a volume fraction dependence of the residual stress, however it was found that this only began to show any significant effects when V_f exceeded 10%. The average V_f for the microbond samples used to generate the data in Figure 8 was found to be 3%. As previously discussed, if the magnitude of the coefficient of static friction at the fibre-matrix interface is known then the contribution of σ_R to the apparent IFSS can be calculated using [6]

$$\tau_{ult}(T) = \tau_0 + \mu_s \sigma_R(T) \qquad (3)$$

where τ_0 is the extrapolated of IFSS at the stress free temperature which, for the sake of simplicity, was assumed to be independent of temperature. There is very little information available on μ_s in the literature, however Schoolenberg reported a value for μ_s=0.65 in a sized glass fibre-polypropylene system [12].

The experimental values for GF-PP IFSS at different temperatures are compared with values of (τ_{ult}) calculated using Equation 3 and various values of μ_s in Figure 11. It can be seen that the residual interfacial stress builds up significantly as the temperature is lowered. Furthermore, the experimental IFSS data fall well within the range of values of interfacial shear strength contribution for coefficients of static friction between 0.35-0.75 which notably covers the value of 0.65 quoted above. One explanation for this range of values may be that μ_s in this system is temperature dependent [6]. Nevertheless, these results appear to indicate that approximately 70% of the value of the apparent

IFSS in this GF-PP system measured at room temperature can be attributed to residual radial compressive stresses at the interface. This would seem to be supportive of the hypothesis that the interface in this system is dominated by residual thermal stresses.

The results for the IFSS of GF-EP in Figure 8 were also fit using Equation 1 but it was found that the friction model was not able to generate a reasonable approximation to the results for GF-EP and required a very high level of μ_s (>6) to give a comparable magnitude of IFSS with the measured values. It is perhaps not surprising to find that the residual frictional stress may not play such a significant role in the GF-EP IFSS as does in neat GF-PP. The former has excellent chemical compatibility, which may give rise to a fibre-matrix interphase with physiochemical properties significantly different from those of either constituent. In such case, chemical bonding may be considered as the main adhesion mechanism accounting for the measured high level of IFSS. On the other hand, for GF-PP it is probably mechanical interlocking and static friction in combination with residual thermal shrinkage stress that serves as the main interfacial stress transfer mechanism.

Despite the different dominant adhesion mechanisms between GF-PP and GF-EP, it is still fascinating to observe that the IFSS obtained from these two systems both exhibit a strong correlation with the temperature dependence of the matrix modulus. It can be clearly seen in Figure 10 that the interfacial tenacity in both GF-PP and GF-Epoxy increases as elastic modulus of the corresponding matrix increases. Similar correlation between IFSS measured by fragmentation test and matrix modulus has been reported for carbon fibre-epoxy [13,14] and related to the change in matrix shear properties. This is an area that requires further investigation.

4 Conclusions

In order to investigate the temperature dependence of the interfacial properties of fibre reinforced composites the microbond test has been successfully adapted to be carried out in the temperature controlled environment of a thermo-mechanical analyser. This novel technique was applied to bare glass fibre-homopolymer polypropylene and APS sized glass fibre-epoxy respectively. Highly significant inverse dependence of IFSS on testing temperature was observed in both systems.

The temperature dependence of the GF-PP IFSS was interpreted with the aid of a model combining static friction with residual radial compressive stresses at the interface. This analysis indicated that approximately 70% of the value of the apparent IFSS in neat GF-PP measured at room temperature could be attributed to residual radial compressive stresses at the interface. In contrast to GF-PP, it was found that this mechanism could not adequately account for the temperature dependence of IFSS in GF-EP.

Nevertheless, the results from both thermoplastic and thermoset systems clearly showed that there existed a strong correlation between the apparent IFSS and matrix modulus. Based on these results it can be concluded that the interfacial stress transfer capability in both thermoplastic and thermoset matrix composites is highly dependent on temperature and that the thermo-physical contribution to the apparent IFSS in these systems can account for a significant proportion of the measured value.

References

[1] J.L. Thomason. *"Glass Fibre Sizings, a review of the scientific literature"*. James L. Thomason, 2012.

[2] J.A. Nairn and P. Zoller. "Matrix solidification and the resulting residual thermal stresses in composites". *J. Mater. Sci*., Vol. 20, pp 355-367, 1985.

[3] H. Wagner and J.A. Nairn. "Residual thermal stresses in three concentric transversely isotropic cylinders". *Compos Sci and Tech*., Vol. 57, pp 1289-1302, 1997.

[4] J.L Thomason. "Interfacial Strength in Thermoplastic Composites – At Last an Industry Friendly Measurement Method?". *Composites: Part A*, Vol. 33, pp 1283-1288, 2002.

[5] J.L. Thomason. "Dependence of interfacial strength on the anisotropic fiber properties of jute reinforced composites" *Polymer Composites*, Vol. 31, pp 1525-1534, 2010.

[6] L. Yang and J.L. Thomason. "Temperature dependence of the interfacial shear strength in glass fibre-polypropylene composites". *Compos Sci and Tech*., Vol. 71, pp 1600-1605, 2011.

[7] L. Yang and J.L. Thomason. "The influence of thermo-oxidative degradation on the measured interface strength of glass fibre-polypropylene". *Composites Pt. A: Applied Science and Manufacturing*, Vol. 42, pp 1293-1300, 2011.

[8] L. Yang and J.L. Thomason. "The role of residual thermal stress in composite interfacial strength by a novel single fibre technique" *Proceedings of ECCM15*, Venice, paper number 327, 2012.

[9] L. Yang and J.L. Thomason. "The development and application of micromechanical techniques for characterising interfacial shear strength in fibre-thermoplastic composites" *Polymer Testing*, Vol. 31, pp 895-903, 2012.

[10] L. Yang and J.L. Thomason. "The thermal behaviour of glass fibre investigated by thermomechanical analysis" *Journal of Materials Science*, In Press, 2013.

[11] R.S. Raghava. "Thermal expansion of organic and inorganic composites". *Polymer Composites*. Vol. 9, pp 1-11, 1988.

[12] G.E. Schoolenberg "*Some wetting and adhesion phenomena in polypropylene composites in Polypropylene: structure, blends and composites*", edited by J. Karger-Kocsis. Chapmann and Hall, London, 3,1995.

[13] V.Rao and L.T. Drzal. "The temperature dependence of interfacial shear strength for various polymeric matrices reinforced with carbon fibers". *The Journal of Adhesion*, Vol. 37, pp 83-95, 1992.

[14] M. Detassis, A. Pegoretti, and C. Migliaresi. "Effect of temperature and strain rate on interfacial shear stress transfer in carbon/epoxy model composites"., *Compos Sci and Tech.*, Vol. 53, pp 39-46, 1995.

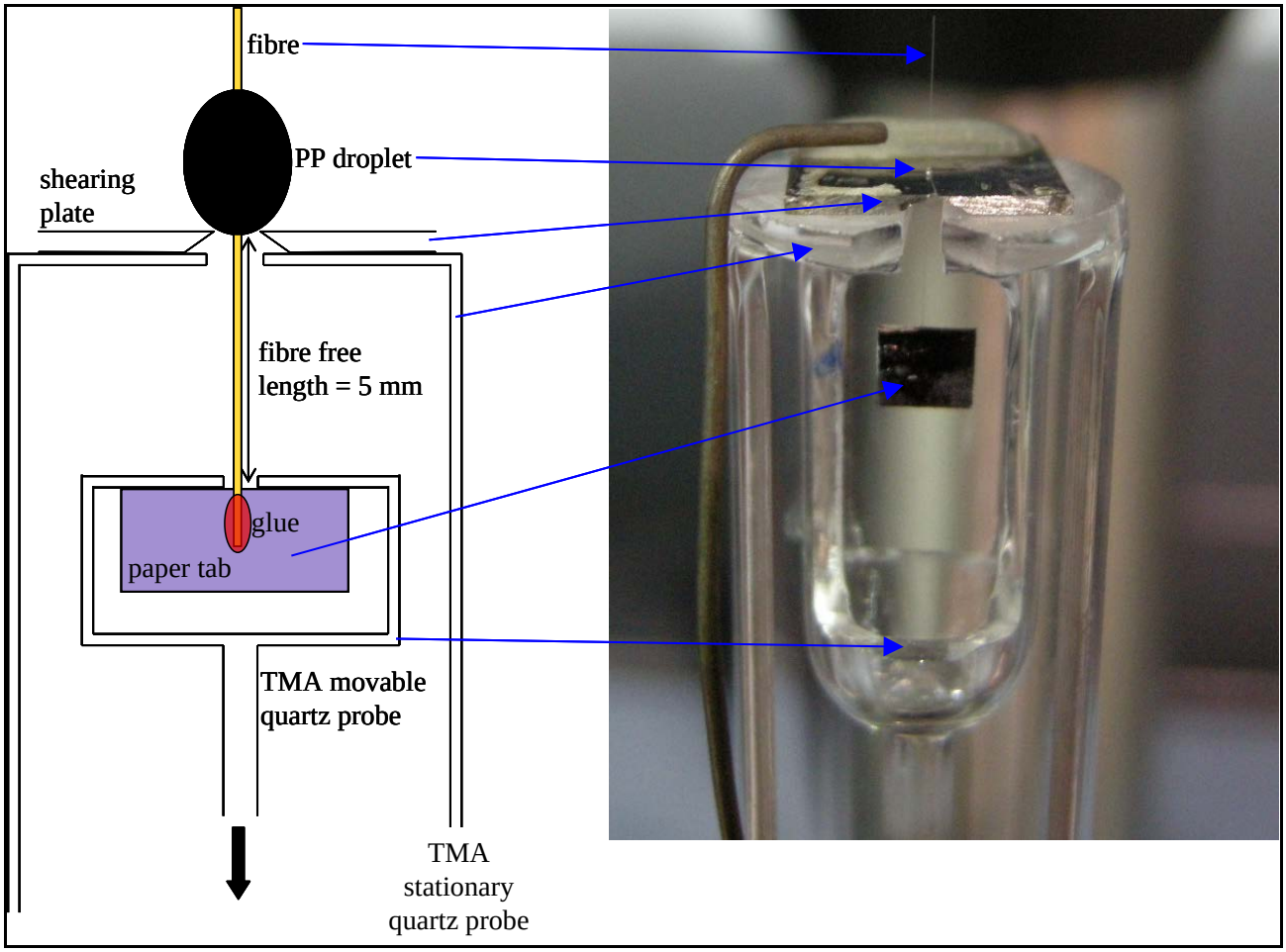

Fig. 1. Schematic diagram and close up photograph of the TMA-Microbond test configuration

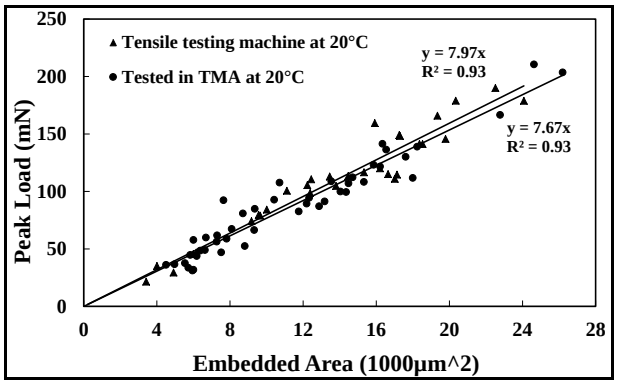

Fig 2. Comparison of results of microbond testing of GF-PP in the TMA and a "standard" testing machine

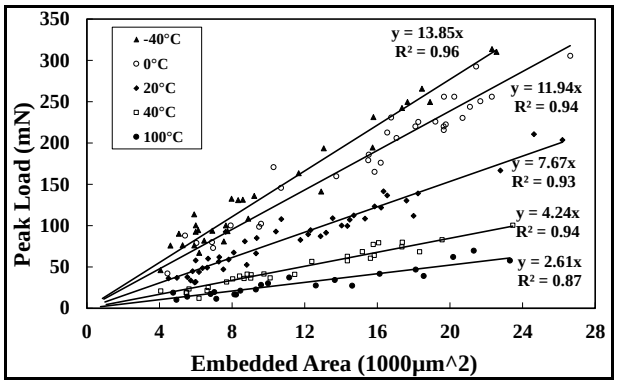

Fig 3. TMA-microbond peak load versus embedded area for GF-PP at various test temperatures

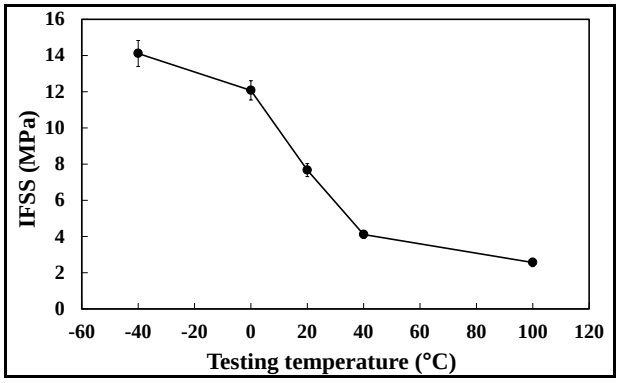

Fig. 4. Temperature dependence of average IFSS for glass fibre-polypropylene

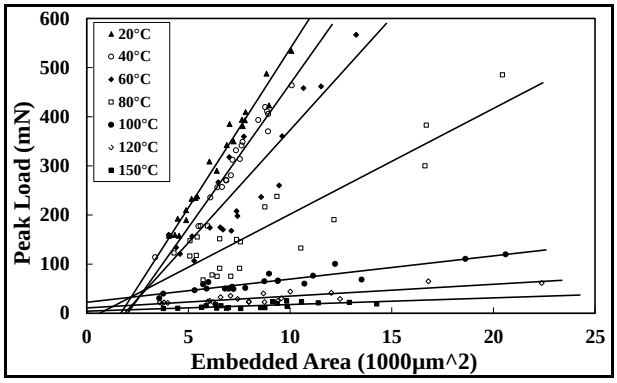

Fig 5. TMA-microbond peak load versus embedded area for GF-EP at various test temperatures

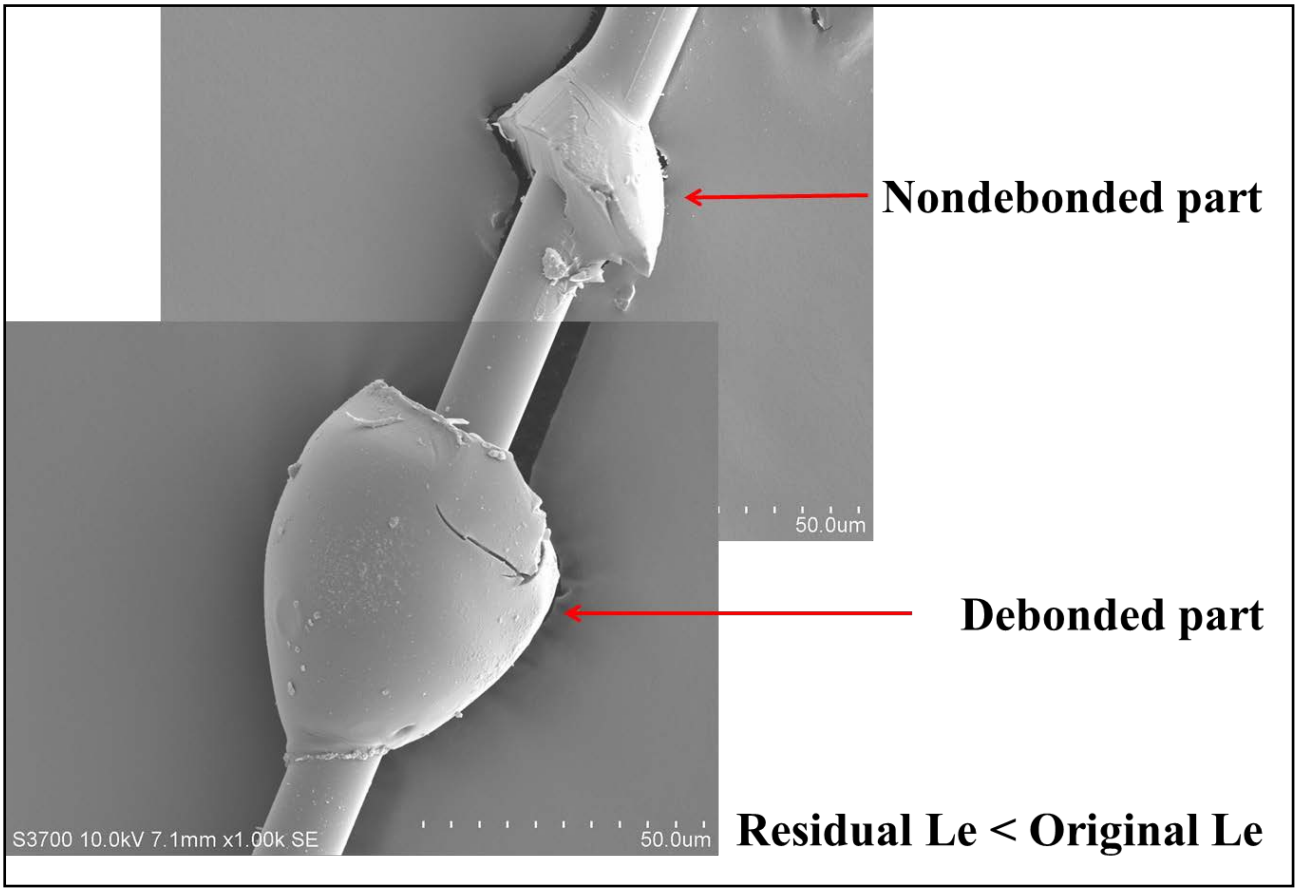

Fig 6. SEM micrograph showing state of epoxy microdroplet after testing below the matrix Tg

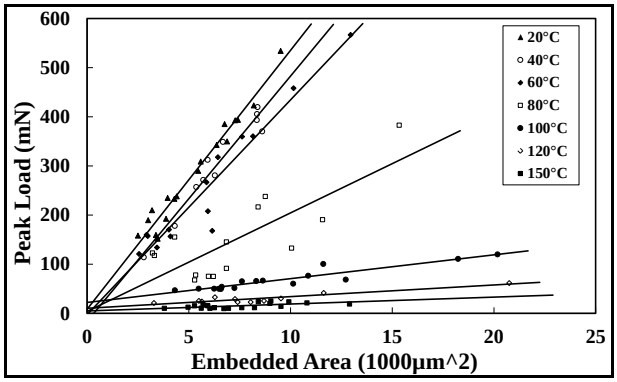

Fig 7. TMA-microbond peak load versus corrected embedded area for GF-EP testing

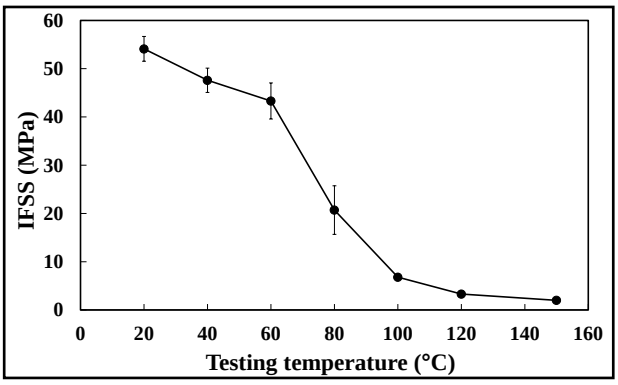

Fig. 8. Temperature dependence of average IFSS for GF-EP

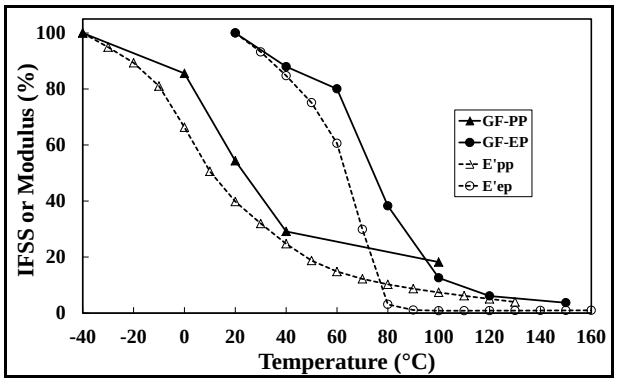

Fig 9. Normalised IFSS and matrix DMA storage modulus vs temperature

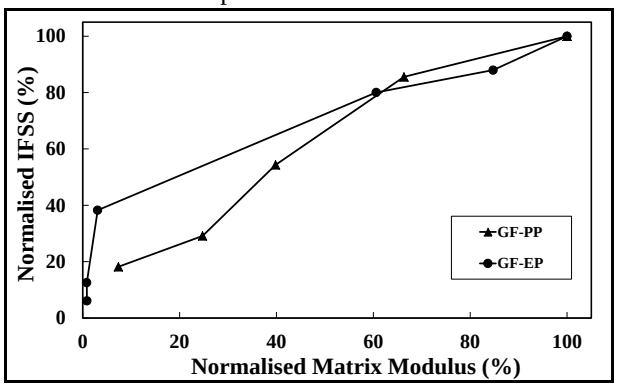

Fig 10. Normalised IFSS vs normalised storage modulus

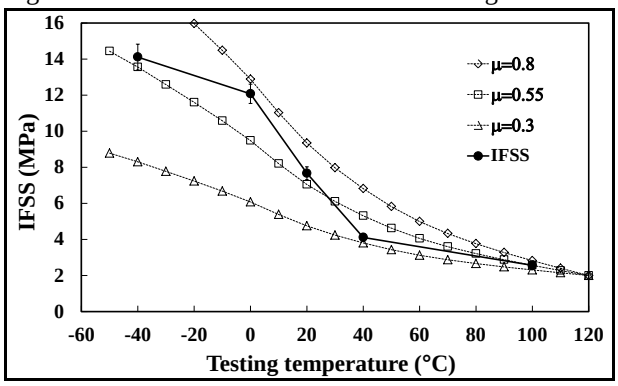

Fig. 11 GF-PP IFSS compared to calculated residual radial interfacial stress component