THE INTERFACIAL PROPERTIES OF GLASS FIBRE/NANO-MODIFIED POLYESTER MATRIX COMPOSITES

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Abstract

The single fibre pull-out (SFPO) test has been used to investigate the interfacial interaction between a glass fibre and a polyester matrix system. However, mechanical data alone cannot explain fully the mechanisms of failure, and time-of-flight secondary-ion mass spectrometry (ToF-SIMS) has been utilised to gain insight into the interfacial chemistry of adhesion.

The present work employs ToF-SIMS for the forensic examination of fibre surfaces following a SFPO test. Regions of interest have been selected for retrospective spectral analysis.

Results are presented which lead to the description of a failure model based upon these complementary analytical techniques. ToF-SIMS has revealed a difference in the surface chemistry at the fibre tip compared to the bulk of the pulled out region, which correlates with stress transfer models in the literature showing higher stress states existing at the embedded fibre tip region.

The application of the methodology to nano-modified polyester matrix composites is discussed.

1 Introduction

The mechanical properties of fibre reinforced composite (FRC) materials depend critically upon the nature of the interface between the polymeric matrix and the reinforcing fibres.

Interfacial properties can be investigated by several means; macromechancial tests such as inter/intra laminar shear stress measurements; and micromechanical tests such as the single fibre pull-out (SFPO), single fibre fragmentation test (SFFT), and microdroplet tests [1]. These micromechanical tests utilise model specimens which examine the interfacial parameters of a composite system at a constituent level.

A particular issue with these micro-mechanical tests is the number of data reduction methods employed by different researchers particularly for the SFFT and SFPO tests.

Given the difficulties in understanding and interpreting the mechanical data in isolation, additional information would be useful to assist explaining the failure mechanism(s). This may take the form of online observation of the stress distribution, or through some form of post analysis.

Further insight into the deformation micromechanics can be gained by utilising spectroscopic methods to study the FRC interface. By far the most widely used approach is that of Raman spectroscopy to deduce the interfacial shear stress (IFSS) distribution along embedded carbon or aramid fibres [2,3]. Microscopy and surface analytical techniques have also been used to provide morphology and chemical interaction information at composite interfaces [3-6].

Secondary-ion mass spectrometry (SIMS) is a particularly useful technique in characterising FRC fracture surfaces [7]. Its use in the fractographic studies of FRC materials enables the precise locus of failure to be determined as interfacial, between fibre and matrix; cohesive, within the matrix; or even within the fibre-matrix interphase. Very thin polymeric layers can be detected increasing the chemical knowledge of a failure to complement mechanical data and fractographic observations.

Preliminary investigations of the glass fibre/polyester matrix interface using the SFPO test and time-of-flight secondary-ion mass spectrometry (ToF-SIMS) have been conducted. These investigations located a change in surface chemistry around the pulled-out fibre tip region [8,9].

Stress transfer models predict a change in the stress state surrounding the embedded fibre tip, as seen in Figure 1 [10]. In order to investigate this, a new methodology to study the interfacial chemistry

associated with the pulled-out fibre surface after SFPO testing, has been devised.

In this work the objective is to use spectroscopy methods to determine interface chemistry directly using ToF-SIMS, and SFPO tests to investigate the fibre/matrix interface of polyester matrix composites.

On the basis of the results to be presented, a failure model has been proposed which has utilised the complementary analytical techniques of surface analysis and fractography to assist explanation of the deformation micromechanics and supplement the mechanical data. The results show that there is a change in the pulled-out fibre tip surface chemistry caused by the increased stress state surrounding the fibre tip, leading to a change in the local failure mechanism. Further work applying the methodology described to investigate nano-modified resin systems is proposed.

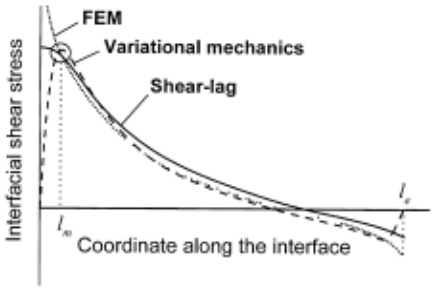


Fig. 1. IFSS distribution along embedded fibre length in an SFPO specimen estimated using the shear-lag approach, after Pisanova *et al* [10]

2 Materials

The resin under investigation was an unsaturated polyester resin, (Crystic 2-406PA, Scott-Bader) supplied without the addition of the silica thixotropic agent. The resin was mixed and cured according to the manufacturer's specification. Sized single glass fibres (2001/600TEX, PPG, NC, USA) were used to manufacture SFPO specimens.

Nano-modification of the polyester resin was made by incorporating phenyl organically modified silica particles (ormosils), with approximate diameter of 150 nm, supplied by the University of Surrey Chemistry Department. Ormosil manufacture and particle dispersion details are explained elsewhere [11,12].

3 Experimental Techniques

Based upon preliminary investigations, a holistic analytical approach has been devised to analyse the SFPO specimen systematically from "cradle-to-grave" using reflected light microscopy (RLM) and ToF-SIMS both pre- and post-mechanical testing, and scanning electron microscopy (SEM) (only after pull-out, as the sample preparation required a gold sputter coating therefore altering the surface composition).

In order to conduct such analyses and ensuring the same analysis region was used throughout, a specially designed mounting cradle was used. The cradle griped the SFPO specimen and could be interchangeably mounted to the ToF-SIMS sample platen, RLM microscope and SEM sample stage. The details of this procedure have been previously described [13].

ToF-SIMS imaging has been used for the forensic examination of fibre surfaces following the SFPO test. Regions of interest have been selected for retrospective analysis. Multivariate techniques have been applied to assist the identification of regions of chemical similarity, enabling better image segmentation and removal of topographic effects [14,15].

4 Results and Discussion

4.1 Mechanical data

A force versus extension plot from an SFPO test can be seen in Figure 2. This follows the expected shape where there is an initial steep rise corresponding to the fibre debonding up to a maximum force F_{max}, then a drop in the force which declines further with a characteristic stick slip behaviour, as the fibre is pulled out from the matrix [16,17]. A basic data treatment has been employed in this paper to calculate the apparent IFFS (τ_{app}) using the following formula:

$$\tau_{app} = \frac{F_{\max}}{A} = \frac{F_{\max}}{\pi d_f L} \quad (1)$$

where d_f is the fibre diameter and L is the embedded length, as measured from microscopic analysis. The data from this test are presented in Table 1.

Table 1. SFPO Mechanical Data

Material	d_f (μm)	L (μm)	F_{max} (N)	τ (MPa)
Glass/Polyester	12.2	849	0.157	4.8

The principal aim of this investigation was not to generate mechanical data, however rather to investigate the surface properties of the pulled-out

fibre. However, the IFSS has been calculated to be 4.8 MPa, which is in agreement with previous investigations of glass fibre/polyester systems [16].

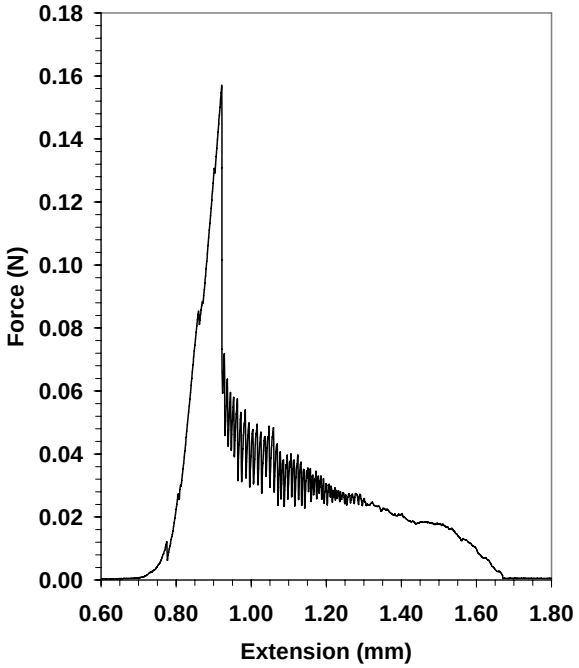


Fig. 2. A force verses extension plot of a SFPO experiment

4.2 ToF-SIMS results

The objective of this investigation was to generate a pulled-out fibre surface and utilise ToF-SIMS to determine the locus of failure and provide further information to model the failure mechanism, and investigate further preliminary observations. Figure 3, presents positive mode spectra of the pre-embedded and pulled-out fibre tip over a 128 µm x 128 µm region using the high mass resolution bunched mode, although as the fibre is some 12 µm in diameter, the area of specimen contributing to the data set is some 12 x 100 μm^2.

It is evident that the two spectra are distinctly different. The characteristic peaks of the spectra, chemical assignments, likely chemical structures and their origin are presented in Table 2. The pulled-out fibre tip, as expected, has high intensity peaks at 91u, 105u, 115u and 149u characteristic of the polyester resin. The pre-embedded fibre has a very intense peak at 135u associated with the epoxy pre-polymer of the size. There are also intense peaks at 58u and 73u characteristic of poly(dimethyl siloxane) (PDMS), a highly mobile surface contaminant which could originate from the manufacturing or storage environments. The presence of this contaminate can assist in the understanding of the failure surfaces. The intensity of the PDMS characteristic peaks on the pulled-out fibre spectrum are very low, the negative spectra, not presented here, also show this. This information, coupled with the appearance of peaks at 28u, 39u and 40u which are characteristic of the underlying glass provide some insight into a failure model. This suggests that the debond has penetrated through the interphase, stripping away the top layer of size on the fibre surface, to reveal the underlying glass.

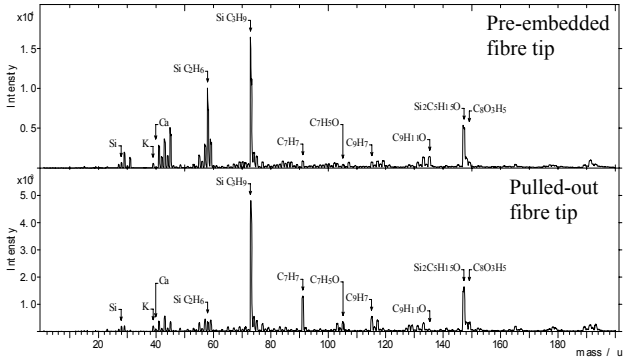


Fig. 3. Positive ToF-SIMS spectra of the pre-embedded and pulled-out fibre tip

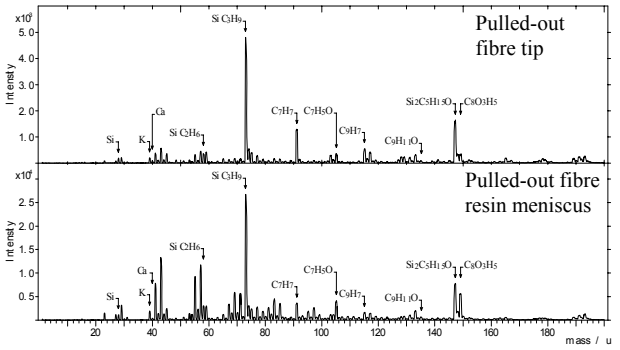


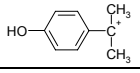
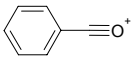
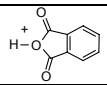
Fig. 4. Positive ToF-SIMS spectra of the pulled-out fibre tip and resin meniscus

Figure 4 compares positive spectra of the pulled out fibre tip and the conical resin fragment region, an artefact of the SFPO failure located at the fibre entry point to the resin. These spectra were generated from retrospective analysis of ToF-SIMS images which used the higher spatial resolution burst alignment mode. A raster area of 128 µm x 128 µm was used for the tip region and a larger 256 µm x 256 µm area for the resin cone, using resolutions of 256 x 256 and 512 x 512 pixels respectively.

As expected, the spectrum of the resin cone region has higher intensity of polyester characteristic peaks and low intensity of the characteristic glass peaks. Therefore there is surface coverage of polyester resin in this region unlike the pulled-out

fibre tip region, suggesting that the debond runs deeper through the fibre/matrix interface at the tip region. As mentioned earlier this observation is not totally unfounded given that the stress transfer models predict that there is a higher stress state located around the fibre tip region [10,16,17,19]. The evidence presented here, and that from previous ToF-SIMS investigations of pulled-out fibres [8,9,13], suggests that this higher stress state has caused the debond to penetrate deeper through the interphase at the tip region therefore revealing the underlying glass.

Table 2. Characteristic peaks and chemical structures [12,20-22]

Mass (u)	Formula	Characteristic	Structure
135	$[C_9H_{11}O]^+$	Glass fibre size (epoxy)	
91	$[C_7H_7]^+$	Polyester resin	
105	$[C_7H_5O]^+$	Polyester resin	
115	$[C_9H_7]^+$	Polyester resin	
149	$[C_8H_5O_3]^+$	Polyester resin	
58	$[SiC_2H_6]^+$	PDMS	$H_3C-Si-CH_3$
73	$[SiC_3H_9]^+$	PDMS	$H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{Si}}-CH_3$

This clear chemical difference at the fibre tip region is in accord with stress transfer model predictions.

5 Application of Methodology

This methodology has shown to be useful from a proof of concept standpoint, characterising the base polyester resin matrix system, and will be particularly instructive when utilised to assess the interface chemistry and IFSS of a nano-particle modified polyester matrix system.

The nano-modification of the base polyester resin with phenyl ormosils has been demonstrated to provide a fourfold toughening effect [23]. This is the rationale for considering its application as a matrix material of an FRC with the aim to produce an overall tougher composite.

The origin of this toughening effect has been studied previously. Fracture surfaces generated from conducting double edge notch (DEN) tests on the base polyester resin and phenyl nano-modified resin system specimens have been examined using SEM and presented in Figure 5, [23].

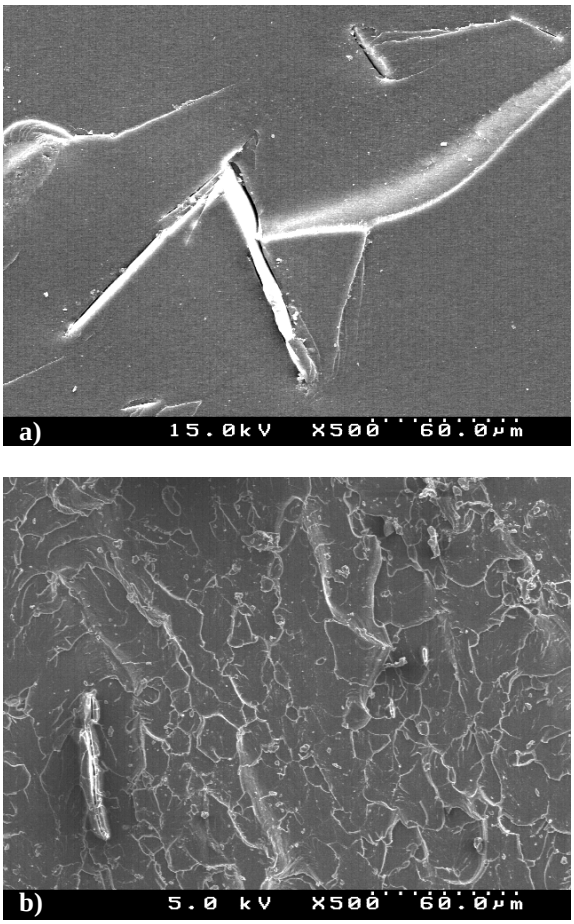


Fig. 5. SEM micrographs of the DEN fracture surfaces of: a) unmodified polyester resin, b) phenyl ormosil modified polyester resin, x500 magnification, after Jesson *et al* [23]

The base polyester fracture surface, Fig. 5a) shows a typical smooth fracture surface, consistent with a brittle failure. In comparison, Fig. 5b), the phenyl ormosil modified resin presents a rougher surface with more crater-like surface features indicative of increased plastic deformation, consistent with a tougher material failure mechanism. Some of this plastic deformation would be accounted for in the debonding of the particle from the matrix, where it is likely that the surrounding matrix becomes deformed.

It has been demonstrated that assessment of the force displacement curve from SFPO tests can enable the comparison of composite toughness values. Tougher composites display a larger area in the pull-out portion of the curve, as shown in Figure

6, attributed to an increase in the interfacial coefficient of friction, μ, which is dependent upon the physical properties of the matrix and fibre and the interphase between them [17].

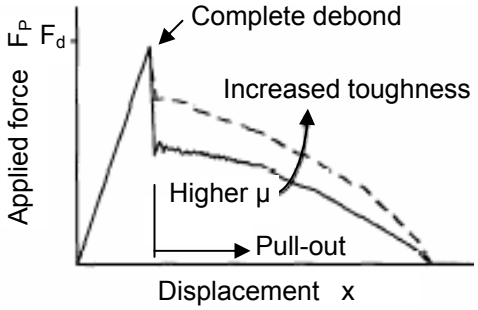


Fig. 6. Schematic diagram showing the effect of an increased μ on the shape of the SFPO test force-displacement curve, after Yue *et al* [17]

How the fracture mechanism of the nano-modified resin system behaves when glass fibres are incorporated is not yet known, and is the basis of current investigations. In parallel, surface analysis techniques will provide insight into the chemistry of the interphase between the ormosil nano-modified resin system and the glass fibre.

6 Further Work

An automated fracture stage for *in-situ* SFPO testing within the ultra high vacuum (UHV) environment of the ToF-SIMS system preparation chamber has been developed. A schematic diagram is shown in Figure 7.

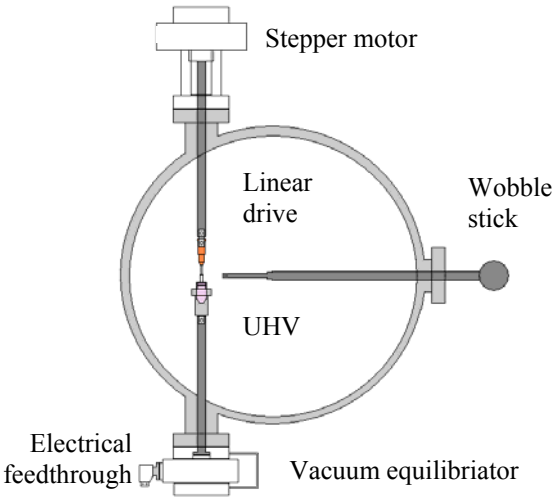


Fig. 7. Schematic diagram of the *in-situ* fracture stage design

This will remove the risk of contamination, principally from test machine lubrication present in the atmosphere of failure, and fracture debris from previously tested specimens, and provide higher secondary ion yields for enhanced spectra interpretation [24-26]. The automated stage will permit quantifiable mechanical data to be collected while also generating contaminant free failure surfaces.

7 Conclusions

This investigation adds further to preliminary studies utilising surface analytical techniques to compliment the mechanical data obtained from SFPO tests of base polyester resin and glass fibres.

A systematic cradle-to-grave analysis methodology has been employed in order to forensically investigate SFPO specimens. This approach confirmed that the change in surface chemistry at the fibre tip region was a result of the pull-out. Stress transfer mechanics models predict a change in stress state at the tip region. With this knowledge, a more informed failure mechanism(s) was proposed [13].

The methodology will be applied to investigate nano-modified polyester resin systems to assist characterisation of the mechanical properties and inform on the chemistry of the interphase, with a view to understand how the toughness of FMC materials can be improved.

8 Acknowledgements

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