Interfacial Strength in Fibre Reinforced Thermoplastics

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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.

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 the test temperature. 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, in the temperature range -40°C to 100°C, obtained 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

Experimental

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 was supplied by SABIC-Europe. IFSS was measured using 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 in air or under nitrogen [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 to obtain the maximum force (F_{max}) which was used with the corresponding fibre diameter (D) and embedded length (L_e) to calculate the IFSS according to equation 1.

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

A transmitted light optical microscope equipped with a Mettler FP 82 hot stage was employed to visualise the formation of PP microdroplet on the glass fibre and the dimensional change of the droplet under the heat

treatment was also measured. The mechanical properties of these droplets were then measured by an Agilent Nano Indenter G200 equipped with the continuous stiffness measurement (CSM) technique [10,11]. The indentation test was conducted with maximum indentation depth and spacing division set to 1μm and 20 μm respectively throughout all the samples.

The temperature dependence of GF-PP 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 [12]. Standard microbond samples were employed [9,10]. To support the resin droplet in the TMA and to provide the droplet shearing force, a small shearing plate which could be positioned on the top of the stationery quartz probe was manufactured. 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. The TMA was configured to measure sample displacement during a linear force ramp at 0.15 N/min until debonding was observed. A preload of 1 mN was required in all cases for the instrument to register the presence of a sample.

Results and Discussion

Figure 1 shows a series of micrographs following the dimensions of a GF-PP microbond sample held at 220°C in the air for 30 minutes. It can be clearly seen that there is a considerable reduction in the volume of the PP droplet over this time. Even in the first 10 minutes the volume loss is significant. This strongly indicates that the PP droplet may undergo severe degradation during the manufacturing process. It can be expected that such high levels of polymer degradation will also result in significant changes (reduction) in the mechanical properties of the droplet. The sensitivity of the droplet degradation to the initial droplet size is examined in Figure 2 where the droplet dimensions were measured regularly during isothermal treatment at 220ºC. The results in Figure 2 reveal that the reduction in droplet diameter begins immediately the time registration starts. Oxidation induction time cannot be observed in these data despite the fact that this commercial polymer contains a full anti-oxidant package. The diameter reduction for all samples appears to follow the same pattern decreasing linearly at a similar rate and then gradually levelling out. Consequently, for a fixed sample preparation time (4 minutes) the smaller droplets undergo a more severe level of average degradation than the larger droplets. It was found that samples with a similar range of dimensions prepared under nitrogen showed no significant change in dimension for times up to 120 minutes at 220ºC.

The nanoindentation results for elastic moduli of PP microdroplets prepared for 4 min and 6 min at 220°C are presented in Figure 3. It can be seen that the PP Young's modulus for a given thermal load is also strongly related to the dimensions of the droplet which correlates well with the above analysis on the levels of degradation in the droplets. Microdroplets prepared under nitrogen showed no such loss in Young's modulus. Although the microdroplets contain much too little material for a standard DSC analysis, DSC analysis carried out on PP film sample exposed to 220ºC in air for different times showed significant reduction in PP crystallinity which is the most likely cause of the drop in Young's modulus observed in Figure 3.

Results for IFSS of sample prepared in air and under nitrogen are presented in Figure 4. It can be clearly seen in Figure 4 that measured IFSS for GF-PP is significantly affected by the thermal load (temperature and time) and the atmosphere (air or nitrogen) in terms of thermal-oxidative degradation in PP matrix. Without degradation of the PP microdroplet the measured average IFSS is over twice the magnitude obtained from degraded PP samples. The fact that the linear fitting lines of the data from non-degraded samples goes through the origin indicates that thermal degradation of PP may be the reason why some regression lines of microbond data do not pass through the origin as would be expected from equation 1.

Results of F_{max} versus embedded area obtained for GF-PP samples, prepared under nitrogen, using the "normal" and the TMA microbond test [12] at room temperature are shown in Figure 5. 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. 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 6. 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 this system at five different test temperatures in the range -40°C to 100°C are summarised in Figure 7 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 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 0.2 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 7 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.

As previously discussed, when the temperature dependence of the fibre and matrix modulus and expansion coefficient are known then the residual compressive stress at the GF-PP interface can be calculated from available models [1-5]. DSC analysis showed the matrix solidification process of PP begins when the temperature drops below 120°C. The data in

Figure 8 shows that the both the modulus and expansion coefficient of the PP matrix are strongly dependent on the temperature and this must be incorporated into the calculations [2,4,5]. Glass fibre properties are also temperature dependent but on a much less significant scale and can be considered constant in this temperature range. In Figure 9 the potential contribution to apparent IFSS of this residual compressive stress is shown calculated using various values of coefficient of static friction and normalised to the IFSS value at 100ºC. 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 0.4-0.8. 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 GF-PP on the test temperature. As discussed above this could be interpreted as direct evidence of the importance of interfacial residual radial compressive stresses on the stress transfer capabilities of the interface.

Conclusions

The results obtained from the microbond test for measurement of apparent interfacial shear strength in fibre reinforced thermoplastics are strongly dependent on the sample preparation history. Hot stage microscopy observation of microbond samples preparation in air clearly shows thermal degradation of polypropylene is an issue. The results for the Young's moduli of PP microdroplets with different heat treatments showed that there was significant stiffness deterioration in degraded samples related to the droplet size for a given heat treatment. Comparison of measured average IFSS for GF-PP between degraded and non-degraded samples shows that degradation of PP can markedly reduce the apparent adhesion of GF-PP. In order to investigate the temperature dependence of GF-PP IFSS the microbond test 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.

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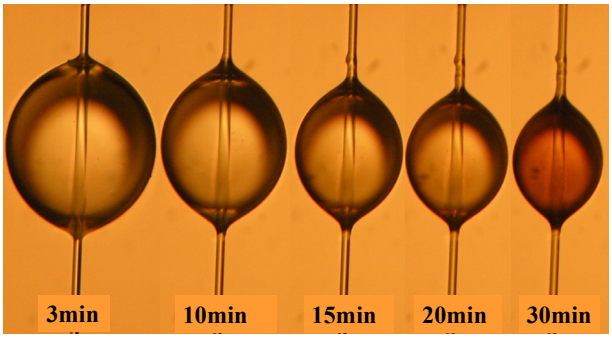

Figure 1 Micrographs of a GF-PP microbond sample heated at 220°C in air.

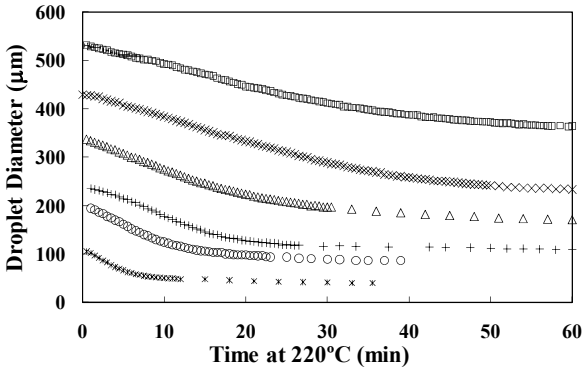

Figure 2 Reduction of the diameter of PP microdroplet heated at 220°C in air.

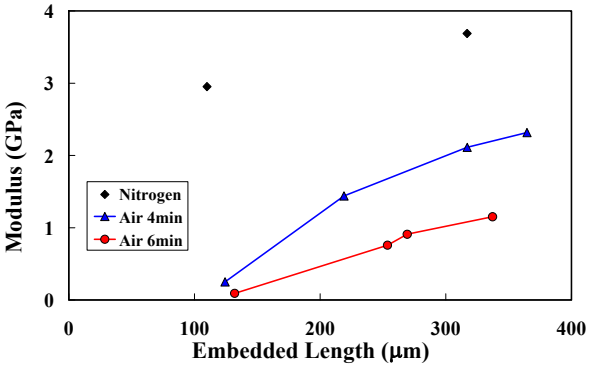

Figure 3 Modulus of PP microdroplets of different size after undergoing different thermal loads.

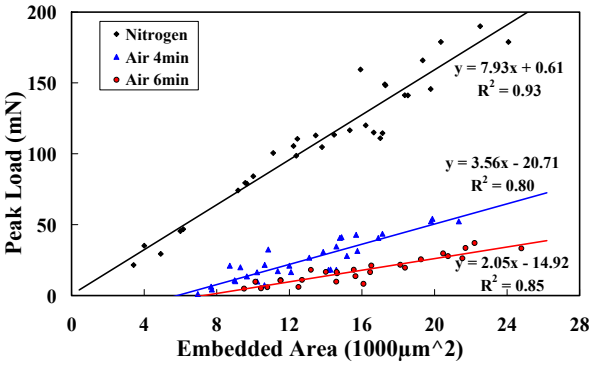

Figure 4 Effect of oxidative-thermal degradation of PP on the microbond measured apparent IFSS of GF-PP.

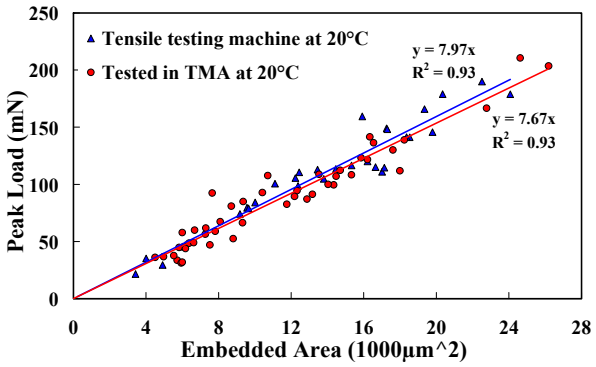

Figure 5 Comparison of results for GF-PP obtained from TMA-microbond and standard microbond testing.

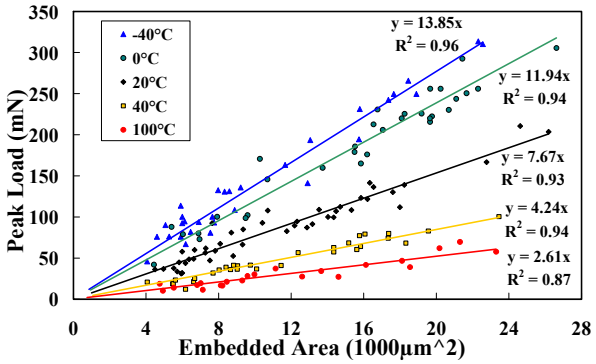

Figure 6 TMA-microbond peak load versus embedded area for GF-PP at various test temperatures.

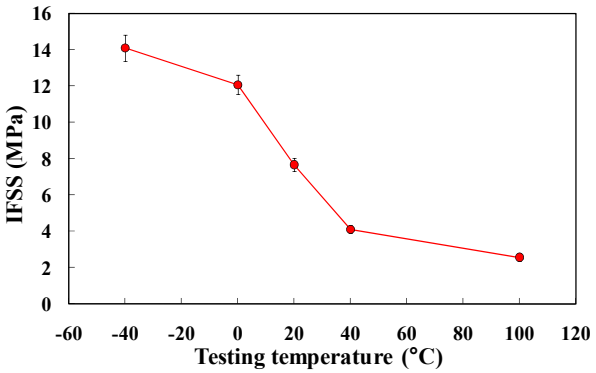

Figure 7 Comparison of average IFSS of glass fibre - polypropylene versus test temperature.

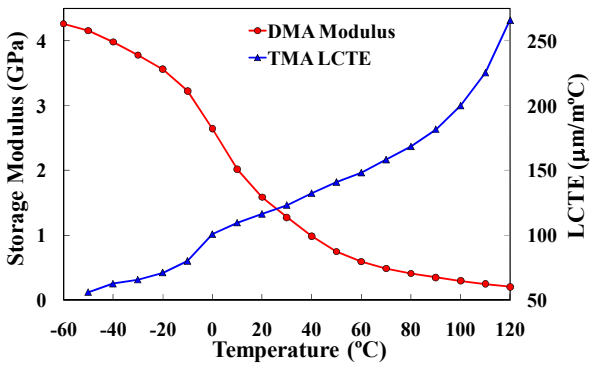

Figure 8 PP matrix properties versus temperature.

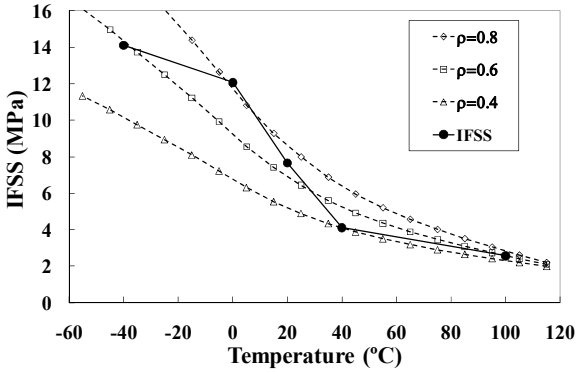

Figure 9 Comparison of average IFSS with residual stress contribution to apparent IFSS.

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