Study of the interface in Kevlar 49–epoxy composites by means of microbond and fragmentation tests: effects of materials and testing variables

H. D. Wagner, H. E. Gallis, E. Wiesel
Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

The work presented in the present paper focuses on the interface in Kevlar 49–epoxy composites. Experimental results for the interfacial shear strength obtained using the microbond test by means of different loading configurations (parallel plate loading, parallel conical plate loading, circular loading), are presented and compared. Contrasting with recent finite-element predictions proposed in the literature, the interfacial shear strength is found to be altogether insensitive to the type of microbond loading configuration. A comparison of the results obtained using two micromechanical tests (microbond and fragmentation) is performed. The interfacial shear strength results obtained by means of the fragmentation test are found to be higher by a factor of about 50% than those obtained by means of the microbond test. A possible explanation for this difference is proposed and discussed, and the value of the “true” interfacial shear strength is conjectured to fall between the values measured by these two tests. The effect of fibre surface chemistry modification (surface desizing) is probed by surface-sensitive techniques (XPS–ESCA and contact angle measurements from droplets) and by micromechanical testing techniques. Surface-sensitive techniques and micromechanical testing provide compatible information for the Kevlar–epoxy system studied here, and the knowledge of the chemical characteristics of the fibre surface can therefore be used as a means of predicting the interfacial shear strength.

1. Introduction
The microstructural features of the interface between a fibre and a matrix in a composite material are of critical importance in controlling the mechanical strength and toughness of the composite. The strength under shearing forces of the interface is viewed by most researchers as a key property since it reflects the ability of the composite to transfer stresses from an external mechanical field to the reinforcing phase (the fibre). Usually, stronger interfaces (or shorter stress transfer – or critical – fibre lengths) result in stronger, but more brittle, composite materials. The so-called “interfacial shear strength” can be measured using either macromechanical or micromechanical tests. Examples of macromechanical tests are the interlaminar shear strength test (ILSS) and the transverse tensile test. Such tests are usually simpler to conduct than micromechanical ones but in many cases it is doubtful whether a true fibre-matrix interfacial property is indeed measured. A number of micromechanical tests such as the fragmentation test, the pull-out test, the microindentation test, and the microbond test, have been used over the last few years and have been the subject of intensive research. This has culminated in an international round-robin exercise, the results of which were recently presented [1]. Micromechanical tests are very sensitive to changes in the interface chemistry and they are unambiguous regarding the failure mode (unlike macroscopic tests). One drawback is the fact that the specimens used are all (except the microindentation specimen) composite model configurations, wherein the stress state is quite different from that in a real-life composite. Another problematic aspect of both macroscopic and microscopic tests is the fact that all give different (albeit reproducible) values for the interfacial shear strength.

The work presented in the present paper has several purposes. First, microbond test results obtained using two different operators as well as different loading configurations are presented and compared. Second, a comparison of the results obtained for the interfacial shear strength using two micromechanical tests (microbond and fragmentation) is performed. Third, the effect of fibre surface chemistry modification (surface desizing) is probed by the surface-sensitive techniques of X-ray photoelectron spectroscopy (XPS) with electron spectroscopy for chemical analysis (ESCA) and contact angle measurements, and by micromechanical testing techniques. The objective of this was to determine whether surface-sensitive tech-
niques and micromechanical testing would provide compatible information, and whether the knowledge of the chemical characteristics of the fibre surface might be used as a means of assessing (or predicting) the interfacial shear strength.

2. Experimental procedure

2.1. Materials
The fibre used in this study was Kevlar 49 poly(phenylene terephthalamide) from Du Pont, with a nominal diameter of 11.9 \( \mu \)m. The filaments were used either in the as-received state, or desized by extraction for 4 h in a Soxhlet apparatus using toluene as a solvent. Desizing was followed by washing in acetone and drying under vacuum at 80 °C. The matrix material was DER 331 (Dow Chemical), a bisphenol A (DGEBA) based liquid epoxy resin with an average epoxy equivalent weight of 186–192, mixed with the curing agent DEH 26 tetraethylenepentamine (TEPA), with an amine equivalent weight of 27. The curing of the samples was performed according to the following schedule: 1 to 3 days at room temperature, followed by 3 h at 80 °C and 3 h at 100 °C, and final (slow) cooling. The resulting cured epoxy resin is a relatively stiff material, with Young’s modulus, tensile strength and failure strain equal to 1.62 GPa, 55 MPa and 0.09, respectively.

2.2. Preparation of microbond specimens
Single filaments were carefully teased out from the fibre bundle and stretched horizontally on a frame using 2 g weights attached to the ends of each filament. Poxipol epoxy cement was then used to fasten the fibre to the frame. Droplets of freshly prepared liquid epoxy were carefully spread on each filament using a boron fibre. The droplet length and thickness, and the fibre diameter were measured after the curing was completed by optical microscopy. Finally, the fibre was cut on both sides of the droplet, and one side was used for tabbing using two roughened square aluminium tabs fastened with cyanoacrylate cement, leaving a 10 mm gauge length between the jaws of the tensile testing apparatus and the droplet. The dimensions of glycerol droplets spread on the fibres were used to calculate contact angle values using a recently developed algorithm [2] that is based on the work of Yamaki and Katayama [3] and Carroll [4].

2.3. Preparation of fragmentation specimens
The preparation procedure for the fragmentation specimens (prepared in the form of 100–200 \( \mu \)m films rather than the more common dog-bone specimens) was identical to that used in our previous work [5], to which the reader is referred.

2.4. Procedures for micromechanical tests
The microbond test has been described and analysed by various researchers since 1969 (see the literature review by Jiang and Penn [6]). Its principle is very simple, consisting of measuring the force necessary to debond the interface between a fibre and a solid droplet encasing it, by pulling the fibre in one direction and restraining the droplet in the opposite direction. Commonly, parallel knife-edges, yielding a two-point loading, are employed to restrain the droplet, although Haaksma and Cehelnik [7] and Andersson et al. [8] have performed their experiments using a circular area of contact (some finite-element work has also recently been initiated by Herrera-Franco and Drzal [9] to assess the possible difference in stress states between the point and circular loading configurations).

Here we performed a series of tests to assess the role of a few variables which we thought might have a strong effect on the pull-out data. First we analysed what would happen if two different operators performed identical tests (same material system, same testing procedure and apparatus). The tests were performed independently by two skilled, well-trained individuals, within a one-year interval. Significantly, these two individuals never had the opportunity to meet and exchange information, but rather they were given a list of instructions and procedures to follow. Second, we studied the effect of the geometry of the microbond loading system by performing three series of tests with parallel knife-edge loading (strictly, a two-point loading configuration), parallel cone-plate loading (also a two-point loading configuration), and circular loading (a uniform loading configuration).

These loading configurations are illustrated in Fig. 1. For the parallel knife-edge configuration we used either 30 \( \mu \)m thick spacers (operator 1) or no spacers at all (operator 2); for the parallel cone-plate configuration we used no spacers; and for the circular loading configuration we used a small metallic disc containing a 30 \( \mu \)m circular hole. All microbond tests conducted with the Instron machine (parallel knife-edge and parallel cone-plate configurations) were performed at a deformation rate of 200 \( \mu \)m min\(^{-1}\), whereas the tests conducted with our custom-made minitensile tester (circular loading configuration) were performed at a deformation rate of 30 \( \mu \)m min\(^{-1}\).

We then performed a series of single-fibre composite (SFC, or fragmentation) tests with the same material systems, and a comparison between the results from these tests and those obtained from micro-pull-out tests was performed. The SFC tests were conducted using our custom-made minitensile tester at a deformation rate of 30 \( \mu \)m min\(^{-1}\), and using a nominal gauge length of 20 mm. The average sample thickness was 150 \( \mu \)m and the test was continuously monitored by videomicroscopic means, as described in our previous publications [5, 10–13].

2.5. X-Ray photoelectron spectroscopy (XPS–ESCA)
The XPS studies of the as-received and desized Kevlar 49 fibres were performed using a PHI model 550 ESCA/SAM, using AlK\(_\alpha\) radiation (\( h\nu = 1486.6 \) eV) as an excitation source. The probing depth was estimated to be 10–30 atomic layers. To avoid peak shifts or