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The Influence of Thermal Stress on the Interface Strength of a Fibre-Reinforced Thermoplastic Investigated by a Novel Single Fibre Technique

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Abstract

The present work focuses on further verification of the hypothesis that the level of apparent IFSS in glass fibre-reinforced thermoplastic composites can be modelled satisfactorily by assuming that the main component of the IFSS is actually due to a combination of thermal residual stress and static friction at the fibre-polymer interface. In order to obtain information on the temperature dependence of glass fibre – polypropylene IFSS we have adapted a thermo-mechanical analyser to enable interfacial microbond testing to be carried out in a well controlled temperature environment. Test results obtained by TMA-microbond testing showed excellent comparability with those obtained by normal microbond testing. The temperature dependence of IFSS of glass fibre – polypropylene was measured in the range from -40°C up to 100°C. The IFSS showed a highly significant inverse dependence on testing temperature.

1. Introduction

There has been a rapid growth in the development and application of fibre-reinforced thermoplastic polymer composites in recent years. Parallel to this growth has been the increasing recognition of the need to better understand and measure the micro-mechanical parameters which control the structure–property relationships in such composites. The properties of thermoplastic composites result from a combination of the fibre and matrix properties and the ability to transfer stresses across the fibre–matrix interphase. Optimization of the stress transfer capability of the fibre-matrix interphase region is critical to achieving the required performance level in thermoplastic matrix composites. The ability to transfer stress across the interphase in thermoplastic 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. Certainly, one of the generally accepted manifestations of 'adhesion' is in the mechanically measured value of interfacial shear strength (IFSS). Despite the high level of attention commonly focussed on the chemical influences, such as silane coupling agents, on the level of IFSS in composites, a number of authors have commented on the role of shrinkage stresses contributing to the stress transfer capability at the fibre-matrix interface [1-7]. Most thermoplastic composite materials are shaped at elevated temperature and then cooled. Since in most cases the thermal expansion coefficients of polymers are much greater than that of the reinforcement fibres this cooling process results in compressive radial stress σ_r at the interface [5]. Assuming that the coefficient of friction (β) at the interface is non-zero these compressive stresses will contribute a frictional component $\tau_f = \beta.\sigma_r$ to the apparent shear strength of the interface. In the case of thermoplastic polymer matrices where there may often be little or no chemical

bonding across the interface these frictional stresses can make up a large fraction of the apparent IFSS.

We recently presented data comparing the apparent IFSS in injection moulded glass fibre reinforced composites based on four different thermoplastic matrices over a range of fibre contents [5,6]. IFSS data were obtained and compared from both single fibre micromechanical testing and also macromechanical composite testing. In all these cases it was shown that the data for the apparent IFSS could be well fitted by the residual stress model when an appropriate value for the static coefficient of friction is selected (see Figure 1). It was further shown how the effect of polymer coupling agents in fibre reinforced polypropylene could be explained by resulting in changes in the coefficient of static friction in these systems as opposed to changes in the level of chemical coupling across the interphase. Most recently analysis of IFSS related to residual compressive stresses has been shown to explain the low levels of apparent IFSS present in natural fibre reinforced polypropylene [6,7].

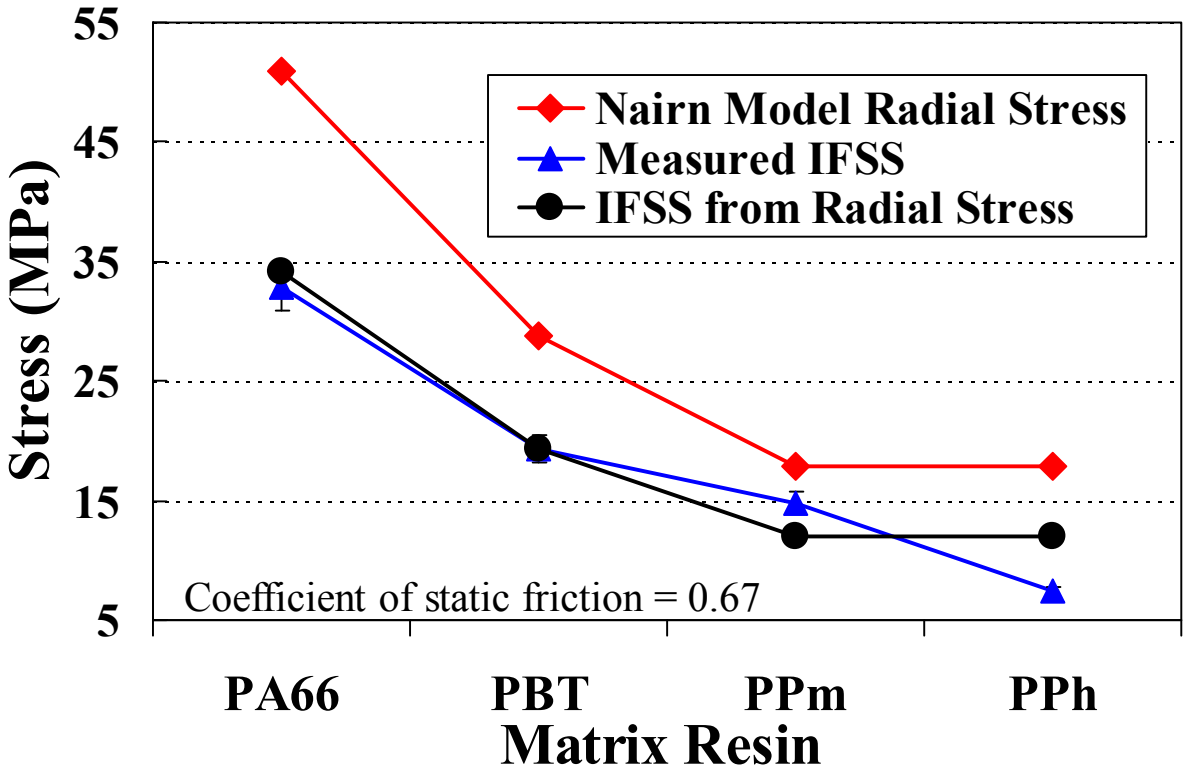

Figure 1. IFSS in glass fibre thermoplastics compared with calculated interfacial residual compressive stress.

Although it is unlikely that these residual stresses provide a full explanation of the apparent IFSS in all composite systems, the above results do underline the need to better understand the role of fibre structure, the levels of residual stress, and the interfacial friction, on the apparent IFSS in thermoplastic composites. Most of the available models [1-7] of these phenomena indicate that the level of residual compressive stress at the composite interphase should be directly proportional to the difference between matrix solidification temperature and the composite operating or test temperature (ΔT). Consequently, this would imply that the apparent IFSS in thermoplastic composites should also be dependent on ΔT. In order to explore this concept an ability to accurately measure IFSS at different temperatures is

required. IFSS is commonly measured using micromechanical test methods such as the fibre fragmentation test, the single fibre pullout test and the single fibre microbond test [8]. In this paper we present data on the IFSS in the glass fibre – polypropylene system obtained at room temperature using the microbond test. Although these micromechanical test methods are commonly employed there is little, if any, standardisation of the testing apparatus. Furthermore, it is certainly the case that accurate control of the temperature of the test sample presents considerable challenges in the building of such micromechanical testing equipment. However, thermal analysis equipment for polymers and composite samples has been developed to a high degree of sophistication. Consequently, we have investigated and report in this paper the possibility of combining a microbond test setup with a thermomechanical analyser in order to generate data on the temperature dependence of IFSS for fibre reinforced thermoplastics

2. Experimental

2.1 Material

In order to minimise the complexity of the interface to be investigated the choice of the materials was limited to uncoated glass fibre and homopolymer polypropylene. Boron free uncoated E-glass fibres (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 (PP47) was supplied by SABIC-Europe.

2.2 Room temperature microbond testing

In this work, the interfacial shear strength (IFSS) was measured by a laboratory-developed microbond test technique. The specific procedure to form a PP microdroplet on a glass fibre and details for the room temperature ("normal") microbond test can be found in [9]. In the present work, the formation of PP microdroplets for the microbond test was carried out under the nitrogen to avoid oxidative-thermal degradation of PP [10]. The free fibre length above the polymer droplet matrix was set at a minimised 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 2) to obtain the maximum force (F_{max}). This was used with the corresponding fibre diameter (D) and embedded length (L_e) to calculate the IFSS according to Equation (1).

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

The tested samples were then examined under the Nikon Epiphot Inverted optical microscope to see if pure debonding process had occurred. Approximate 30 tests for each method were carried out to obtain both IFSS for each sample by Equation.1 and average IFSS for the entire data by a least-squares regression (i.e. slope of linear fitting line for the entire data).

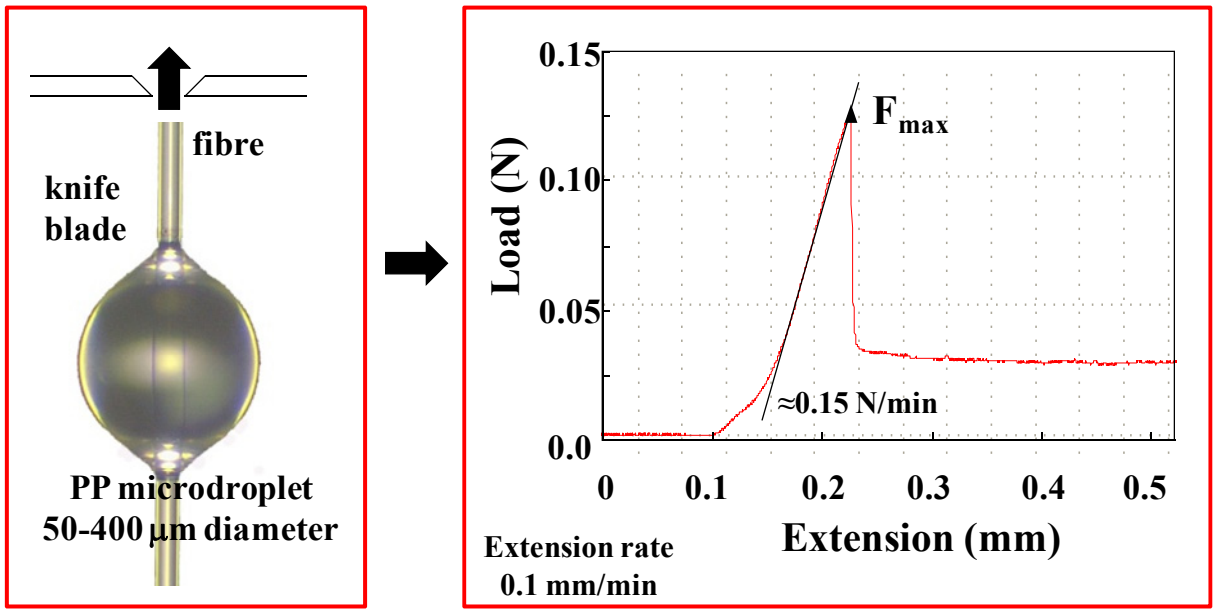

Figure 2. Sample configuration and typical Load-Displacement curve for the "normal" microbond test

2.3 TMA-Microbond testing

The temperature dependence of glass fibre–polypropylene IFSS was investigated by adapting the "normal" microbond test configuration to fit into the well controlled temperature environment of a Thermomechanical Analyzer (TMA Q800EM from TA Instruments) using the TMA film/fibre clamping mode. This system consists of two concentrically installed probes (see Figure 3). The outer one is fixed on a flat stage, while the inner probe is driven up and down by a shaft. Both of them have a 1.2 mm slot on the top for supporting two clamps normally used at each end of the specimen when measuring the sample expansion coefficients. Such a fixture provides the potential of conducting the microbond test in TMA, where the resin droplet could sit on the outer stationary probe and the fibre could thread through both slots and end up with some attachment that can just fit under the slot of the inner movable probe.

There were three main challenges to overcome in carrying out the microbond test in a TMA.

1. Sample mounting - how to connect the fibre to the inner movable quartz probe.
2. Droplet restraint - the width of the upper slot in the stationary quartz probe is approximately 2 mm which is much too large to engage the microbond polymer droplets with a normal diameter range of 40-400 µm.
3. Development of an appropriate TMA testing protocol for an instrument not initially designed for quasi-static tensile testing.

The TMA Q800 fibre/film accessory is supplied with a pair of stainless steel clamps for gripping thin film samples and cleaved aluminium balls for gripping fibre samples. Such clamping mechanisms work quite well with tough materials such as polymer films and natural fibres. However, brittle 17µm diameter glass fibres do not survive such severe clamping. In addition, heavy clamps would lead to underestimation of the maximum load for interfacial failure or even premature sample failure, since the weight of the clamps could excessively pre-strain the sample. Thus, we used two small paper tabs to sandwich the fibre end. Approximately 0.5 mN is applied on the fibre by the weight of the paper tab which is

negligible in comparison to the normal measured debonding forces. To support the resin droplet in the TMA and to provide the droplet shearing force, a small shearing plate (Figure 3) which could be positioned on the top (Figure 4) of the stationery quartz probe was manufactured. The shearing plate was machined from high carbon content stainless steel and consisted of three separate parts, as shown in Figure 3. Two plates had been polished so that there was a sharp edge formed along one of the surfaces. A small angle of approximately 1.2° was deliberately designed between these knife plates to facilitate sliding of the fibre (i.e. the sample) into the gap. Moreover, this ensured the required experimental condition that there was no gap between the fibre and the shearing knives for each fibre, despite the individual variations of fibre diameter from sample to sample. Compared to perfect parallel shearing plates, this angle leads to the difference of 0.33% in the fibre perimeter in loading points around the fibre on each side. For the maximum fibre diameter in this investigation, about 22 µm, the arc length between the loading point applied by the parallel plate and that by the angled plate is only 0.23 µm. Consequently, this slight non-parallel alignment of the shearing plate knives was not expected to make any significant difference in the loading pattern of the resin droplet in comparison with the conventional parallel slot. The third upper plate was used to hold the other two knife plates together.

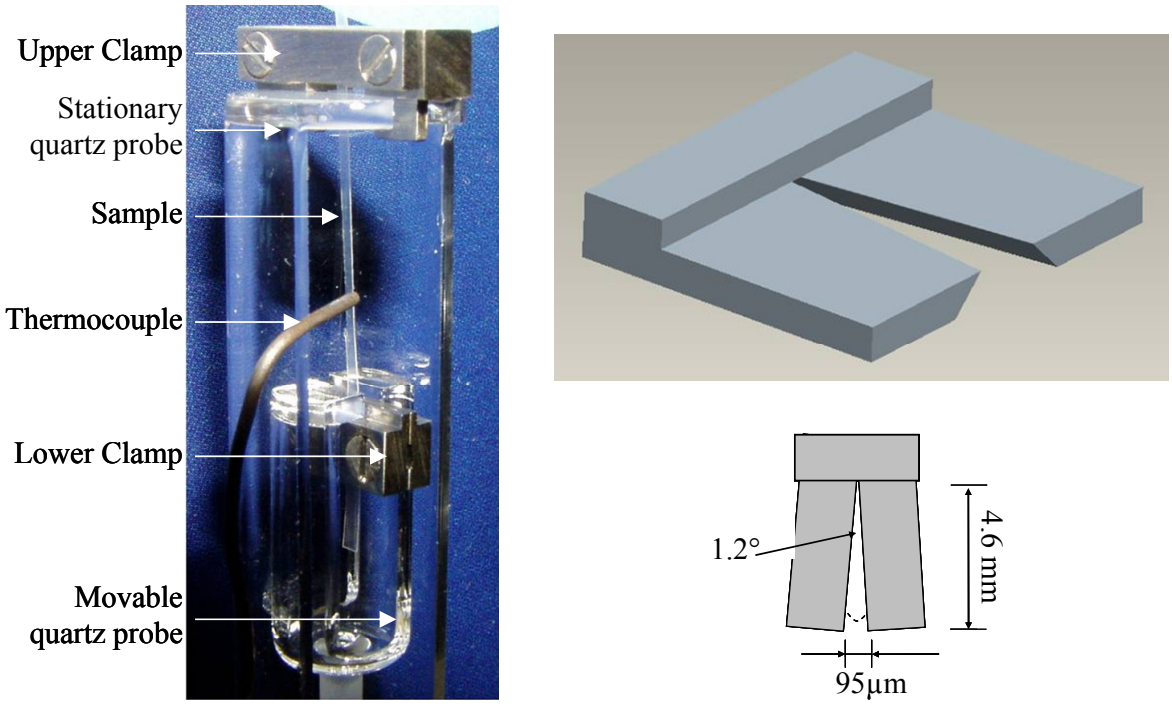

Figure 3. TMA film/fibre probe and TMA-Microbond shearing plate

The TMA configuration proved to be a challenging part in the process of achieving TMA-Microbond since this instrument was not originally developed to carry out the microbond test. In a normal TMA test with the film/fibre probe in use, a static pre-load on the sample is required to remove the slack of the fibre or film and put them under slight tension. The choice of this parameter mainly depends on mechanical properties of materials to be tested. Given that we were attempting to investigate the IFSS of the system, then the interface strength was considered as the criterion for choosing the static pre-load. Hence, the pre-load should be significantly smaller than the maximum load required to cause interfacial failure (found to be in the range 40-230 mN for room temperature testing of IFSS). It was found that a minimum preload of 1 mN was required for the instrument to register the presence of a sample. Hence 1

mN was adopted as the preload level with the consequent error in the debond force being found to be acceptably low at <2.5%.

The "normal" microbond test is carried out by measuring the load generated during the displacement of the droplet at constant rate, however the TMA was unable to operate in this mode. The TMA was consequently configured to measure sample displacement during a linear force ramp. It can be seen that the rate of force increase in the "normal" microbond test force displacement plot shown in Figure 2 is approximately linear during most of the strain ramp up to the debonding force. The average value of the slope of the force-displacement curve for all of the measurements shown in Figure 5 was found to be 0.15 N/min (with a 95% confidence limit = 0.007 N). In order to keep the TMA-Microbond test as comparable as possible to the "normal" test we therefore adopted 0.15 N/min as the applied force ramp rate in the TMA.

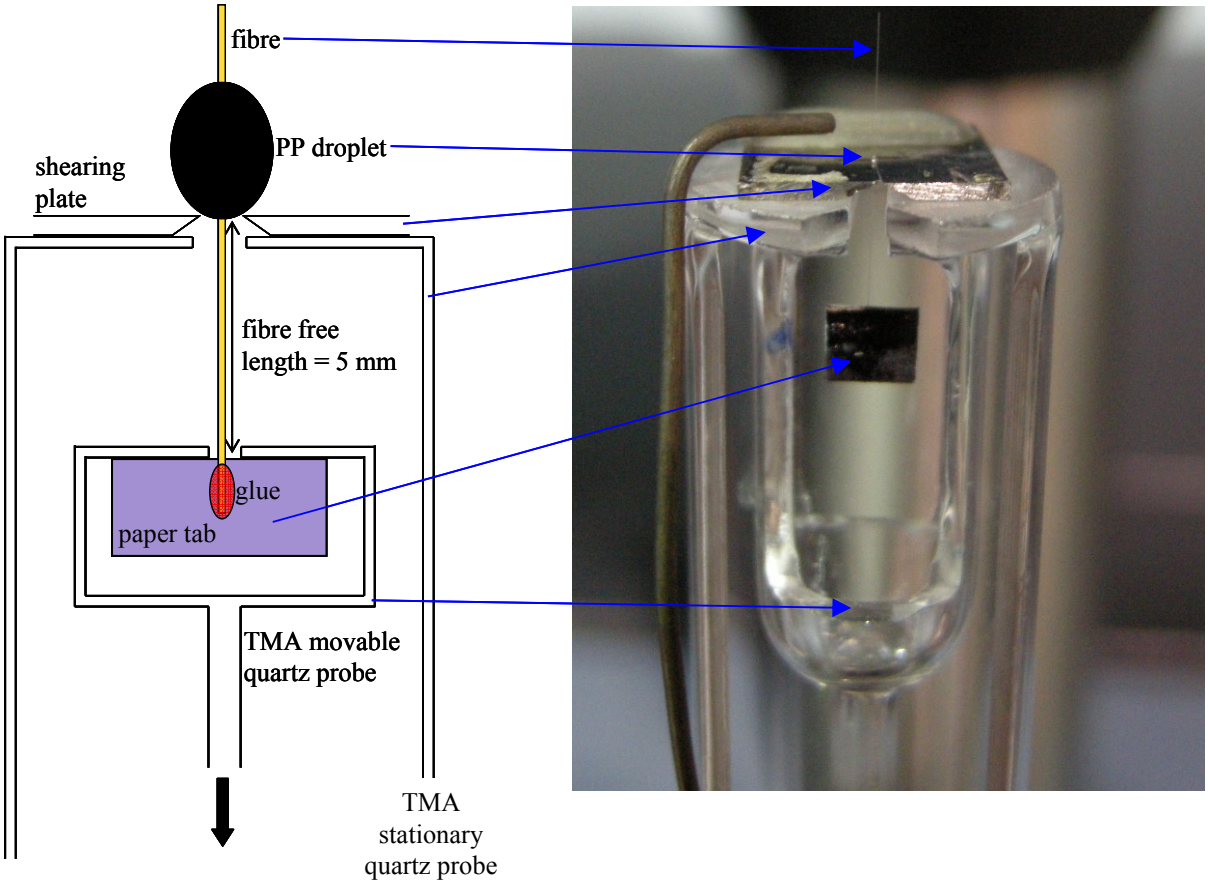

Figure 4. Schematic and close up photograph of the TMA-Microbond test configuration

The measurement protocol then proceeded as follows. The probe displacement was electronically zeroed and the single fibre microdroplet sample was loaded into the shearing plate with the lower paper tab hanging freely below the movable quartz probe. With the movable probe immobilised above the paper tab the furnace was closed. The initial sample length and probe position was recorded and then the furnace was equilibrated at the desired test temperature (in the -40ºC to 100ºC range) with an addition 3-5 minutes isothermal segment to ensure a constant equilibrium temperature was attained. The movable quartz probe was then lowered very gently to contact the paper tab and the force ramp was initiated

at 0.15 N/min. The increasing probe displacement was then recorded until debonding occurred. A typical result obtained from a TMA-microbond test is plotted as a Force-Displacement curve in Figure 5. The general form of the curve is clearly different than that obtained in a "normal" force-displacement experiment. However, the maximum value of force required to obtain a debonding event is still obtained. The major difference is what occurs after debonding. Since the TMA continues to attempt to increase the applied force above F_{max} after debonding there is a rapid downward displacement of the debonded fibre. Consequently, in this test configuration, there can be no further information obtained on post-debond dynamic friction in a similar manner to the "normal" microbond test.

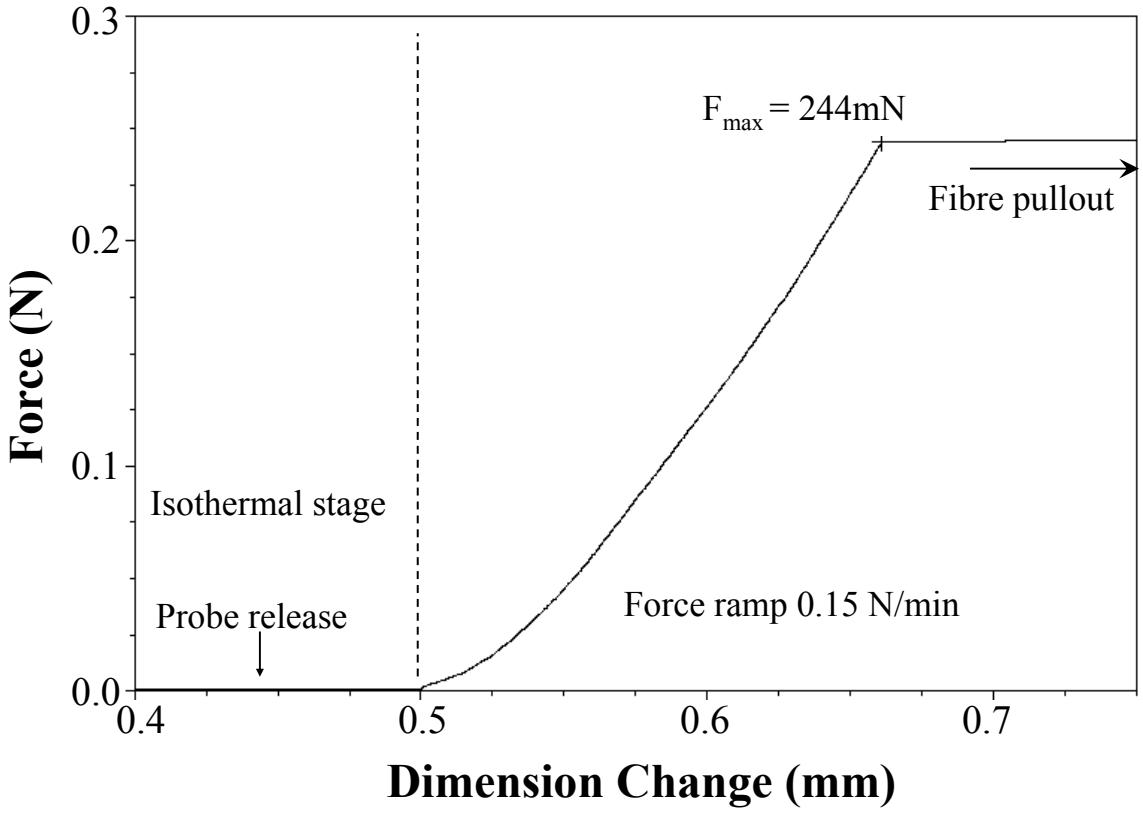

Figure 5. Load-Displacement curve from a typical TMA-Microbond test

3. Results and discussion

Results obtained for F_{max} versus embedded area obtained for glass fibre – polypropylene samples in the "normal" microbond test at room temperature are shown in Figure 6. The data clearly exhibit a significant linear relationship and the least squares fitted line illustrated gives a value for apparent IFSS = 8.0 MPa (with a 95% confidence limit = 0.3 MPa) in this system. In Figure 7 the results for the same system obtained in the TMA-microbond test at room temperature are overlaid. It can be seen that the comparison of the two test configurations indicate an excellent level of reproducibility of the apparent IFSS of PP47 with bare glass.

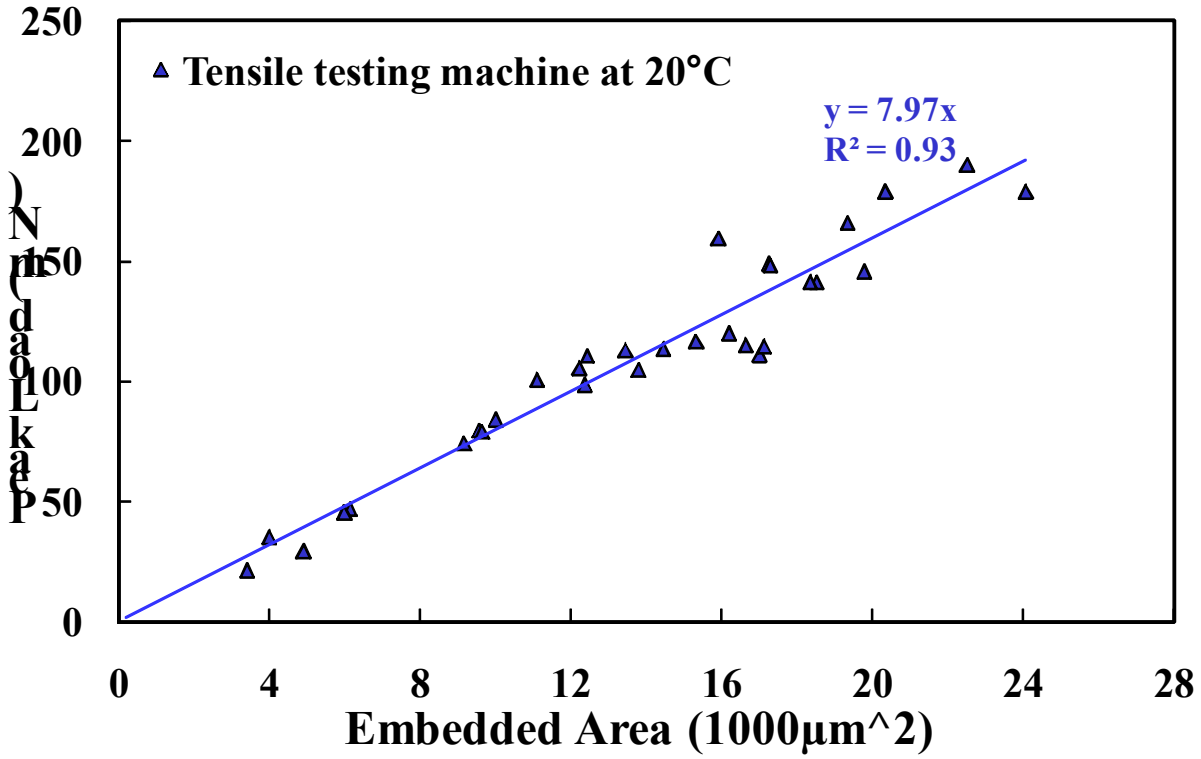

Figure 6. IFSS for GF-PP from microbond maximum load versus embedded area plot

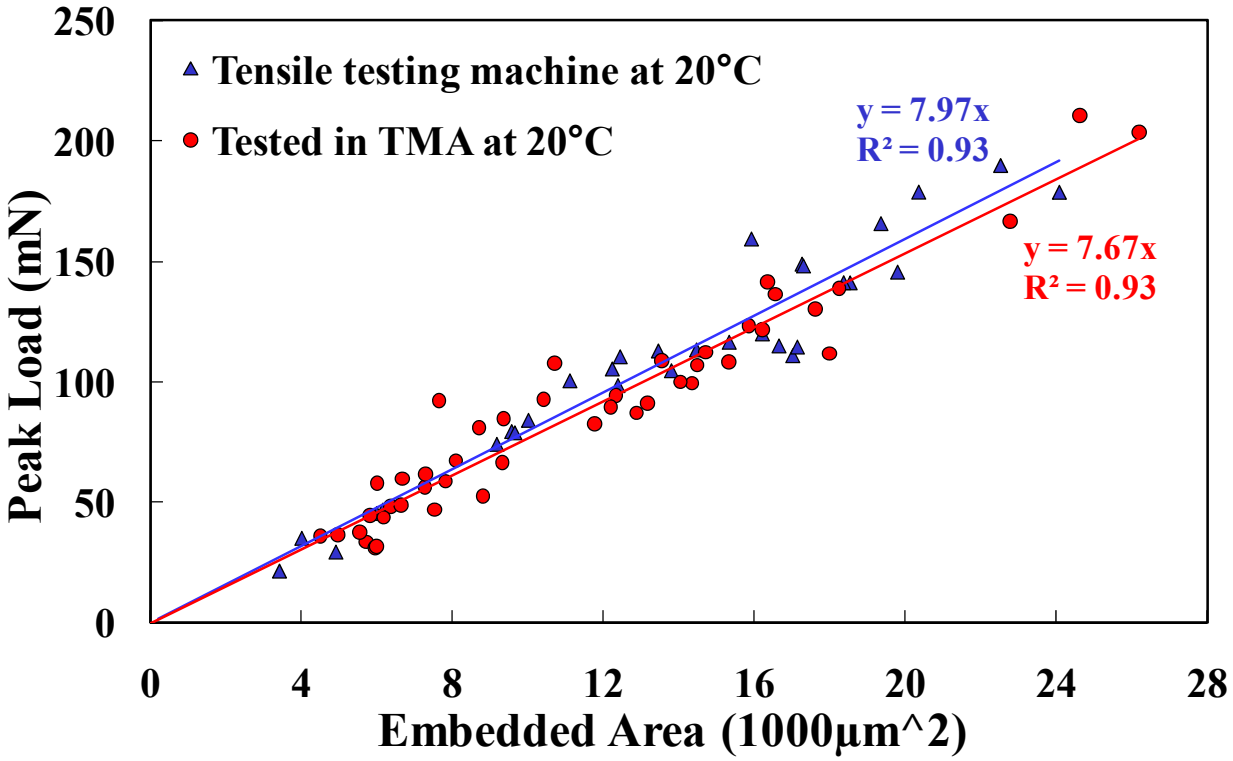

Figure 7. Comparison of results for GF-PP obtained from TMA-microbond and standard testing

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 8. Once again the data for each test temperature exhibit a strong linear relationship with (in comparison to many published studies using the microbond test) a low level of scatter and high values of R^2.

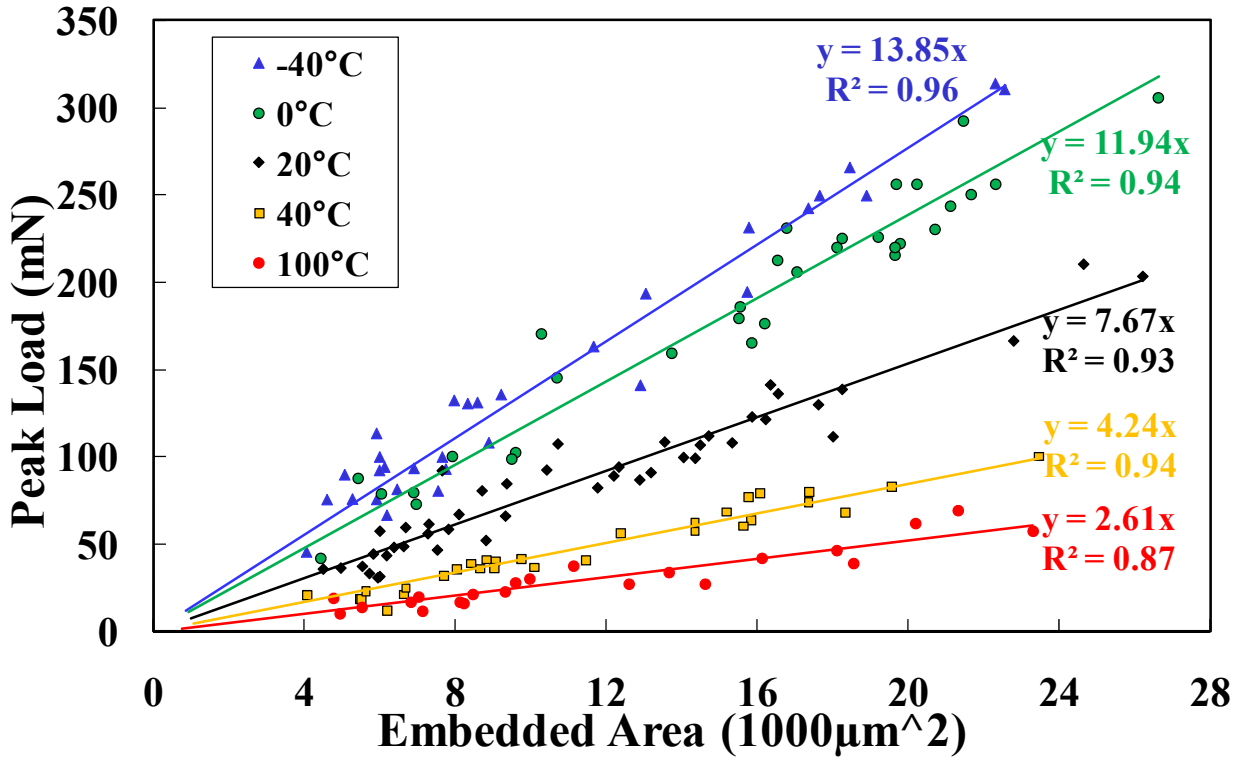

Figure 8. TMA-microbond peak load versus embedded area for glass fibre - polypropylene at various test temperatures

These results are summarised in Figure 9 which shows the average values of apparent IFSS (with 95% confidence limits) plotted versus the testing temperature. It is clear from this Figure that the IFSS of glass fibre – polypropylene is significantly dependent on testing temperature. IFSS is low at higher temperatures above 40°C. As the test temperature is lowered below 40°C there is a sharp increase in IFSS which then appears to level out as the temperature is further lowered below 0°C. The sharp increase of IFSS in this system appears to occur in the region of the glass transition temperature of polypropylene (in the range -10°C to 10°C depending on measurement method). Indeed the general form of the results in Figure 9 is very reminiscent of a typical storage modulus versus temperature plot that might be obtained in a dynamic mechanical analysis measurement on polypropylene. It is worth noting that the rate of change of IFSS with temperature is highest around room temperature (approximately 0.2 MPa/°C at 20°C). 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 9 indicate that, at least with polypropylene matrices, small variations of the sample test temperature could contribute significantly to observed scatter in the results for IFSS.

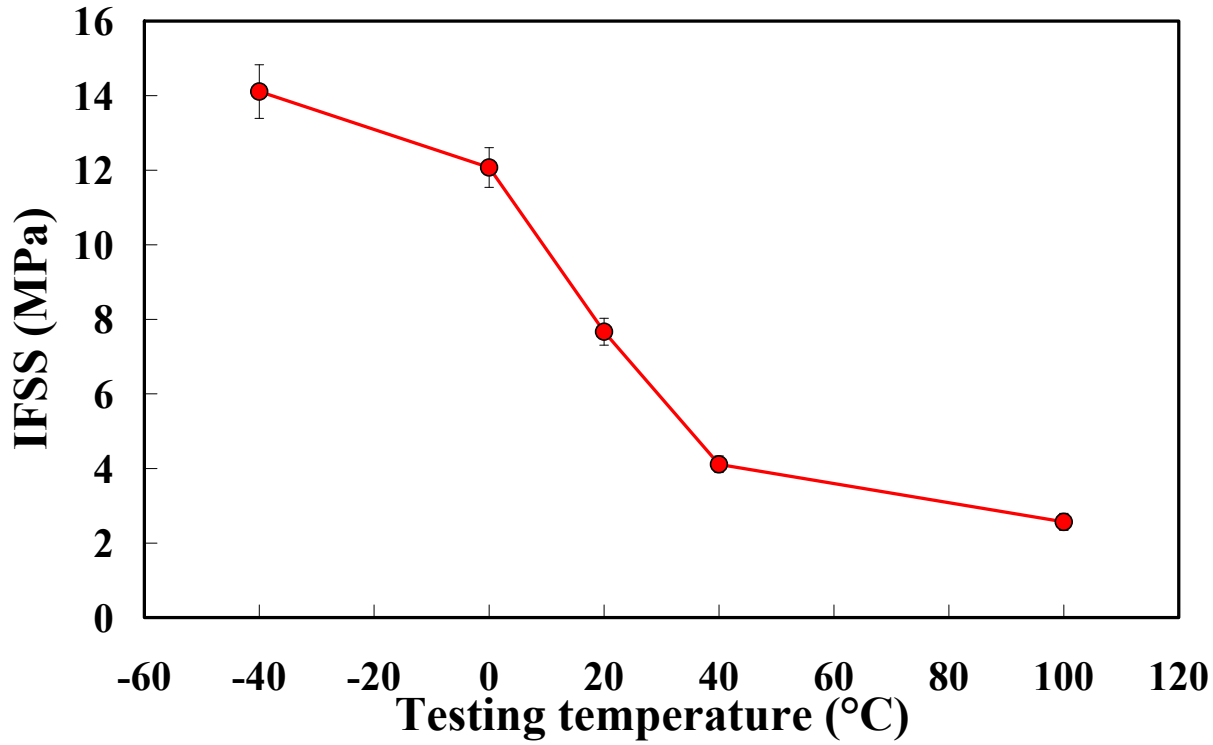

Figure 9. Comparison of average IFSS of glass fibre - polypropylene versus test temperature

The detailed dependence of the IFSS on temperature will clearly require further investigation; however it is clear that there is a strong dependence of the apparent IFSS in glass fibre – polypropylene on the test temperature. As discussed in the introduction this could also be interpreted as direct evidence of the importance of residual radial compressive stresses at the interface on the stress transfer capabilities of the interface. Further characterisation of the stiffness and thermal expansion characteristics of the glass fibres and polypropylene used in these experiments will enable us to comment further on this possibility.

4. Conclusions

The microbond test for measurement of apparent interfacial shear strength in fibre reinforced thermoplastic has been successfully adapted to be carried out in the temperature controlled environment of a thermo-mechanical analyser. Excellent comparability was obtained for the room temperature IFSS of glass fibre – polypropylene measured by the TMA-microbond and the "normal" microbond test configurations. The temperature dependence of IFSS of glass fibre – polypropylene in the range -40°C up to 100°C showed a highly significant inverse dependence on testing temperature.

Acknowledgements

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