Composites Science and Technology 96 (2014) 7–12

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Temperature dependence of the interfacial shear strength in glass–fibre epoxy composites

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ARTICLE INFO

Article history:
Received 18 December 2013
Received in revised form 6 March 2014
Accepted 8 March 2014
Available online 18 March 2014

Keywords:
A. Glass fibres
B. Fibre/matrix bond
B. Interfacial strength
C. Residual stress

ABSTRACT

The present work focuses on further investigation of the hypothesis that a significant fraction of apparent interfacial shear strength (IFSS) in fibre-reinforced composites can be attributed to a combination of residual radial compressive stress and static friction at the fibre–polymer interface. The temperature dependence of the interfacial properties of a glass fibre–epoxy system has been quantified using the laboratory developed TMA-microbond technique. The temperature dependence of apparent IFSS of glass fibre–epoxy in the range 20 °C up to 150 °C showed a significant inverse dependence on testing temperature with a major step change in the glass transition region of the epoxy matrix. It is shown that the magnitude of the residual radial compressive stress at the interface due to thermal and cure shrinkage is of the same order of magnitude as the measured IFSS. It is concluded that it possible to suggest that residual stress combined with static adhesion could be the major contributor to the apparent interfacial adhesion in glass fibre–epoxy systems.

1. Introduction

There has been a rapid growth in the development and application of fibre-reinforced 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 that control the structure–property relationships in such composites. Composite properties result from a combination of the fibre and matrix properties and the ability to transfer stresses across the fibre–matrix interface. Optimisation of the stress transfer capability of the fibre–matrix interface region is critical to achieving the required composite performance level. The ability to transfer stress across this interface is often reduced to a discussion of 'adhesion' that is a simple term to describe a combination of complex phenomena on which there is still significant debate as to their relative significance and their characterisation. Certainly, one of the generally accepted manifestations of 'adhesion' is the mechanically measured value of interfacial shear strength (IFSS). Despite the high level of attention commonly focussed on chemical influences, such as the application of silane and polymeric coupling agents, on the level of composite IFSS. A number of authors have also commented on the role of shrinkage stresses contributing to the stress transfer capability at the fibre–matrix interface [1–10].

Most composite materials are processed at elevated temperature and then cooled. Since in most cases, the thermal expansion coefficients of matrix polymers are much greater than that of the reinforcement fibres, this cooling process results in a build-up of compressive radial stress (σ_R) at the interface. Assuming that the coefficient of static friction (μ_s) at the interface is non-zero these compressive stresses will contribute a frictional component $\tau_{fs} = \mu_s \cdot \sigma_R$ 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 static frictional stresses can make up a large fraction of the apparent IFSS [9,10]. Most of the available models [1–6] of this phenomenon indicate that the level of residual compressive stress at the interface should be directly proportional to ΔT, the difference between matrix solidification temperature and the composite operating or test temperature. Consequently, this implies that the apparent IFSS in composites should also be dependent on the test temperature.

We recently reported the development of the TMA-microbond apparatus that allows for the measurement of IFSS using the microbond test operated in the temperature controlled environment of a thermo-mechanical analyser [9,11]. Using this equipment to measure the apparent IFSS in a glass fibre–polypropylene (GF–PP) system it was found that the IFSS showed a highly significant inverse dependence on testing temperature with a major increase in the glass transition region of the PP matrix [9]. Further analysis showed that approximately 70% of the apparent room temperature IFSS in this system can be attributed to residual radial compressive

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http://dx.doi.org/10.1016/j.compscitech.2014.03.009
0266-3538/

stress at the fibre–matrix interface. These results are in good agreement with those of Wenbo et al. who recently reported the use of similar methods to show that 80% of the apparent IFSS in a carbon fibre reinforced poly(phthalazinone ether ketone) system could be attributed to residual radial compressive stress at the interface [10]. Whereas this concept is readily understandable in thermoplastic systems where there may be little or no expectation of chemical bonding across the interface, it becomes challenging to expectations in thermosetting matrix systems where there is a long history of the use of chemical bonding theory at the interface. The microbond test was originally developed [12] to deal with the challenge of characterising the fibre–matrix interface in systems with high levels of apparent adhesion such as those often experienced with epoxy resin matrices. Despite the long history of the application of the microbond test in this area there appears to have been little, if any, investigation of temperature effects such as those suggested above. Nevertheless, a number of authors [3–5] have reported temperature dependence of the apparent IFSS in epoxy-based systems obtained using the fragmentation test. However, this has not been investigated systematically and there has been little work recently reported on this important subject. In order to explore these concepts further we have investigated the application of the TMA-microbond technique to the characterisation of the IFSS in a glass fibre–epoxy (GF–EP) system. In this paper we present and discuss results on the apparent IFSS of the GF–EP system over the temperature range 20–150 °C.

2. Materials and methods

2.1. Materials

Boron free E-glass fibres (average diameter = 17.5 μm) coated with γ-aminopropyltrimethoxysilane were supplied by Owens Corning-Vetrotex [13]. IFSS was measured using the in-laboratory developed TMA-microbond test technique. The reproducible preparation of microbond samples is critical to the outcome of the measurement and the avoidance of erroneous interpretation of test results [9,11]. Individual fibres were carefully selected from the roving bundles and 80 mm lengths were mounted on wire frames. The epoxy resin and curing agent used were Araldite 506 (Sigma–Aldrich) and Triethylenetetramine (TETA) hardener (Sigma–Aldrich). The resin and hardener were thoroughly mixed in stoichiometric proportions (22:3) recommended by the manufacturer and degassed under vacuum for 12 min. Epoxy droplets were then deposited on a single fibre using a thin wire that had a small resin bead on its tip. Approximately 40 droplets were placed on individual fibres before these samples were transferred into a convection oven, where they were heated first to 60 °C and held isothermally for 1 h followed by another 2 h heating at 120 °C. After heating, the samples were left in the oven to cool down. The state of cure of the epoxy resin system was examined using differential scanning calorimetry (DSC) in a TA Instruments Q2000 DSC with a heating/cooling rate of 10 °C/min and a 5–6 mg sample size. Results 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 (200× magnification) in order to determine the fibre diameter (D_f), embedded fibre length (L_e), and the maximum droplet diameter (D_m).

2.2. TMA-Microbond

Development of the TMA-Microbond test (TMA-MBT) has been reported previously [9,11]. Fig. 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 Fig. 1. This assembly is enclosed in the TMA temperature controlled programmable oven. 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 between the tab and the polymer droplet 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 to obtain the maximum force (F_{max}) at debonding. This was used with the corresponding fibre diameter and embedded length to calculate the apparent IFSS using to Eq. (1).

$$\tau_{ult} = \frac{F_{max}}{\pi D L_e} \quad (1)$$

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 the cured epoxy matrices and single glass fibres using dynamical mechanical analysis, differential scanning calorimetry and thermo-mechanical analysis. Dynamic mechanical analysis (DMA) was carried out on cured samples of the epoxy system with dimensions 60 × 12.6 × 3.2 mm using a TA Instruments Q800 DMA. Three-point bending configuration was used with a support span length of 50 mm and a heating rate 3 °C/min from 20 °C to 200 °C, frequency 1 Hz, oscillating amplitude 100 μm, static pre-load 0.1 N, and force track: 150%. The coefficient of linear thermal expansion (CLTE) of discs with dimensions of 6 × 1.6 mm was measured using a Q400EM TMA with heating rate 3 °C/min from 20 °C to 200 °C with a 0.1 N static force. Axial CLTE of 20 mm lengths of single unsized glass fibre was also determined using a Q400EM TMA heated at 3 °C/min from −60 °C to 500 °C under 50 ml/min nitrogen [14].

3. Results

The TMA-microbond results for F_{max} versus interfacial area obtained for the glass fibre–epoxy (GF–EP) system at seven different test temperatures in the range 20 °C to 150 °C are shown in Fig. 2. 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 glass transition temperature (Tg) show low levels of scatter with high levels of

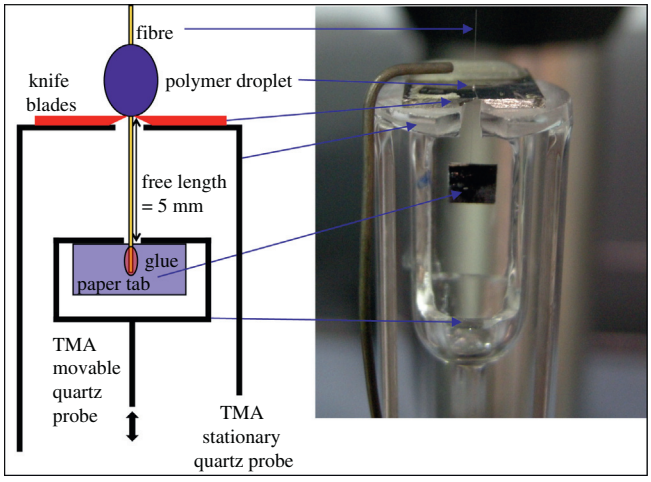

Fig. 1. Schematic and close up photograph of the TMA-Microbond test configuration.