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**Characterising Micro and
Nanoscale Interfaces in
Advanced Composites: A
Review**

**W R Broughton, L E Crocker
and M J Lodeiro**

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Characterising Micro and Nanoscale Interfaces in Advanced Composites: A Review

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ABSTRACT

This report critically examines test methods and predictive analysis for characterising interfacial and interphase properties of micro- and nanofilled polymer systems, in order to ascertain the influence of these properties on the overall composite behaviour. The report covers both conventional fibre-reinforced composites and nanocomposite materials. Particular emphasis has been placed on the ability of test methods to provide reliable, quantitative data for modelling and design purposes. Novel measurement techniques, such as nanoindentation, nanoscratch, scanning probe microscopy (SPM), Raman spectroscopy and ultrasonic techniques are assessed, as well as micromechanical interface test methods (single-fibre fragmentation, fibre pull-out, microdrop/microbond and microindentation). The test methods are assessed in terms of the data generated, fitness for purpose, ease of use, sensitivity and spatial resolution, and consistency of data.

The modelling approaches considered are those in which the interface is included as one of the constituents. Predictive analysis techniques assessed include micromechanical models used for predicting elastic and strength properties of conventional composites, and modelling approaches such as molecular modelling, continuum based modelling and computational methods used for characterising the behaviour of nanocomposites. The models are discussed in terms of applicability to material type (continuous and discontinuous, aligned and random), data provided and comprehensiveness in covering all the many parameters affecting the interface in composite materials from micro- to nano-scale.

The review highlights the limitations of micromechanical interface test methods in providing reliable quantitative interfacial data. There is no single ideal or universally applicable interfacial test method nor any standard method in existence. However, scanning probe microscopy consists of a powerful set of techniques, which could potentially provide in-situ quantitative mechanical and chemical measurements for characterising interfacial and interphase properties of composite systems ranging from the micro- to the nanoscale. Combined with atomic force, acoustic, thermal and electrochemical probes, as well as nanoindentation and nanoscratch facilities, SPM could provide a comprehensive set of data sufficient to fully characterise the interface and interphase properties. It is not limited to ambient conditions, and thus could be used for in-situ environmental studies.

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1 INTRODUCTION

The engineering properties and performance characteristics of complex multiphase polymeric systems, such as continuous and discontinuous fibre-reinforced polymers (FRPs) and polymeric nanocomposites (PNCs), are dependent upon a number of factors:

- Spatial and compositional nature of the filler;
- Size, orientation and spatial distribution of the filler in the matrix;
- Filler and matrix engineering properties;
- Interfacial region between filler and matrix (i.e. interface and interphase); and
- Constituent volume fractions.

There is a wide range of commercially available filler formats differing in geometry, size and chemical composition, which include nanoparticulates (clays, particles, nanotubes and nanofibres), short (~1 mm) and long discontinuous fibres (< 10 mm), flakes, continuous fibres and woven fabrics. For many of these formats there are mathematical models available for predicting elastic and strength properties from the properties of the resin and filler. In the analysis for most of these models, a number of assumptions are made about the interfacial properties. These are [1]:

- Filler, matrix and hence the composite exhibit linear elastic behaviour;
- Interface is infinitesimally thin;
- Perfect interfacial bonding between filler and matrix (i.e. no strain discontinuity across the interface);
- Material in the vicinity of the filler is identical to material in the bulk matrix;
- Fibres are uniform and regularly spaced;
- Fibres are perfectly aligned if unidirectional or perfectly random if random;
- A void free composite; and
- Strains experienced by the fibre, matrix and composite are equal under tensile or compressive stresses.

Most of these assumptions are incorrect, but are necessary in order to obtain solutions to the mathematical models. The predictive analysis will often be sufficiently accurate for many design purposes and provide important information on material behaviour. In reality, the filler is surrounded by a complex environment, consisting of areas of imperfect bonding, residual thermal stresses and high stress gradients produced by localised stress concentrators (i.e. voids, micro-cracks and inclusions), with the filler-matrix interface being an inhomogeneous layer of variable thickness and distinct physiochemical properties from the bulk matrix [2]. This layer is defined as the interphase and consists of a transition region where chemical, physical and mechanical properties vary between the fibre and matrix [3].

Interfacial (interphase) properties play an important role in determining the mechanical behaviour of FRPs [1-8]. Intralaminar (in-plane) and interlaminar (through-thickness) shear, transverse and interlaminar tension, and compression behaviour are particularly sensitive to the quality of the interface. These properties degrade more than axial properties because of interfacial failure.

The interface is also important in determining fracture toughness, and long-term property retention under fatigue and hostile chemical environments (including moisture). Composites with weak interfaces have relatively low strength and stiffness, but high resistance to fracture. Weaker interfaces promote interfacial debonding, delay the onset of fibre failure and lead to increased energy absorption during the fracture process. Environmental resistance tends to be compromised in laminates with weak interfacial bonding. Composites with strong interfaces are intrinsically stronger and stiffer but tend to be brittle (i.e. low fracture toughness). A strong interface helps to ensure good off-axis properties, delays the onset of microstructural damage formation and reduces the rate of damage accumulation, thus contributing to improved product reliability and service life.

As the pace of nanocomposite research has intensified, it has become apparent that the conventional approach to understanding and optimising material performance of PNCs is not applicable. The misconception is that it is simply a case of scale and that technology applicable to discontinuous reinforced composites is directly transferable to nanocomposites. At the nanoscale, the boundary between a material and a functional device may become blurred [8]. The conventional approach used to determine structure-property relationships is unsuitable when the length scale of the morphology of the reinforcement and the critical length of the fundamental physics of a given property coincide (i.e. the onset of non-bulk (localised) properties).

Note: Particles with sizes below 100 nm are characterised by extremely large surface-to-volume ratio. For particles with a diameter of 10 nm, 15 % of all atoms are located on the particle surface compared to 0.015% for 1 μm diameter particles. The thickness of a human hair is approximately 10,000 nanometres.

It could be argued that the same factors that influence the performance of PNCs are equally applicable to the performance of conventional FRPs, but for six interrelated characteristics associated with nanoscopic dimensions and inherent surface areas of nanofillers. These distinguishing characteristics have been identified as [8]:

- Low percolation threshold ($\sim 0.1\text{-}2.0$ vol.%) – critical volume fraction at which an infinite network of randomly dispersed particles form a continuous path across the composite;
- Particle-particle interactions arising at low volume fractions affecting orientation and position of adjacent particles (short range order or correlation);
- High particle density per particle volume ($10^6\text{-}10^8$ particles/ μm^3);
- High surface (interfacial) area to volume ratio ($10^3\text{-}10^4$ m^2/ml);
- Short inter-particle separation (of the order of 10-50 nm for 1-8 vol.%); and
- Comparable dimensions for particulate particle separation and relaxation volume of polymer chains.

Not all of these characteristics apply to the same degree for all forms of nanofillers. It is self-evident that for spherical nanoparticles the aspect ratio is low, thus it may be argued that orientation correlations between particles is not an issue, however that is not the case. Particle size, inter-particle distance and the extent that the interfacial (interphase) region between filler and matrix penetrates the bulk matrix are of a similar order of magnitude to the radius of gyration R_g of the polymer matrix. R_g is a key spatial parameter of the order of 10-20 nm used to relate static and dynamic properties.

The internal interfacial area generated by fully exfoliated and dispersed high aspect ratio plates or rods is comparable to that of macro-molecular dendrimers (spherical polymeric molecules) and proteins.

Note: Fully exfoliated refers to when the mean distance between particles becomes a maximum for a given filler content.

PNCs are intrinsically anisotropic, exhibiting a domain-like structure resembling grains within which these domains have a preferred filler orientation. At a global level, the orientation can be considered isotropic. PNC structures tend to have far more commonality with meso-structured macromolecular systems, such as semi-crystalline polymers, block co-polymers and liquid crystal polymers than with conventional FRPs. There is the additional factor of interaction between nanoparticles and crystalline and amorphous phases, which has an impact on order-disorder transitions (e.g. glass transition temperature, T_g), relaxation processes and phase behaviour.

The amount of particulate filler needed to enhance the material performance of PNCs is also on a reduced scale (typically 1-5 vol.%) compared with conventional FRPs. The addition of nanoparticles has a beneficial effect on a wide suite of mechanical and physical properties (e.g. stiffness, strength, thermal stability, fire retardancy, fracture toughness, etc.), improving functionality to levels not achievable using larger scale fillers in the same quantities. These enhancements can be achieved without compromising processibility, weight and cost.

A number of different approaches including coupon testing, micromechanical methods and more recently surface and chemical techniques have been used to provide information pertaining to interfacial and interphase properties. A common issue with most of these techniques is that there is a need for further work in establishing procedures for ensuring accurate and repeatable measurements that represent actual material properties. Surface and chemical analysis techniques that are applicable to conventional and nanocomposites are listed below.

Analytical Technique	Property
Atomic Force Microscopy (AFM)	Interfacial/interphase properties (inc. stiffness)
Atomic Force Acoustic Microscopy (AFAM)	Interphase elastic properties
Differential Scanning Calorimetry (DSC)	Phase transitions (melting and glass transition)
Dynamic Mechanical Analysis (DMA)	Damping coefficient (energy dissipation at interface)
Flow Microcalorimetry (FMC)	Absorption/desorption – surface reactivity
Fourier Transform Infrared Spectroscopy	Polymer chemistry – state of cure
Infrared Spectroscopy (IRS)	Molecular structure and chemical composition
Inverse Gas Chromatography (IGC)	Filler-matrix interactions
Nanoindentation	Stiffness, interfacial strength and fracture toughness
Nanoscratch	Interphase dimensions
Nuclear magnetic resonance	Moisture absorption and fibre/matrix chemical bonding
Raman Spectroscopy	Strain measurements (stress-transfer)
Scanning Electron Microscopy (SEM)	Surface topography and failure analysis
Scanning Electrochemical Microscopy (SECM)	Chemical composition of interphase and diffusion
Scanning Thermal AFM	Thermal conductivity and glass transition temperature
Scanning Tunnelling Microscopy (STM)	Surface topography (high resolution)
Secondary Ion Mass Spectroscopy (SIMS)	Chemical composition of filler surfaces
Thermo Gravimetric Analysis (TGA)	Thermal stability (flammability)
Transmission Electron Microscopy (TEM)	Molecular structure - dispersion
Wide-Angle X-ray Diffractometry (WAXD)	Degree of exfoliation and intercalated spacing
X-Ray Photoelectron Spectroscopy (XPS)	Chemical composition of fibre/filler surfaces

This report critically examines test methods and predictive analysis for characterising interfacial and interphase properties of micro- and nanofilled systems, in order to determine the influence of elastic and strength properties of these constituents on the overall composite behaviour. The report covers both conventional composite materials and PNC systems. The report provides an assessment of micromechanical interface test methods (single-fibre fragmentation, fibre pull-out, microdrop/microbond and microindentation) and more novel measurement techniques, such as nanoindentation, nanoscratch, scanning probe microscopy (SPM), Raman spectroscopy and ultrasonic techniques. The test methods are assessed in terms of the data generated, fitness for purpose, ease of use, sensitivity and spatial resolution, and consistency of data. The modelling approaches considered are those in which the interface is included as one of the constituents. Predictive analysis techniques assessed include micromechanical models used for predicting elastic and strength properties of conventional composites, and modelling approaches such as molecular modelling, continuum based modelling and computational methods used for characterising the behaviour of PNCs.

The report consists of five sections including the Introduction (Section 1). Micromechanical interfacial test methods and new/novel techniques are covered in Sections 2 and 3, respectively. Section 4 covers predictive analysis techniques. Discussion, general conclusions and recommendations for future work are presented in Section 5.

2 INTERFACIAL TEST METHODS

Matrix dominated properties, such as transverse tension and interlaminar shear strengths are strongly influenced by the quality of the interface bond, and hence the traditional approach has been to employ coupon tests to investigate the interfacial properties of continuous fibre-reinforced laminates. Coupon tests most strongly affected include longitudinal compression, transverse tension, short beam and double notch shear, longitudinal and transverse flexure, intralaminar shear ($\pm 45^\circ$ tension, V-notched beam, etc.), and Mode I and Mode II fracture. There are national or international standards available for the majority of these test methods. Arguably, transverse flexural strength of continuous unidirectional laminates is the most appropriate mechanical property that could be used for assessing fibre/matrix adhesion, and preferable over transverse tensile strength. Unpublished research conducted at the National Physical Laboratory (NPL) has shown that the former is less sensitive to the effects of flaws, and thus generally higher than transverse tensile strength. Transverse flexural strength is strongly dependent on the degree of fibre/matrix adhesion with the surface appearance generally commensurate with the degree of interfacial bonding. The greater the extent of bare (or resin free) fibre surface the weaker the interfacial bonding between fibre and matrix.

Although coupon specimens yield qualitative and quantitative information that can be used to determine the relative degree of interfacial strength, it is impossible to isolate the contributions of the interface from the contributions of the other constituents (i.e. fibre and matrix) to the measured strength. It was because of the inability of these methods to provide a definitive quantitative value for interfacial adhesion that researchers focused attention on micromechanical interface tests employing single fibres.

The most common of these test methods are [2, 4, 7]:

- Single-fibre fragmentation;
- Fibre pull-out;
- Microdrop/microbond; and
- Microindentation.

These methods offer a number of benefits including minimised fibre-fibre interaction, simplified stress states and modelling, minimal material requirements, full control of interface loading, and in-situ monitoring techniques. However, none of the aforementioned micromechanical interfacial test methods provide accurate and unequivocal interface property measurements [4, 9].

There are a number of concerns with these methods in terms of the stress state (stress concentrations), failure processes and whether interfacial strength has any physical meaning [2]. Published data indicates very high data scatter associated with all of these methods and the results obtained differ widely. Data reduction methods associated with the different test methods are also heavily oversimplified. Other concerns include the large variability in specimen geometry and dimensions, methods of specimen manufacture, test equipment and procedures used, parameters measured and/or monitored, and methods of data reduction and analysis employed. It should also be noted that micromechanical tests are generally difficult to perform and that only a small number of specialised laboratories are equipped for carrying out these tests. This section will examine in detail micromechanical test methods used for interfacial characterisation.

2.1 SINGLE-FIBRE FRAGMENTATION TEST

The fragmentation test has gained considerable attention because of its applicability to a wide variety of fibre systems (including brittle fibres), simplicity of specimen preparation and test equipment (i.e. microscope and tensile tester) requirements. This test consists of a single fibre aligned axially in a dogbone resin coupon, loaded in tension. The tensile load applied is transferred to the fibre through shear transfer at the interface.

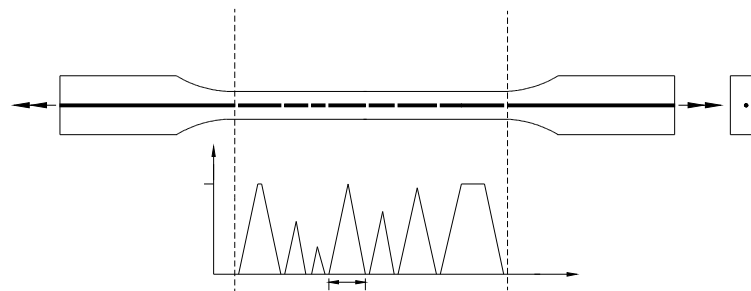


Figure 2.1: Fragmentation specimen geometry and associated axial fibre tensile stress distribution of fragments.

As loading proceeds, the tensile forces exerted on the fibre exceed its tensile strength and the fibre breaks, first at its weakest point (largest flaw) and then at successively weak points (smaller flaws). The embedded fibre fractures into shorter lengths as the test continues and the stress gradients on the fibre ends begin to merge (Figure 2.1).

This fragmentation process halts when the shear stress transfer through the interface can no longer build up enough tensile stress within a fragment to cause any further failures. This is termed the saturation point and the corresponding maximum final fragment length of the fibre is termed the critical length (affected by flaw size, density and distribution) [10].

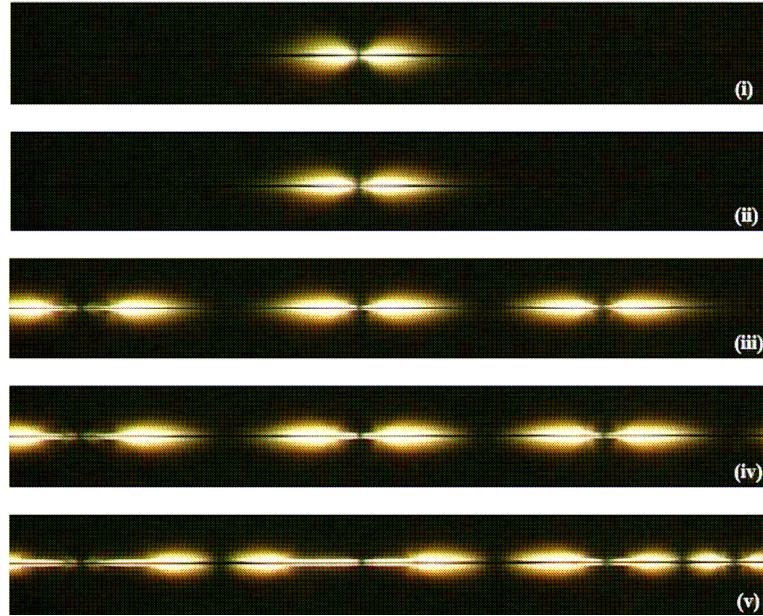


Figure 2.2: Photoelastic microscopy images detailing damage progression in a single break in a carbon fibre fragmentation specimen under full extinction with increasing stress: (i) ~45 MPa, (ii) ~52 MPa, (iii) ~57 MPa, (iv) ~60 MPa and (v) ~66 MPa.

The number and spacing of fibre breaks are monitored with respect to the load/strain applied to the specimen, either continuously or at intervals, until saturation. At saturation, the positions of the fibre breaks or the length of the fragments formed are measured and recorded. A matrix possessing a failure strain three times that of the fibre ensures that saturation is successfully achieved. Figure 2.2 shows photoelastic microscopy images detailing damage progression in a single carbon fibre specimen for increasing applied stress.

Analysis of the fragmentation test is complicated because of the different modes of stress transfer and rupture mechanisms operating at the interface, such as elastic shear loading, debonding, friction, brittle failure and plastic yielding [11]. All of these factors would need to be included in order to provide an accurate, rigorous analysis. However, simple analyses tend to be used, which require only the critical fibre fragment length and the strength of the fibre at the critical length. The critical fibre length, l_c , can be correlated to the interfacial shear strength, τ_i , by the equation:

$$l_c = \frac{d\sigma_f}{2\tau_i} \quad (2.1)$$

where σ_f is the fibre strength at the critical length and d is the fibre diameter.

The critical length is defined as either the longest length from the experimental distribution of fragments or $4/3$ of the average fragment length (as final fragment lengths of between $l_c/2$ and l_c can be expected with an average $3/4 l_c$). In turn, the average fragment length can be defined as the arithmetic mean (monitored length divided by the number of breaks observed within the length) of the experimental fragment length distribution. All other factors being equivalent (fibre and surface treatment, resin specimen geometry, test method, etc.), longer fragment lengths and fewer fragments are indicative of a weaker interface.

The experimentally recorded data are usually presented as plots of cumulative number of fragments with applied stress/strain or as histograms of saturation fragment length distributions [12]. The specimen dimensions used by researchers vary from 43-130 mm long (with gauge-lengths between 15 and 50 mm), 10-25 mm wide (with gauge-widths between 2 and 10 mm) and 0.2-3 mm thick. In order to improve the consistency and repeatability, and reduce scatter in fragmentation data, the gauge-length should be as long as possible, and specimen width and thickness $\geq rE_f/E_m$ (r is fibre radius, E_f is longitudinal modulus of the fibre and E_m is the Young's modulus of the matrix) [5]. A large gauge-length is more suitable for statistical studies; as the population of fragments are more representative of the interaction between defects.

The test is normally accompanied by bare (resin free) single fibre strength tests to enable the strength of the fibre at the critical length to be determined. These tests are performed on long fibre lengths at several gauge-lengths to ascertain the relationship between fibre length and strength. These data are then used to extrapolate to the strengths of the very short fragment lengths achieved at saturation, using statistical methods. The single fibres for these tests are randomly selected from a tow and contain flaws of different sizes. However, this may not necessarily correspond to an equivalent length of fibre resulting statistically from the fragmentation process. As the fibre in a fragmentation specimen fractures at large flaws and is subsequently repeatedly broken at smaller flaws, the fragments comprise non-random material and the fragmentation strength actually increases. As a result, the tensile strength of the critical length is commonly under predicted using this method. In addition, the fibre properties in air may differ to those of the fibre when embedded in resin and uniformly along its length.

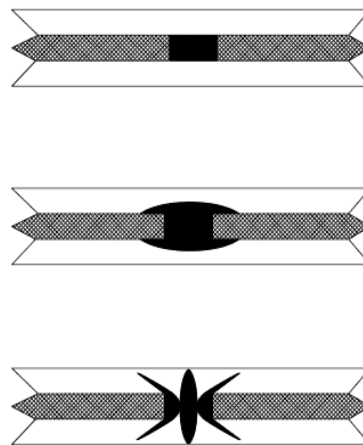


Figure 2.3: Schematic diagram of typical fragmentation failure modes associated with fibre fracture in thermoset matrices: (top) frictional debonding; (middle) interfacial crack growth and (bottom) matrix crack growth.

A variety of failure events are possible when performing the fragmentation test, since depending on the strength and integrity of interfacial adhesion and the properties of the fibre and matrix, the balance of competing failure processes may change depending on the test environment. It is possible to observe and differentiate between the different failure modes using photoelastic microscopy (see Figure 2.3 [5]).

For weak interfaces: a crack propagates down the interface extending along the fragments on either side of a fibre break.

For strong interfaces: elliptical matrix cracking in the region surrounding a fibre break occurs, which may form at 45° or 90° to the fibre:

- **For ductile matrices:** matrix yielding may occur at the interface extending along the fragments on either side of a fibre break with continued loading; and
- **For brittle matrices:** first fibre fracture may result in catastrophic failure of the specimen.

Several useful variations to the conventional single fibre fragmentation test geometry and analysis have been developed. These include:

Coaxial Geometry Fragmentation Test: Attempts to extend the fragmentation test to brittle resin systems, which cannot successfully achieve saturation. A thin coating of the brittle resin of interest is applied to the surface of the fibre prior to being encased in a tough resin dogbone specimen [11, 13].

Multi-Fibre Fragmentation Test: Consists of several continuous fibres aligned in parallel, at pre-defined inter-fibre spacing in a dogbone specimen. This test is useful for analysing fibre-fibre interactions [14].

Strand Test: Prepared with fibre tows rather than single fibres, aligned parallel or perpendicular to the dogbone specimen axis [15].

In-situ Fibre Strength Test: Performed using the fragmentation test specimen to provide data on the strength of fibres whilst embedded in the matrix of interest [12].

A detailed and comprehensive study conducted at NPL [5-6] into the single-fibre fragmentation test method has shown that the method can be used to discriminate between different levels of interfacial adhesion. The test enables detailed inspection of the failure mode, thus enabling a clear interpretation of interface quality and consistency/homogeneity. The fragmentation method is suitable for quality control and for comparative purposes (e.g. comparing interfacial adhesion strength of different fibre sizings), but less effective at providing accurate quantitative data for design or predictive models.

Interfacial strengths determined using the fragmentation test are usually high because of the nature of the test; a fragmentation will only occur if minimum bond strength is achieved. The stress state in the specimen is also a contributing factor. High interfacial shear stresses are induced in the vicinity of the fragment ends causing either localised plastic deformation of the matrix or interfacial crack growth. These stresses diminish more slowly than for other micromechanical test methods.

In addition, the applied tensile load also induces high intensity compressive radial stresses, such that further stress transfer can occur at the interface after debonding, through frictional forces. Advantages and disadvantages of the fragmentation test are listed at the end of this section.

The results of tests conducted at NPL, together with modelling of the fragmentation process, revealed that the widely used interpretation of this test is inappropriate when describing the essential features of interface failure [4, 16]. Instead, local stress or energy analysis is recommended. One particular limitation of existing models [2, 9] is their poor description of the stress field at low volume fractions. A simple, closed-form, shear-lag based model [16] was chosen to describe the distributions of the axial stress in the fibre and the interfacial shear stress. This approach simplified to a great extent the modelling and simulation work. While approximate, this method enables a quantitative assessment of the quality of the interface in single carbon and glass fibre epoxy composites.

The good quality of the results obtained using the analysis could not disguise the fact that information obtained on fibre properties is still subject to a large uncertainty, that the existing stress transfer models are still unable to solve all the equations of equilibrium with all boundary conditions satisfied. The consequence is that the stress state is not fully known, and thus interfacial strength values are, at best good approximations. Recent developments have seen the use of Raman spectroscopy to measure strain in the fibre and interfacial shear stress – see Section 3.4.

Advantages	Disadvantages
• Simple specimen handling. • Large statistical sampling of the interface. • Replicates the stress transfer characteristics in real composites. • Critical length is sensitive to and reflects changes in the level of fibre-matrix adhesion. • Energy and fracture mechanics analysis methods being developed which do not require specimen saturation. • Variety of methods available for observing/analysing failure processes directly: • Acoustic emission, • Photoelasticity, • Raman spectroscopy. • Useful variations on the fragmentation test provide additional/complementary information: • Coaxial test, • Multi-fibre test, • Strand test, • <i>In-situ</i> fibre strength test.	• Indirect method of interface loading. • Time consuming: • specimen preparation, • testing and data collection, • data analysis. • Additional fibre strength tests required. • Limited material applicability (tough, high strain to failure matrices). • Highly complex/non-uniform stress state at the interface: • interfacial shear stress concentration near fragment ends, • neighbouring fractures, • affected by fibre pre-tension, • sensitive to level of interface adhesion. • Multiple failure events: • interfacial debonding, • matrix cracking • plastic yielding, • frictional slip. • Does not allow determination of the coefficient of friction/interface pressure. • Interfacial shear strength value depends on the constituent properties. • Relationship between critical fibre length and average fragment length unknown. • Extrapolation of Weibull fibre strength data to short fragment strengths is not understood. • High radial compression stresses can give rise to overestimated interfacial strengths.

2.2 FIBRE PULL-OUT

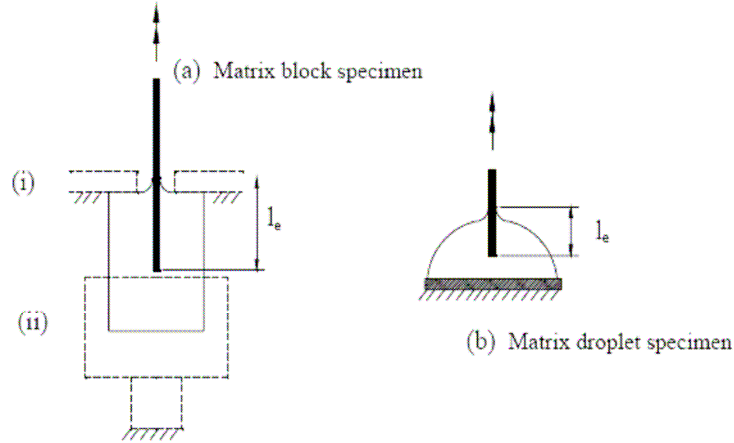


Figure 2.4: Pull-out specimen geometries showing fibre embedded lengths and different geometries and loading configurations: (a) matrix block sample (i) restrained from above and (ii) restrained from below; and (b) matrix droplet sample.

This test consists of a fibre embedded in a neat resin (matrix) block of known geometry (Figure 2.4). The free end of the fibre is gripped and a steadily increasing tensile force is applied to the free end of the fibre until the fibre is pulled from the matrix. The fibre may be pulled out of a resin disk, block or droplet [10]. There is considerable variation in geometry and specimen fabrication procedure.

The interfacial shear strength, τ_i , is usually determined using shear lag analysis (as in the fragmentation test) from the applied force required to pull the fibre out the block (also known as debonding force), F , and the fibre length embedded in the block, l_e and fibre diameter, d as shown below:

$$\tau_i = \frac{F}{\pi d l_e} \quad (2.2)$$

In order to determine the shear stress at the interface during pull-out with reasonable accuracy, it is necessary to use very short (< 1 mm) embedded lengths, and very short (< 2 mm) free lengths of fibre. The free length is the distance between the place where the fibre is gripped and the surface of the matrix. In practice, the embedded lengths that are achievable range from 30-500 μm . Data are presented as plots of debonding force versus embedded length.

At low strains the behaviour follows elastic shear-lag analysis, but as the fibre strain is increased, Mode I dominated, mixed mode failure (i.e. debonding) occurs at the fibre/matrix interface. This is due in part to the Poisson contraction of the fibre away from the surrounding matrix [17]. Subsequent interfacial crack propagation may be rapid or stable depending on the system stiffness. After debonding, friction at the interface must be overcome for pull-out to proceed.

Strongly bonded interfaces, may fail initially within the resin meniscus, leaving a conical residue on the fibre, followed by interfacial debonding [2]. A test device optimised for stiffness encourages stable crack propagation [18]. Raman spectroscopy can be used to analyse the distribution of fibre strain in the pull-out test by mapping the variation of strain along a fibre undergoing pull-out from the resin matrix.

A major drawback is the large uncertainty associated with test results. The pull-out test is very sensitive to small variations in specimen preparation and the conditions under which it is carried out. The stress state at the location of the fibre/matrix contact is complex; particularly in the vicinity where the fibre enters the matrix surface. As a result, deformation is very complex. It is therefore questionable if the results that are obtained using the pull-out test can be used to realistically simulate fibre/matrix interactions in composite laminates (see also list of advantages and disadvantages below).

Advantages	Disadvantages
• Direct method of loading interface. • Single force value recorded at failure. • Applicable to most fibre-matrix combinations. • Simple test to perform. • Simple basic analysis. • Provides information on friction coefficients and shrinkage pressures.	• Difficult specimen preparation and handling. • Variability in specimen geometry and fabrication procedure. • Highly complex/non-uniform stress state at interface: • high shear stress concentration near point of fibre entry into matrix, • lower shear stress concentration at embedded fibre end, • affected by elevated meniscus and embedded fibre length. • Restrictions on embedded length: • lower bound due to meniscus formation, • upper bound limited by fibre strength. • Large scatter obtained. • Single data point per test. • Local interface measurement. • Meniscus failures are invalid. • Test device stiffness affects nature of failure and results. • Radial stresses on fibre change with thermal and moisture expansion mismatch between fibre, resin and resin holder; fibre strength degradation due to environmental ageing.

2.3 MICRODROP/MICROBOND TEST

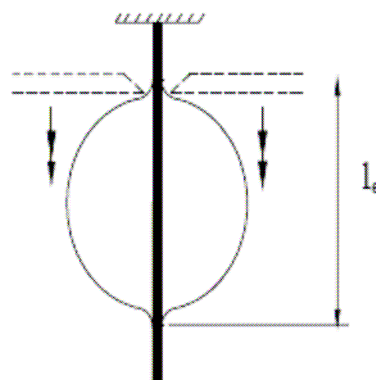


Figure 2.5: Microdrop specimen geometry showing fibre embedded length [4].

This is a specific type of pull-out test that aims to deal with some of the limitations/problems associated with the conventional pull-out test (see Section 2.2). A droplet of cured resin is formed axisymmetrically on a fibre. After the resin is cured, the fibre is gripped and a shear force is applied to the interface via an adjustable pair of knife edges (flat-ended, bevelled or semi-circular) exerting a downward force on the droplet causing debonding (Figure 2.5) [10, 19].

As with the conventional pull-out test, data are presented in the form of debonding force (maximum load) versus embedded length plots with the interfacial shear strength determined using Equation (2.2). The droplet lengths vary from 40-200 μm . As in the conventional pull-out test, the interface fails in a mixed mode with Mode I dominating initially (due in part to the Poisson contraction of the fibre away from the surrounding matrix). Once a debond initiates, it propagates rapidly and catastrophic failure occurs. After this point, some load transfer due to frictional sliding occurs, as the fibre is pulled through the droplet. As in the conventional pull-out test, the microbond test can be used for both thermoset and thermoplastic resin systems.

Advantages	Disadvantages
• Direct method of loading interface. • Single force value recorded at failure. • Applicable to most fibre-matrix combinations. • Simple specimen preparation. • Simple test to perform. • Simple basic analysis. • Requires very small amounts of material. • Cohesive or adhesive nature of failure can be ascertained through SEM examination of the fibre surface after failure. • Reduced meniscus.	• Difficult specimen handling. • Variability in droplet shape and dimensions. • Restrictions on embedded length: • lower bound due to droplet formation, • upper bound limited by fibre strength and droplet formation. • Highly complex/non-uniform stress state at interface: • high shear stress concentration near point of fibre entry into matrix, • affected by stress concentrations at loading points of contact, • affected by location of loading points on droplet, • affected by shape of loading blades, • affected by droplet shape and size. • Large scatter obtained. • Single data point per test. • Local interface measurement. • Meniscus failures are invalid. • Droplet mechanical properties vary with size. • Resin plasticisation at loading points following hygrothermal exposure; high diffusion rates demand prompt post-conditioning testing.

2.4 MICROINDENTATION TEST

Microindentation was originally developed as a hardness test for metals and polymers, but has in recent years been adapted for determining interfacial shear strength of fibre-reinforced systems (including FRPs, ceramic matrix composites (CMCs) and metal matrix composites (MMCs)). The major advantage with this test method is that it can be applied to actual composite components. In this technique, single fibres perpendicular to a cut and polished surface of a high volume fraction composite are compressively loaded in the axial fibre direction with an indenter to produce debonding or fibre slippage (Figure 2.6) [10]. This test is less commonly used for reinforced polymers than the other interface test methods.

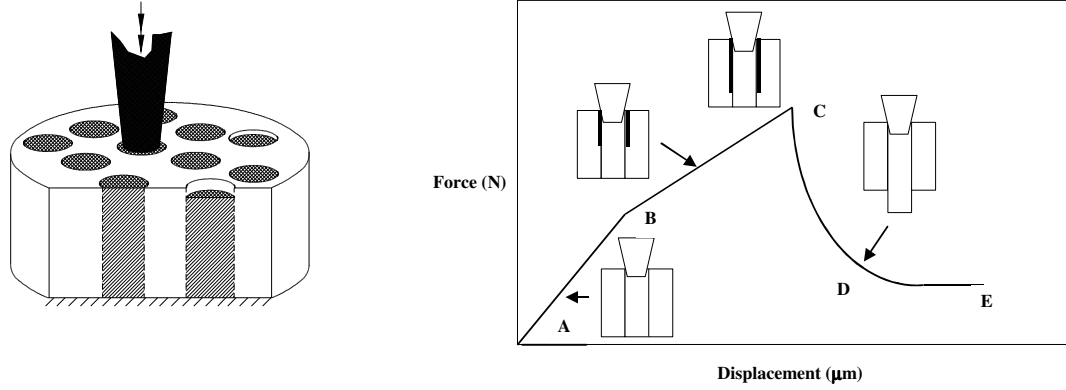


Figure 2.6: Micro-indentation test specimen and force-displacement response.

With the aid of an optical microscope a fibre is manoeuvred into position directly beneath a flat/rounded end indenter, whose diameter is less than the fibre diameter. The fibre is loaded via high stiffness apparatus in a cyclic loading-and-observation process or at a constant rate, with the load and depth of indentation monitored continuously. Detection of fibre debonding is recorded as a characteristic change in the load-depth trace (Figure 2.6), by monitoring acoustic emission events or by unloading and observing the fibre optically. Specimen dimensions vary in order to accommodate specific indenting equipment, but are approximately 10x 10x 3-10 mm in size.

As a first analytical approximation the debonding strength of the interface can be calculated from the following equation [20]:

$$\tau_i = \frac{nF}{2\pi r^2} \quad (2.3)$$

where F is the applied force, n denotes the volume fraction and fibre/matrix stiffness parameter and r is the fibre radius.

Because of the complexity of the resultant stress state produced by microindentation, interfacial shear strength is usually calculated using either finite or boundary element analysis (in conjunction with shear lag theory) of the stressed area, for each fibre tested, to include the effect of neighbouring fibres located at various distances and distributions [19]. The results obtained using microindentation tend to agree with other direct methods provided testing is rigorous.

Mode II dominated failure occurs superimposed with compressive stresses (due to the Poisson expansion of the fibre) [17]. It is likely that debonding initiates within the maximum shear stress region, below the contact surface, and quickly spreads over the circumference up to the specimen surface. Figure 2.6 shows the different stages of single-fibre push-out: (A-B) linear-elastic fibre deformation, (B) initiation of debonding, (B-C) region of progressive (stable) debonding and sliding (push-in), (C) instability, (C-D) unstable debonding, (D) initiation of push-out, and (D-E) progressive push-out: stable extraction of the embedded fibre (plateau). In some cases, especially for thermoplastics with weak interfaces, the polishing process can destroy the interface.

Advantages	Disadvantages
• Direct method of loading interface. • Single force value recorded at failure. • One specimen provides many data points. • Applicable to most fibre-matrix combinations. • Simple specimen preparation. • Simple specimen handling. • <i>In-situ</i> test providing a real environment for assessing the interface. • Independent of fibre tensile strength.	• Difficult specimen testing: • high position accuracy required, • difficulty detecting debonding load. • Failure criterion is subjective and arbitrary. • Highly complex/non-uniform stress state at interface: • high shear stress concentration near fibre contact surface, • stress concentration at loading region of contact, • affected by proximity/configuration of neighbouring fibres, • affected by indenter shape/size/stiffness and position on the fibre cross-section, • affected by the polishing protocol. • Fibre damage is common, limiting material applicability. • Failure mode and locus cannot be observed. • Finite or boundary element analyses required for accurate data reduction.

2.5 DISCUSSION

The primary concern with micromechanical interfacial test methods is that strength properties of composites depend on the properties of all the constituents, fibre content and format, fabrication quality and other factors in addition to fibre/matrix interfacial adhesion. As previously stated, there is no complete and unambiguous interface measurement method. The stress states associated with each of the four methods discussed are complex, and not fully known. There is a lack of consensus and understanding regarding the fundamental failure processes occurring at the interface and the data reduction analyses, which best provide meaningful and reliable data. Data reduction methods are oversimplified, using constant shear assumptions when non-uniform distributions and mixed mode failures occur in all cases.

There is generally a high scatter in the data generated due to the intrinsic random nature of the interface, the small areas considered in the tests and the sensitivity to specimen and test details. Results differ significantly between tests due to differences in, specimen geometry and loading methods, stress distributions, thermal mismatch and curing stresses, friction and Poisson's effects and stiffness mismatch effects. An inherent problem with the tests is the determination of an interfacial property that is independent from the specific test arrangement.

Despite these problems, it is possible that by tightening the controls on specimen preparation, dimensions, and test parameters, and by formalising the analysis methods, that consistency can be achieved. The fragmentation and pull-out techniques are the most favourable techniques for achieving these aims, giving the best balance between testing and modelling aspects. A round-robin exercise [21] highlighted the potential for harmonisation of each of the interface test methods, where initial results showed a promising correlation in results for each of the four tests between 12 separate sites, each using their own in-house procedures, specimen geometries and equipment.

There are no test standards currently in existence for evaluating interfacial properties, although efforts have been initiated in ASTM to develop a guide on how to conduct and analyse single fibre push-in/push-out tests for ceramic composites. Another test method being developed for CMCs is the load/unload tensile test (i.e. measurement of the interfacial frictional shear stress obtained by cycled tension on mini-composites). The test geometry is similar to fibre fragmentation (see Figure 2.7). The size and magnitude of stress-strain hysteresis loops can be used to extract information about residual stress state and interfacial shear strength. Although this type of test has not been standardised, it is potentially a simple mechanical test for “interrogating” the bulk composite to extract in-situ constituent properties and performance.

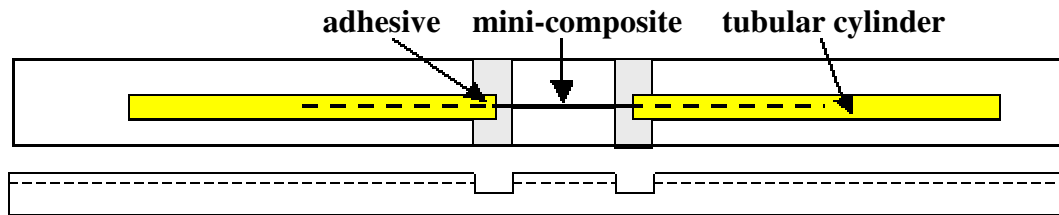


Figure 2.7: Mini-composite tensile CMC specimen.

3 NOVEL TECHNIQUES

It is clear from the previous section that direct methods, such as the single-fibre pull-out/push-in and fragmentation tests are far from satisfactory in providing quantitative interfacial property data that can be used for quality assurance (e.g. assessing surface treatments and environmental resistance), and design and modelling purposes. A quandary remains as to alternative techniques that could be suitable for characterisation of interfacial properties of actual composite systems. Recent developments have seen the emergence of novel techniques, such as nanoindentation, nanoscratch, atomic force microscopy (AFM), and Raman spectroscopy, etc., used for characterising interfacial properties. These techniques have attracted considerable interest because of the potential for direct quantitative measurement of interfacial (interphase) properties (chemical, physical and mechanical) in actual multiphase polymeric systems. This section examines a number of new/novel techniques that potentially could provide interfacial information.

3.1 NANOINDENTATION

Indentation hardness testing is routinely used in engineering and metallurgy for quality assurance purposes, as it is a quick and simple test for characterising a material's hardness (i.e. its resistance to permanent, and in particular plastic, deformation) [22]. Conventional hardness testing, such as Rockwell, Vickers and Brinell, usually consists of loading a material in compression with an indenter of specified geometry and measuring the dimensions of the resulting indentation after retraction of the indenter (Figure 3.1). Elastic deformation in these tests is ignored. The indenter may be spherical (Brinell test), pyramidal (Vickers and Knoop tests) or conical (Rockwell test). An optical microscope attached to the hardness test apparatus is used to measure the lateral size of the residual indentation (i.e. imprint).

In contrast to conventional hardness methods, instrumented indentation testing has the ability to measure the indenter penetration, h , under the applied force, F , throughout the testing cycle (i.e. as a function of time), and is therefore able to measure both the plastic and elastic deformation of the material under test [23-24]. As the force is increased, the instrument measures both the plastic and elastic deformation of the material under test. As the force is removed, the indentation recovers elastically and the stiffness of the contact may be related to the elastic modulus of the material under test using knowledge of the area of contact. It is possible to infer the size of an indentation from the measured penetration depth. Instrumented indentation renders a separate measurement of the indent size unnecessary and allows indentation testing at indent sizes much smaller than previously possible using conventional methods. As with conventional indentation testing, knowledge of the indenter geometry is required.

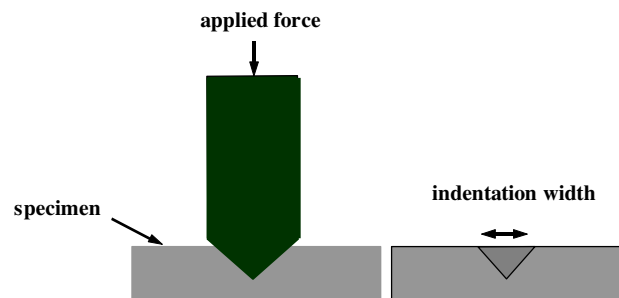


Figure 3.1: Indentation test.

For most hardness measurements an indentation load of 30 N (or greater) is used and the size of the indentation is approximately 300 μm in size in the plane of the tested surface. Nano-hardness testing involves smaller indenters and significantly smaller loads (100 μN to 100 N). The corresponding indentation is far smaller (100 nm or less) and is associated with local properties, whereas standard hardness tests provide bulk hardness measurements of the surface region. Indentations of the order of 10 nm are not uncommon. Higher force instruments are also now available, capable of applying forces up to 1500 N. Instrumented nanoindentation is one of the very few techniques that can measure both the elastic and plastic properties of very small volumes of materials. Instrumented indentation can be used in combination with acoustical measurements to provide Poisson's ratio, and thickness or density values for coatings.

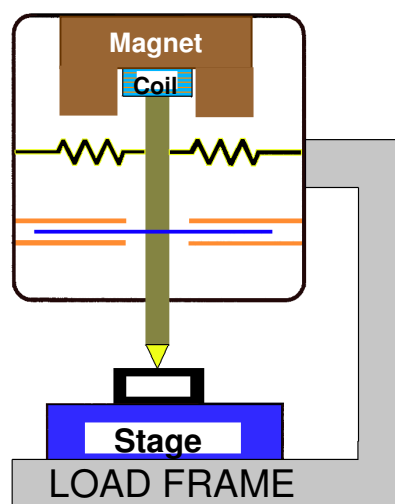


Figure 3.2: Schematic of instrumented indentation test system [24].

The principle of a typical instrumented nanoindentation system is shown in Figure 3.2 [24]. The indenter is mounted on an indenter shaft, which is suspended by flexure elements and is pressed against the test sample by a force actuator (electromagnetic, electrostatic or piezoelectric system). A parallel plate capacitor is commonly used to measure the displacement of the shaft (and therefore the indenter) into the sample. Instrumentation of the indentation displacement removes the need to inspect the indents in order to determine indent size, and thus indents can be much smaller in size.

For large indents in the upper microindentation range ($h > 6 \mu\text{m}$), the indentation area of contact can be calculated from measurements of indentation depth assuming the indenter has the “ideal” or “perfect geometry” [24]. The error in area is less than 1% for a Vickers or Berkovich indenter that complies with BS EN ISO 14577-2 [25]. For smaller indent depths (i.e. $0.2 \mu\text{m} \leq h \leq 6 \mu\text{m}$), more detailed knowledge of the indenter shape, as a function of depth is required. The key parameter A_s , known as the “area function” (i.e. area as a function of depth) can be determined using a traceably calibrated AFM. The area function needs to be calibrated for each indenter. Figure 3.3 shows a typical 3D indentation map and “area function” obtained for a modified Berkovich indenter using AFM.

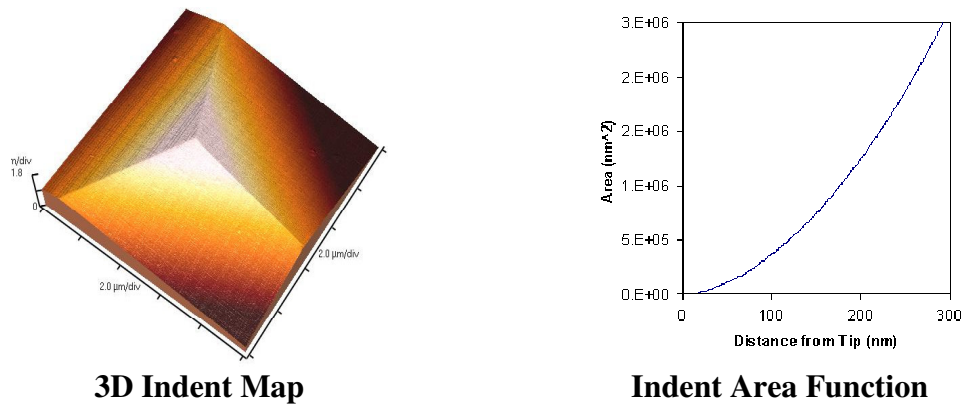


Figure 3.3: 3D map and area function obtained by AFM for a modified Berkovich indenter [24].

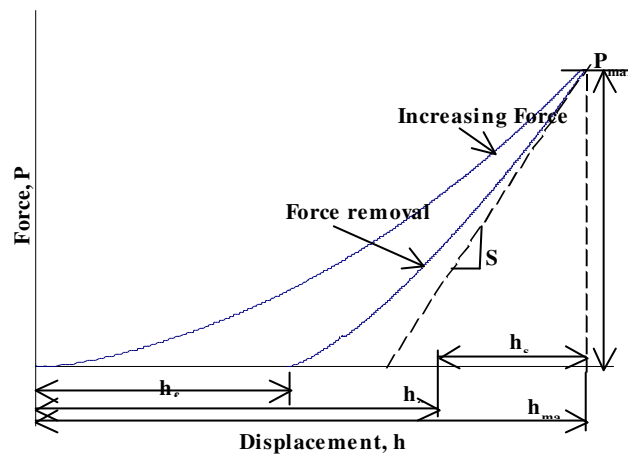


Figure 3.4: Typical force-displacement curve showing measured (P , P_{max} , h , h_{max} , h_f) and derived parameters (S , h_s , h_c) [24].

In a typical quasi-static indentation cycle, force is progressively applied and the indenter is steadily pressed into the sample. As a result, the sample deforms elastically and plastically under the indenter until a maximum force is reached. The force is often held for a short period of time before being progressively removed with the sample relaxing elastically as the indenter is removed from the surface. Applied force and displacement is recorded either continuously or at frequent time intervals throughout the loading-unloading cycle (see Figure 3.4). The force-displacement response on its own can provide considerable information, for example, the ratio of the areas under the force loading and unloading curves is an immediate indicator of the balance between elastic and plastic deformation of the material under test.

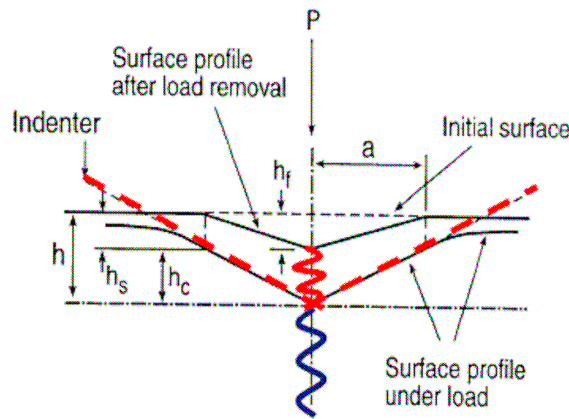


Figure 3.5: Schematic of displacements observed during an indentation experiment (after Oliver and Pharr [26] – see also [24]).

Figure 3.5 shows a schematic representation of the indent at maximum applied force and after the force has been removed (after Oliver and Pharr [26]). The overlay in the schematic diagram shows the elastic response as a combination of the sample and the indenter, which can be considered as two springs in series. The gradient of the force-displacement curve as the force is removed is a measurement of the contact compliance $C (= 1/S)$ from which the contact depth, h_c , can be calculated by taking into account the bowing of the surface in response to the exact shape of the indenter. S is the slope of the tangent of the force-displacement (indentation) curve during the unloading cycle (Figure 3.5). Surface bowing is calculated using contact mechanics equations [27-28]. In reality, the actual contact depth is also a function of the test material response to indentation. Sinking-in and piling-up of the material around the indenter can affect the value, reducing and increasing the actual contact depth, respectively. Both phenomena are a function of material processing history and, as in conventional hardness testing, are not included in the standard analysis.

Instrumented nanoindentation may be used to determine the stiffness of contact, and therefore indentation modulus E_{IT} and indentation hardness H_{IT} (equivalent to Meyer Hardness and similar to HV for a Vickers indenter) and the Martens hardness HM (previously known as Universal hardness, HU) of a material [24]. The HM value is calculated by dividing the test force P by the surface area of the indenter penetrating beyond the original surface of the test piece $A_s(h)$. The Martens hardness is a combination of elastic and plastic indentation responses, and therefore has no direct correlation either to a physical property such as elastic modulus, or to traditional hardness scales (see [24] for further details).

Time-dependent material properties may also be investigated by measuring the continued displacement under a constant applied force. Fracture toughness properties may also be determined by calculating the ratio of elastic to plastic work done during an indentation. The indentation hardness H_{IT} is calculated from the test force, P , divided by the projected area of the indenter in contact with the test piece at maximum load:

$$H_{IT} = \frac{P}{A(h_c)} \quad (3.1)$$

The indentation modulus, E_{IT} , is calculated from the slope of the unloading curve through the formula:

$$E_{IT} = (1 - \nu_{IT}^2) \left/ \left\{ \frac{2}{\sqrt{\pi}} \frac{\sqrt{A(h_c)}}{S} - \frac{(1 - \nu_{indenter}^2)}{E_{indenter}} \right\} \right. \quad (3.2)$$

where ν_{IT} and $\nu_{indenter}$ are the Poisson's ratios of the sample and indenter respectively, S is stiffness, and h_c is the contact depth value, which is dependent on the shape of the indenter (Figure 3.5). Power law or splines fitting routines are used to determine the slopes of the high portion of the unloading curves (Figure 3.4). For homogeneous and isotropic materials, E_{IT} approaches the Young's modulus of the material.

A wide range of indenter geometries is available including cube corner, Knoop or ball indenters, Berkovich and diamond sphero-conical indenters. Berkovich is possibly the most popular indenter geometry used with instrumented indentation. Since three facets cannot form a line of conjunction and must meet at a point, this geometry can be used down to very small depths (see Figure 3.3). The most commonly used version of the Berkovich indenter is now the “modified Berkovich” with a facet angle of 65.3°. This angle ensures that the cross sectional area to depth ratio of a modified Berkovich is almost the same as that of a Vickers indenter, thus enabling direct measurement correlation between the two geometries. The cube corner geometry, which is used for indenting very thin coatings and generating cracks, is a three-sided indenter with a much higher aspect ratio (lower opening angle) than the Berkovich. At very shallow depths its main advantage is an ability to support a tip with a very small radius of curvature. This geometry concentrates the force into a smaller indent area, and thus higher energies can be generated. The literature suggests that this geometry is more difficult to calibrate and may exhibit an indentation response that deviates from the standard contact mechanics employed in BS EN ISO 14577-2. Corner cube indenters are more fragile than other geometries and have a tendency to wear more rapidly [24].

The resultant contact area, and hence penetration depth is dependent on the surface roughness of the sample. For the same contact area, indentation depth is higher for a roughness peak compared to an ideal plane horizontal surface, which is higher than for a roughness valley. In order to exclude (or minimise) the effect of surface roughness, which can be significant, it is advisable to carry out an appropriate number of tests commensurate with the magnitude of surface roughness (i.e. scatter increases with increasing surface roughness). An average of 15-25 tests should ensure a reasonable representation of surface properties [29].

A number of researchers have carried out instrumented nanoindentation on polymeric composites in order to determine the elastic modulus, hardness and dimensions of the interphase region surrounding fibres [3, 30-35]. Generally, researchers use a Berkovich indenter for these measurements. There are a number of uncertainties associated with nanoindentation measurements in addition to surface roughness, and “pile-up” and “sink-in” of material around the tip-sample contact previously mentioned. Sources of measurement uncertainty include: load frame compliance, detection of a true zero and measurement errors in load and displacement, variability of elastic properties of the sample and indenter materials, indenter tip geometry (i.e. deformation and wear) and thermal drift. The area values obtained for real tips corresponding to a given contact depth will be much different to those values expected for an ideal tip geometry; particularly for contact depths less than 100 nm (commonly used for nanoindentation). The point assumed to represent initial contact ($h = 0$) could in fact correspond to a significant applied load. The actual penetration could also be a significant proportion of the maximum displacement, h_{max} .

The elastic modulus of polymeric materials is known to increase with decreasing indentation depth (often referred to as indentation size effect). The discrepancy may be due to surface effects, but there is no evidence to support the hypothesis that E (surface) $> E$ (bulk). The most likely cause is indenter tip defects near the tip apex and decreased signal-to-noise ratios at low load and displacement levels. Viscoelastic creep during unloading can dramatically affect the slope of the unloading curve, and hence result in errors in modulus and hardness measurements.

A number of researchers [30, 36-37] have attempted to characterise the interfacial mechanical properties of fibre-reinforced composites using nanoindentation. The main approaches used are: (i) nanoindentation profiling to determine changes in hardness and elastic modulus of the modified matrix within the interphase region; (ii) single indentations in close proximity to the fibre/matrix interface to evaluate interfacial fracture; and (iii) individual push-out tests on perpendicularly aligned fibres to the composite surface. SEM and TEM are used for studying resultant fracture mechanisms.

Advantages and disadvantages of nanoindentation are summarised below. Most of the factors that adversely effect nanoindentation measurements can be avoided or at least minimised through good measurement practice (see [24]).

Advantages	Disadvantages
• Straightforward specimen preparation and handling. • Direct method of <i>in-situ</i> characterisation of interfacial and interphase properties: • hardness, • elastic modulus (fibre, matrix and interphase), • yield stress, • true stress/strain curves, • interfacial adhesion strength, • fracture toughness, • strain hardening, • surface residual stresses, • glass transition temperature, • interphase dimensions. • Time-dependent (creep/stress relaxation) behaviour. • Applicable to most fibre-matrix combinations. • Straightforward data analysis.	• Large uncertainty in measured data: • load frame compliance correction, • calibration errors, • difficulty in establishing true zero for load and displacement, • variability in indenter tip geometry, • wear and deformation of indenter tip, • “pile-up” and “sink-in” of material around indentation, • variability of elastic properties of the sample and indenter materials. • Surface roughness effects measurements. • Viscoelastic behaviour effects unloading slope. • Thermal drift. • Vibration – need anti-vibration table.

3.2 SCANNING PROBE MICROSCOPY

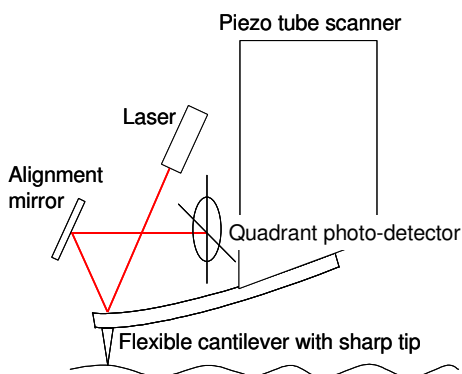


Figure 3.6: Schematic of scanning probe microscope.

Scanning probe microscopy (SPM) describes any technique where the surface is imaged at high (or atomic scale) resolution by rastering (or scanning) an atomically sharp tip in close, but not in direct contact (see Figure 3.6) [38]. The measurement of the interaction between the probe tip and surface is combined with the measurement of the relative position of the probe tip to produce an image of the interaction strength as a function of position in the x-y plane and providing information on surface topography, lateral force, conductance, magnetic attraction or electrochemical response.

Atomic Force Microscopy (AFM) is a subset of SPM and measures surface characteristics, such as topography (Figure 3.7), on the atomic scale [31, 39-43]. A small tip mounted on a flexible cantilever attached to a measuring device is used to analyse the small vertical movements of the probe as it travels over the contours of the surface of the sample (similar principle of operation to the stylus profilometer). The cantilever is typically silicon or silicon nitride (typically 100 - 200 μm in length) with a tip radius of curvature of the order of 5 - 10 nm.

The surface deflection of the cantilever, caused by changes in topography, is usually measured using a laser spot reflected from the top of the cantilever into an array of photodiodes. The deflection of the cantilever behaves according to Hooke's law. Optical interferometry, capacitive sensing and piezoresistive AFM probes are also used for measuring deflection. These probes are fabricated with piezoresistive elements that act as a strain gauge. A Wheatstone bridge is used to monitor strain in the AFM probe due to deflection, but this method is not as sensitive as laser deflection or interferometry. A feedback mechanism is generally employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample, and also to prevent the tip colliding with the sample and damaging the tip. High-resolution scans can take some time, and effects from thermal drift and probe shape de-convolution must be considered.

AFM has a spatial and depth resolution of the order of a few nanometres. Maximum scan range is typically 100 μm in the x- and y-directions, and 7 μm in the z-direction. Forces of the order of a few pico-newtons can now be routinely measured. AFM can be used to monitor interaction forces, such as van der Waals, magnetic, electrostatic, capillary and chemical bonding forces as a function of the separation distance between the probe tip and the sample surface.

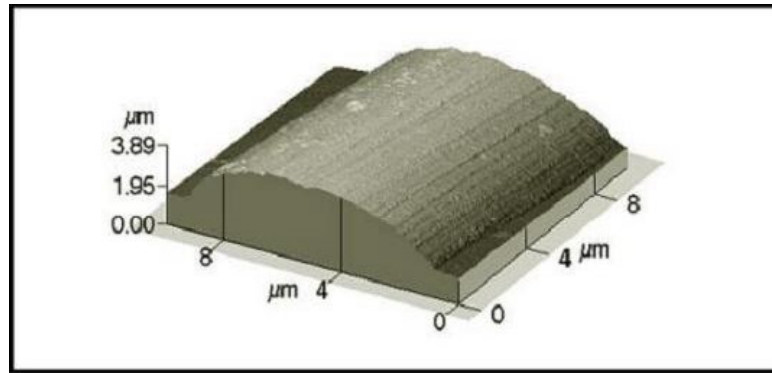


Figure 3.7: AFM surface map of a treated carbon fibre [40].

AFM has several advantages over SEM. Unlike the SEM, which provides a 2-D projection or a 2-D image of a sample, the AFM provides a true 3-D surface profile. Additionally, samples viewed by AFM do not require any special treatments (such as metal/carbon coatings) that would irreversibly change or damage the sample. While SEM needs an expensive vacuum environment for proper operation, most AFM modes can work perfectly well in ambient air or even a liquid environment. Almost all materials can be studied without the need for sample preparation.

There are two main modes of operation: static (**contact**) and dynamic (**non-contact**), which maintains a constant force or separation to the sample surface, respectively. In **contact mode**, the probe is brought into contact with the surface with a low force (nN to μ N) and rastered across the surface; the force between the tip and the surface is kept constant during scanning by maintaining a constant deflection. Measurement of static signals is prone to noise and drift, hence low stiffness cantilevers are used to boost the deflection signal. However, close to the surface of the sample, attractive forces (i.e. lateral (shear) and normal forces) can be quite strong, causing the cantilever tip to “snap-in” to the surface. The combination of lateral and normal forces can result in reduced spatial resolution and may cause damage to soft materials, such as polymer samples, due to scraping between the tip and sample. Consequently, **contact mode** AFM is almost always done in contact where the overall force is repulsive. Atomic resolution images can only be achieved using **contact** mode AFM.

In dynamic mode (i.e. **tapping mode** and **non-contact mode** imaging), the cantilever is externally oscillated, at or close to its resonance frequency with oscillation amplitude ranging typically from 20 nm to 100 nm. In **tapping mode** AFM, the cantilever tip “lightly” taps on the sample surface during scanning, contacting the surface at the bottom of its swing. Tip-sample interaction forces modify the amplitude, phase and resonance frequency of the oscillating signal with changes in oscillation with respect to the external reference oscillation providing information about the sample's characteristics. By maintaining constant oscillation amplitude, via a feedback loop, a constant tip-sample interaction is maintained during imaging. The vertical position of the scanner at each position in the x-y plane is recorded to form a topographical map of the sample surface. Samples are less prone to being damaged, as lateral forces are virtually eliminated. Scanning speeds are slightly less compared with **contact mode** AFM.

In **non-contact mode**, the tip does not contact the sample surface, but oscillates above the surface at a frequency slightly higher than the resonance frequency of the cantilever. Amplitude of oscillation is less than 10 nm. Van der Waals forces, which extend approximately 1 nm to 10 nm above the surface, interact with the cantilever tip causing the resonant frequency of the cantilever to decrease. The decrease in resonant frequency is accompanied by a decrease in amplitude of oscillation. The feedback loop is used to either maintain constant oscillation amplitude or frequency and the distance the scanner moves vertically recorded to form a topographic image of the sample surface. The advantage of **non-contact mode** AFM is that no force is exerted on the sample surface. Limits on the tip-sample separation results in lower lateral resolution. In order to avoid surface contact, scan speeds need to be reduced, and hence scan speeds are lower than contact and tapping modes.

Schemes for dynamic mode operation include frequency modulation and the more common amplitude modulation [44-45]. In frequency modulation, changes in the oscillation frequency provide information about tip-sample interactions. Frequency can be measured with very high sensitivity and is used for atomic resolution imaging in ultra-high vacuum (UHV) conditions. In amplitude modulation, changes in the phase of oscillation can be used to discriminate between different types of materials on the surface. Amplitude modulation can be operated either in the non-contact or in the intermittent contact regime.

AFM nanoindentation has been used to measure and map nanohardness and elastic modulus (see also Section 3.1) [31]. Problems with the technique include no direct measurement of the tip-sample separation and the common need for low stiffness cantilevers, which tend to “snap-in” to the surface. The “snap-in” can be reduced by measuring in liquids or by using stiffer cantilevers, but in the latter case a more sensitive deflection sensor is needed. By applying a small dither to the tip, the stiffness (force gradient) of the bond can also be measured. The radius of curvature of the probe tip limits the quality of an image, and an incorrect choice of tip for the required resolution can lead to image artefacts. Surface contamination and dust can also adversely affect test results.

As previously mentioned, there are also shear forces acting on the AFM tip, which lead to torsion of the cantilever. These forces can be used to measure the friction between the tip and sample. Lateral forces can be measured using regular AFM instrumentation. The term **Friction Force Microscopy (FFM)** or **Lateral Force Microscopy (LFM)** is frequently used to describe this form of measurement. A quadruple photodiode is used to simultaneously detect deflection and torsion of the cantilever, thus enabling both topographic and lateral force imaging.

Micro-scale thermal properties of materials, such as FRPs, can be investigated using **Scanning Thermal AFM** [46]. The technique may be used with either a passive or active thermocouple probe. Although passive thermal probes have been used in a number of applications, particularly for evaluating heat generation in small-scale electronic devices, the passive nature of the probe limits the capability of the technique. Passive probes are unable to detect property-based variations at the micro-scale. In contrast, active thermocouple probes when coupled with an AFM are able resolve material differences based on thermal properties instead of mechanical force.

As with traditional AFM, the probe is held in contact with the sample using a feedback control loop to maintain a constant load on the surface. Using a separate feedback loop to maintain the probe at a fixed temperature, it is possible to raster the probe over the surface generating a thermal map of the sample surface. This provides information on localised thermal conductivity of the surface, and enables visualisation of the micro-scale heterogeneity in composite materials. By comparing the response of the active probe with a reference probe, differential thermal analysis can be performed. Samples as small as several cubic microns can be examined. Modulated local thermal analysis AFM (LTA-AFM) has been used to measure transitions in thermoplastics and in-situ glass transition temperature, T_g , of glass and carbon fibre-reinforced epoxy laminates [45]. The transition temperature measurements have correlated well with results obtained using differential scanning calorimetry (DSC). Tillman et al [46] showed that there was clearly an interphase region of soft (loss stiffness) matrix material surrounding the fibres. The T_g of the matrix decreases near the fibres. For the glass fibre-reinforced epoxy, a 15% reduction in T_g was measured at the fibre surface compared with the bulk matrix material.

Atomic Force Acoustic Microscopy (AFAM) is a hybrid acoustic/AFM technique that involves vibrating the cantilever at ultrasonic frequencies (10 kHz – 10 MHz) to excite its mechanical resonances [47-53]. The resonant frequencies of the AFM cantilever shift when the cantilever tip is in contact with the sample surface. AFAM can be used to obtain elastic property data. The cantilever can be considered a miniaturised elastic beam that can vibrate in different types of modes (i.e. flexural, torsional and extensional). A piezoelectric ultrasonic transducer is used to excite either longitudinal or shear acoustic waves in the sample under examination. Longitudinal and shear waves cause out-of-plane surface vibrations and in-plane surface vibrations in the sample, respectively. Surface vibrations are coupled to the AFM cantilever beam through the tip when it is in contact with the sample. The AFM photodiode sensor using a lock-in amplifier detects changes in the amplitude of the cantilever vibration.

As the excitation frequency approaches the resonance frequency of the cantilever, the detected amplitude of the cantilever vibrations increases, enabling its resonance frequency to be determined. The amplitude and phase of the cantilever vibration, as well as the shift of the cantilever resonance frequencies contain information about local tip-sample contact stiffness. Quantitative elastic property data can be extracted by measuring the resonant frequencies under both free-space and surface-coupled conditions. Elastic forces dominate tip-sample interactions. AFAM systems are fitted with small diameter tips capable of lateral resolutions of 5-10 nm. Frequency-tracking electronics have been developed to enable rapid imaging of the contact resonance frequency in a given area on the sample surface, thus enabling maps of the contact stiffness and the indentation modulus to be obtained.

In order to generate reliable quantitative data, further work is required to understand and control tip wear and tip-contact sample behaviour. Silicon tips have been known to experience considerable wear during testing, which can cause large uncertainties in elastic property measurements. Using diamond-coated tips, however, the wear can be avoided (or at least minimised). Tip abrasion/erosion and deformation can limit measurement accuracy. Concerns also exist about the effects of viscoelastic damping and the need for finite element analysis (FEA) to account for geometric effects on the resonant frequency for cantilever beams.

Scanning Tunnelling Microscopy (STM) has revolutionised surface science enabling real space atomic resolution images of surfaces [38, 47-48]. The technique consists of rastering a conductive sample with a fine metallic tipped probe with the probe in close proximity to the sample surface. A voltage is placed between the probe tip and the sample surface. As the probe tip approaches to within 10-20 nm of the surface, a tunnelling current (0.01-50 nA) can be induced in either direction between the tip and the surface with current flow being sensitive to the distance between the tip and the surface, and conductivity of the sample. The exponential dependence of the tunnelling current on the probe tip to surface distance results in a high vertical resolution. The current between the probe tip and sample surface is continuously monitored and by maintaining a constant current (**constant current mode**) it is possible to generate a topographic image of the surface. As the current is proportional to the local density of atomic states, the probe tip follows a contour of constant density of atomic states during scanning.

Constant current mode of operation is only suitable for atomically flat surfaces otherwise the tip would inevitably collide with the surface damaging the probe tip and sample. A conductive sample is needed to generate a current flow between probe tip and sample surface. The STM needs to be operated under UHV conditions in order to produce atomic resolution images. In **constant current mode**, image generation is slow. A single image may require seconds to a few minutes to generate, whereas images can be generated within 10^{-4} seconds using constant height mode.

Typical spatial resolution is 3 nm with a vertical feature resolution of < 0.1 nm. A wide range of scan sizes from 100 μm down to the atomic level can be covered in a single experiment. Hence, it is possible to obtain an overview image of the surface and then zoom-in on structural features at higher resolution to investigate local defects, such as dislocations. Although STM measurements are usually undertaken in UHV conditions, STMs can also be operated under ambient conditions.

Scanning Electrochemical Microscopy (SECM) is a scanning probe technique that is based on Faradaic current changes as an ultramicroelectrode (UME) is scanned in an electrolyte solution a few microns above a sample's surface (Figure 3.8) [54-55]. The electrochemical response of the UME is recorded as it approaches or scans over a surface. The images obtained depend on the sample topography and surface reactivity. The response of the scanning electrochemical microscope is sensitive to the presence of conducting and electro-active species, which makes SECM useful for imaging heterogeneous surfaces and studying dynamic electrochemistry processes.

The SECM uses piezoelectric based controllers to position the tip in any of the three axes at scan speeds from 0.05 to 1000 $\mu\text{m/s}$, although 1 to 20 $\mu\text{m/s}$ is a more typical scan rate. In addition, the position controllers allow movements of less than 0.1 to 300 μm during imaging. The tip and substrate potential will often be simultaneously controlled and the Faradaic current flow monitored during imaging. A video microscope is used to observe the tip electrode as it approaches the substrate.

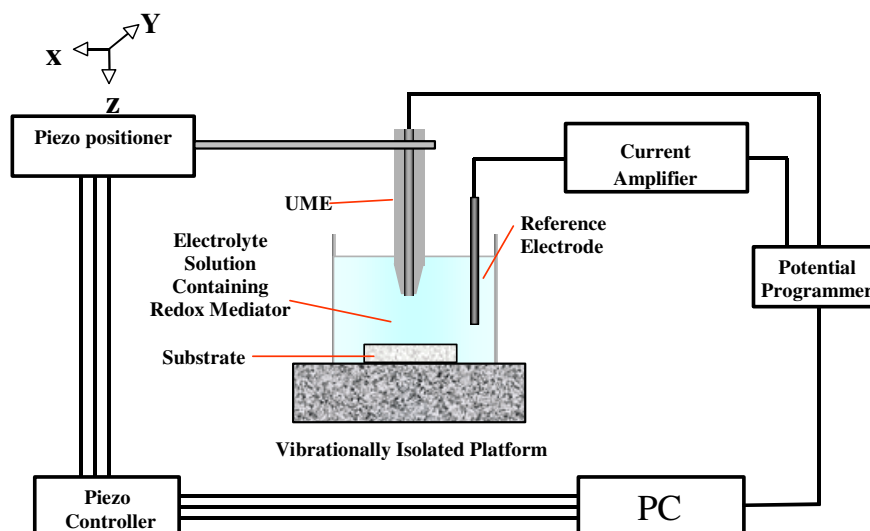


Figure 3.8: Schematic diagram of a scanning electrochemical microscope.

A commonly used tip is based on an embedded disk-shaped geometry (Figure 3.9), which are made by heat sealing microscopic wires (platinum, gold, silver or carbon fibres) in an insulating sheath of borosilicate glass (or a polymeric resin). The end is then polished to expose an embedded disk. The tip is ground so that the glass insulator forms a truncated cone, thus enabling the tip to approach the sample surface more closely. A typical disk electrode would have a radius of 1 to 25 μm . An insulator radius of 3 to 10 times larger than the electrode radius surrounds the electrode. Spatial resolution of SECM is limited by the size of the SECM tip and the minimum current that can be accurately measured. SECM spatial resolution is comparable to the size of the UME probe (typically 0.1 - 25 μm in diameter). For high-resolution SECM measurements, laser-pulled platinum nanoelectrodes and electrochemically etched carbon fibre UMEs with a tip diameter of 1 μm are routinely being used.

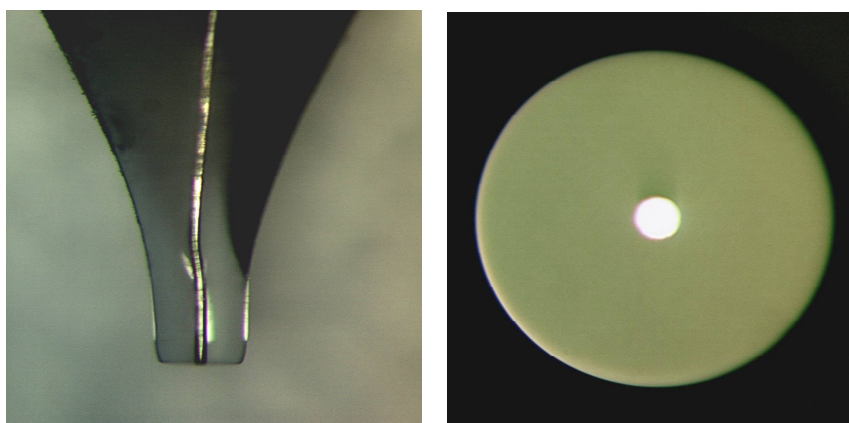


Figure 3.9: SECM disk-shaped UME viewed side on (left) and end on (right).

SECM has excellent chemical selectivity, and therefore is an excellent tool for examining local interfacial electrochemical properties and reactions. The technique could potentially be used to determine absolute rates of diffusion and for monitoring chemical degradation at the fibre/matrix interface in composite materials. Strong electric fields need to be avoided as these may affect physical conditions at the sample surface. A Faraday cage is recommended to shield the equipment.

Scanning Kelvin Probe (SKP) is an electrochemical technique similar to SECM, which is used to measure the electrode potential at metal/polymer interfaces (e.g. conductive adhesives). The probe tip and sample surface form essentially a parallel plate capacitor with height regulation achieved through the application of a small modulation voltage (300 mV) across the tip-sample gap and then monitoring the modulated current, which is proportional to the average tip-sample separation. The modulated current is measured at the desired distance and then kept constant by a piezo-position controller (see reference [56] for a full description of the basic principles of operation). The technique enables both topography and voltage potential to be measured simultaneously. SKP can detect changes in sub-surface metal oxide structures (50 μm in depth) and variations in the interfacial ionic conductivity, hence it is possible to study the kinetics of interfacial reactions and de-adhesion processes that cause interfacial degradation. For moisture degradation studies, it is usual that tests be conducted under normal atmospheric pressure and high humidity. Spatial resolution is typically 50 μm .

3.3 NANOSCRATCH

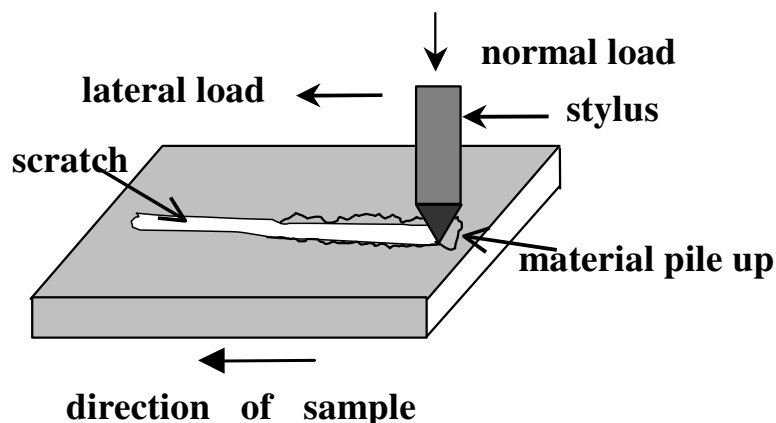


Figure 3.10: Scratch test.

The scratch test (Figure 3.10) is a variant on a hardness test and is commonly used for assessing abrasion resistance and coating adhesion [57-59]. A loaded diamond tipped stylus (10 to 60 N) is drawn across the target surface (or the sample is displaced beneath the stylus) under an increasing load (typically 100 Nmin^{-1}) until some well-defined failure occurs, usually flaking or chipping. The horizontal displacement rate is nominally 10 mm.min^{-1} with sample size being typically $25 \text{ mm} \times 15 \text{ mm}$.

During the test, the penetration depth and stylus position are recorded. These data can be supplemented with the vertical indenter load, the horizontal force on the indenter and acoustic emission to enable the coefficient of friction and the point of failure to be determined. The scratch can be subsequently analysed with a profilometer, SEM or optical microscopy to ascertain the scratch shape (residual depth, scratch width and pile-up height) to allow the failure mechanism to be identified. Varying the loading rate, the scratch speed and the indenter shape markedly affect the results of the test. Commercial scratch testing equipment can run in single or multi-pass modes. There has been recent collaborative work involving NPL to provide a scratch test calibration procedure, draft standards and reference materials [59].

The usefulness of conventional scratch test is limited to relatively thick coatings of the order of 1-10 μm . The test is inappropriate for studying thin (sub-micron to sub-100 nm) coatings; as damage may be induced in the underlying material and substrate deformation has been known to strongly influence test results [60-61]. The nanoscratch by employing much lower load and a smaller tip radius is able to achieve surface sensitivity and contact pressure to enable the study of deformation and fracture modes not possible using conventional the scratch test. Nanoscale versions of the scratch test are available with depth-sensing nanoindentation and AFM systems. These systems have the added advantage in that surface profile is recorded directly before, during, and after the scratch with vastly improved load resolution. The load capacity typically varies from 50 μN to 600 mN with a spatial resolution of 400 nm (or better). Scan speed is 1-2 $\mu\text{m/s}$ and probe tip radius is of the order of 50 nm.

Nanoscratching is accomplished by applying a normal load, W , in a controlled manner while measuring the tangential (or friction) force, F , required for moving a diamond tip probe across the sample surface (see also FFM or LFM). Test probe displacement is measured with a parallel plate capacitor capable of achieving sub-nanometre resolution. The measured forces are converted to friction coefficients. The coefficient of friction, μ , is calculated using the relationship [3]:

$$\mu = \frac{F}{W} \quad (3.5)$$

Single and repetitive scratch tests can be performed. Sequential constant load scratches over the same wear track with a low load topography measurement performed between each scratch enables simultaneous acquisition of elastic and plastic depth, and friction data. Information attainable using the nanoscratch test includes scratch-resistance, wear-resistance, friction coefficient and critical load for inducing adhesion failure (i.e. coating-substrate adhesion strength). Adhesion failure may manifest itself by an abrupt change in the probe displacement or a sudden change in the tangential (frictional) force between the tip and sample. Detection of adhesion failure is also possible using optical or SPM imaging of the wear track or by monitoring acoustic energy release. Nanoscratch testing is now being widely used to investigate nanotribological and naomechanical properties of thin (5-10 nm) coatings and oxide layers. The nanoscratch test is potentially more accurate and reliable compared with nanoindentation for measuring the effective thickness of the transition (or interphase) region surrounding fibres in composite materials [3]. It is possible to obtain measurements 20 nm apart.

3.4 RAMAN SPECTROSCOPY

Raman is based on the inelastic scattering of monochromatic light. A laser (e.g. Ar+ or He-Ne) excites the material, which is usually in the visible region of the spectrum (Figure 3.11). The frequency of scattered light is analysed compared with incident values. The technique is similar to infrared spectroscopy (IRS) in determining the nature of molecular structures and is a complementary technique to IRS when characteristic frequencies are weak or for highly absorbing materials (see Section 3.5). Raman spectroscopy is sensitive to a material's composition and structure and can distinguish between different structural arrangements of similar atoms.

The vibrational spectrum of a material is a function not only of its constituent atoms, but also the spatial arrangement and the strength of bonding between atoms. Samples require minimal preparation, but need to be stable to high intensity light and contain no species that fluoresce when excited by visible radiation.

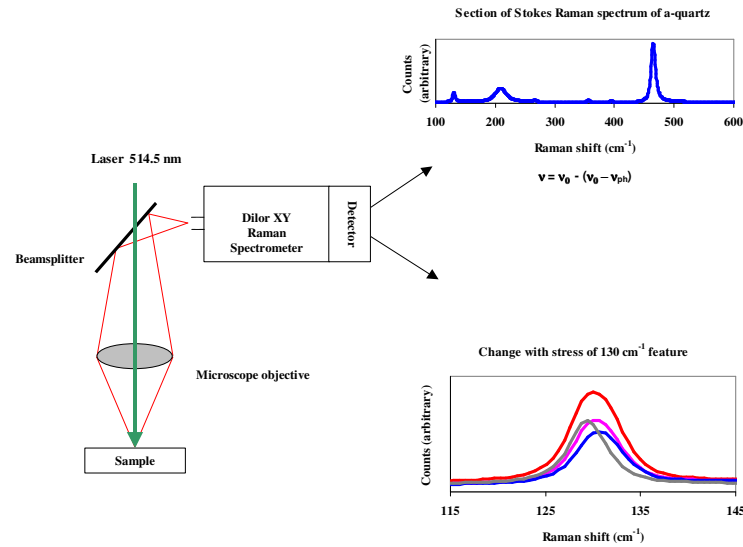


Figure 3.11: Schematic of scattering from α -quartz (SiO_2). (Dilor XY Raman spectrometer)

Raman spectroscopy can be used to determine near surface strain distribution. The use of the technique for determining strain relies on detecting frequency shifts in Raman modes (phonons) under mechanical stress. The frequency and intensity (peak height) of the scattered peak will change with stress. Frequency is dependent on the strain state of the material (i.e. residual strains will cause the peak to shift). Figure 3.11 shows a schematic diagram depicting inelastic scattering from α -quartz (SiO_2) in which the frequency and intensity of the scattered peak changes with stress. In general, compressive stresses result in an increase in Raman frequency and conversely tensile stresses cause a reduction.

The relation between strain or stress and Raman frequency is usually complex, however under uniaxial and biaxial loads the relationship tends to be linear. Using the linear relationship between the peak frequency position of a strain sensitive Raman band and the applied strain, the true axial strain distribution in an embedded fibre can be determined at the microscopic level. By monitoring the Raman scattering frequency at different positions on the sample, a strain map can be produced with a spatial resolution of $0.5\ \mu\text{m}$ (or better). Raman spectroscopy systems are capable of measuring frequency changes of $\sim 0.02\ \text{cm}^{-1}$. It should be noted that the intensity or peak height is dependent not only on the strain state of the inspected area, but also on the separation distance between the optical microscope objective lens and the inspected surface. In order to use the peak height, the beam needs to be focused identically at each location on the sample surface; a difficult task on structures that have undergone out-of-plane deformation as a result of twisting. Hence, it is recommended that the Raman frequency shift, which is independent of focal path, be used in preference to the peak height. Residual strains and thermal effects will also cause the Raman peak to shift.

The technique is readily adaptable to uniaxial loading conditions, but requires additional experimental and analysis work in order to interpret the data in terms of strain measurement. The technique is sufficiently sensitive to provide in-situ information on the strain distribution, residual stresses and micro-damage in composite laminates, and therefore has been used extensively as a laboratory tool for investigating interfacial behaviour in continuous and discontinuous fibre-reinforced systems, and fragmentation and microindentation tests [62-63]. Raman spectroscopy is particularly suited to inspecting polymers reinforced with aramid fibres, carbon fibres [63] or carbon nanotubes [64-65]. The matrix needs to be sufficiently translucent for in-situ analysis of the embedded fibres. Raman spectroscopy has been used to check dispersion, evaluate nanotube/matrix interactions and detect polymer phase transitions [65]. Raman can also be used to determine the orientation of nanotubes, and stress or strain transferred to the nanotubes from the surrounding environment. Well-defined Raman spectra can be obtained from the dispersed phase enabling the effective modulus of the nanotubes to be determined. Small amounts of nanotubes may need to be distributed in the composite matrix in order to make the polymer Raman sensitive.

An area of major concern relates to the inability to obtain well-defined Raman spectra from glass fibres. Glass fibre-reinforced systems are the most common systems in use, and unless this problem is resolved then the use of Raman spectroscopy will be limited to mainly aerospace/defence applications. A solution is to coat the glass fibres in a polymer (e.g. diacetylene-containing urethane copolymer) that allows Raman spectra to be obtained. This approach has been used to map strain distributions along large diameter ($> 100\ \mu\text{m}$) glass fibres embedded inside an epoxy matrix resin (i.e. fragmentation test) [62]. The glass coating was relatively thick (typically $15\ \mu\text{m}$). The next step required is to apply this approach to in-situ measurements of laminates with conventional glass reinforcing fibres with diameters of the order of $10\text{-}15\ \mu\text{m}$. This will also require the use of significantly thinner coatings. For practical purposes, these coatings will need to be both compatible with the surrounding matrix ensuring good intrinsic interfacial strength and environmentally durable.

3.5 INFRARED SPECTROSCOPY (IRS)

IRS provides information on molecular structure based on specific frequencies associated with internal vibrations of groups of atoms in molecules using a laser in the infrared region to excite the target material and analyse the frequencies absorbed. It makes use of the fact that for polymeric materials the chemical bonds between the atoms in the polymer molecules can vibrate at frequencies in the IR range of the electromagnetic spectrum (i.e. at wave numbers from $100\text{-}4000\ \text{cm}^{-1}$). By directing IR light at a polymeric material and measuring the absorption (or transmission) of the various frequencies, it is possible to characterise, or “finger-print”, the polymeric material since it will have specific frequencies at which it is seen to absorb strongly. This “finger-print” of the various frequencies at which the material absorbs is referred to as the IR spectrum. By monitoring the IR spectrum (i.e. absorption intensities) of a polymer during cure it is possible to determine the formation/transformation of chemical species. Change in intensities, the basis of cure monitoring techniques, gives direct information about the timescale within which the chemicals involved in the cure reaction have been used and the reaction is complete. The technique can be used to analyse gases, liquids and solids. Both qualitative and quantitative chemical analysis data can be obtained.

IRS is a key tool for assessing polymer chemistry (e.g. monitoring state of cure and determining environmental effects) and is used to provide information on the effects of processing and environmental exposure on interphase chemistry in filled polymeric systems. IRS is often used in conjunction with Raman spectroscopy as a complementary identification technique. It requires minimal sample preparation, but samples need to be transparent to infrared, the method is less useful for inorganic materials. Water is problematic as it obscures the spectrum. IRS is not inherently surface-specific (analysis is possible to within 0.5 to 3 μm of the sample surface), but variants improve this aspect. One variant, attenuated total reflectance uses a prism in optical contact with the sample resulting in total internal reflection after penetrating a small way into the sample surface and is particularly useful for investigating adhesion problems and surface treatment for strong IR absorbers provided the surface is flat. There are various ways of performing IR spectroscopy on a material, and probably the most widely used is known as Fourier transform infra-red or FTIR. Computerised databases of spectra for common polymeric materials are available to enable characterisation of molecular structure by observing spectral differences between known materials and the test sample.

3.6 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

This is an analytical technique that measures the energies of photoelectrons emitted from atoms of a sample when it is irradiated with soft (or low energy) X-rays. XPS is surface-sensitive and is frequently used for quantitative elemental analysis of fracture surfaces in fibre-reinforced systems, and hence the relative amount of cohesive and adhesive failure. XPS is also used for determining the surface chemistry of treated fibres and fillers (i.e. sizing). The technique, which is capable of detecting all elements with the exceptions of hydrogen and helium, can provide information on chemical structure (e.g. oxidation states) and element distribution present on the surface of any solid material. The technique is surface-sensitive with a maximum operational depth of less than 10 nm with a spatial resolution of less than 10 μm . XPS can be used to determine the effect of elevated temperature and surface preparation on surface chemistry and is used to examine the cause of adhesion problems. The technique can be used in conjunction with inert gas ion sputtering to determine the variation in chemical composition with depth (NB. Many polymeric material samples are sensitive to ion beam damage).

3.7 NUCLEAR MAGNETIC RESONANCE (NMR)

NMR spectroscopy is one of the principal techniques used to obtain physical, chemical, electronic and structural information about a molecule. Nuclear magnetic resonance of complex molecules, such as polymers, is usually achieved by aligning the molecules in a material using a very strong magnetic field, and then perturbing the alignment by applying an alternating electromagnetic (radio-frequency (RF)) field perpendicular to the original magnetic field [66]. The frequency range for RF signals is typically between 10 and 30 MHz. The nuclei absorb or emit energy at characteristic frequencies of the RF field with the amount and frequency of the energy providing an indication of the chemical structure of the material. All nuclei that contain odd numbers of nucleons and some that contain even numbers of nucleons have an intrinsic magnetic moment. The most often-used nuclei are hydrogen-1 and carbon-13, although certain isotopes of many other elements nuclei can also be observed.

Magnetisation will relax back to the equilibrium state over time. As excited nuclei relax, free induction decay (FID) signals are generated. FID is a sine function modulated by a decay function. The FID is then manipulated using Fast Fourier Transforms to create NMR spectra. The FID can be applied directly for quantitative determination of many physical properties, providing information on molecular coupling and on nuclei in different chemical states. NMR has been used to determine moisture content and degradation in fibre-reinforced polymers. Absorbed moisture as low as 0.2 wt% can produce measurable changes in NMR signals [66]. The technique is capable of distinguishing free moisture entering the composite via cracks and fissures from chemically bound moisture attached to fibre surfaces. As the level of absorbed moisture increases, the decay time of FID signals also increases, thus indicating that the motion of water molecules is increasingly constrained. The amplitude of FID signals also decrease as the amount of absorbed moisture increases. Spatial mapping of moisture distribution is possible using NMR.

NMR can also be used to measure degree of cure, variations in modulus as observed for the interphase regions surrounding fibres and fillers and degree of chemical bonding between coupling agents (e.g. organosilanes) used for fibre sizing and the surrounding matrix material. It is capable of resolving less than a monolayer equivalent of coupling agent on a fibre surface. Surface impurities and inhomogeneities (defects) can be detected; as both affect the degree of chemical cross-linking between the coupling agents and surrounding matrix material (i.e. line broadening in NMR spectra).

3.8 NUCLEAR REACTION ANALYSIS (NRA)

NRA is a nuclear method that can be used to obtain concentration versus depth distributions for certain target chemical elements in thin solid films. By irradiating the target elements with select projectile nuclei having specific kinetic energies these target elements can undergo a nuclear reaction under resonance conditions for a sharply defined resonance energy. The reaction product is usually a nucleus in an excited state, which immediately decays, emitting ionizing radiation. To obtain depth information the initial kinetic energy of the projectile nucleus (which has to exceed the resonance energy) and its stopping power (energy loss per distance travelled) in the sample has to be known. In order to contribute to the nuclear reaction, the projectile nuclei have to slow down in the sample to reach the resonance energy. Each initial kinetic energy corresponds to a depth in the sample where the reaction occurs (the higher the energy, the deeper the reaction). The energetic emitted γ ray is characteristic of the reaction and the number of γ rays detected at any incident energy is proportional to the concentration at the respective depth of hydrogen in the sample.

NRA analysis can be used to directly measure localised moisture content through the thickness of polymeric materials. Specimens are conditioned in D_2O instead of H_2O and the resultant deuterium concentrations in the specimen are measured. The surface is bombarded with a finely collimated ^3He beam, which reacts with the deuterium in the sample, releasing high-energy protons. The proton yield is directly proportional to deuterium in the reaction volume. Moisture profiles with a resolution of 12 μm have been measured.

3.9 ULTRASONIC TECHNIQUES

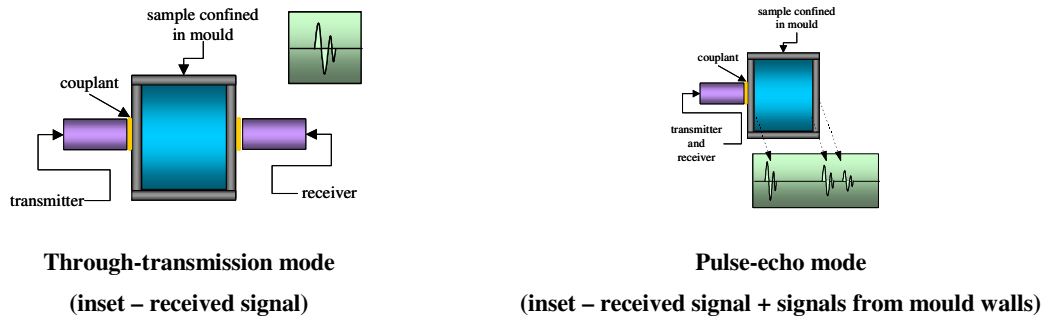


Figure 3.12: Time-of Flight [67].

Ultrasonic techniques (e.g. time-of-flight – see Figure 3.12) may be used to establish relationships between changes in the characteristics of propagating ultrasound and the real-time mechanical properties. The longitudinal velocity, V_L , of a sound wave is directly related to the longitudinal elastic modulus (stiffness), E_L , and density, ρ , of the material, through the relationship:

$$E_L = \rho V_L^2 \quad (3.6)$$

By using probes that emit and detect ultrasound these changes in modulus can be detected, which then provide information on the viscosity and hence state-of-cure of the matrix [66]. It is also possible to determine information about the viscoelastic properties of the matrix by monitoring the attenuation of the ultrasound signal. The attenuation of the ultrasound is at a maximum when losses due to viscous effects in the polymer are at a maximum, and this coincides with the glass transition temperature, T_g .

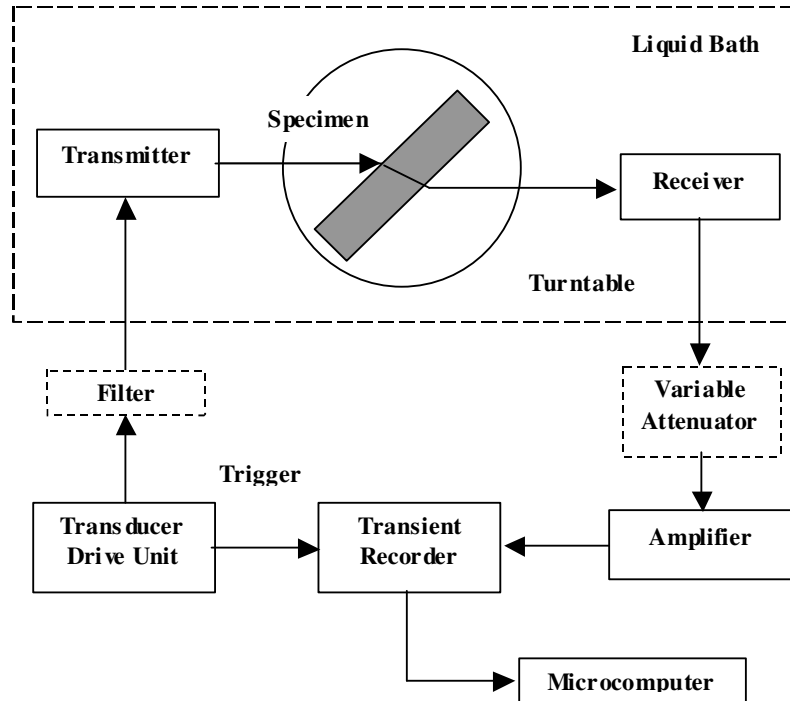


Figure 3.13: Schematic representation of the immersion equipment.

Elastic Property Measurements: Ultrasonics offers an alternative to the conventional mechanical test method for the determination of elastic properties, although its use for characterisation of composite materials has been limited [68-71]. Many of the difficulties encountered in mechanical testing, particularly for evaluating through-thickness properties, are obviated by the ultrasonic pulse method since the applied stress is negligibly small, and a high sensitivity can be obtained on small, thin specimens. Two methods are available for the ultrasonic determination of elastic properties: contact and immersion. The immersion method allows a full set of elastic properties to be determined for a single specimen (80 mm x 20 mm x 5 mm). The material under investigation immersed in a liquid, which acts as an ultrasonic couplant. In order to obtain all the stiffness components, the sample is placed on a turntable to facilitate wave propagation in the required directions (Figure 3.13).

Alternatively, the contact method requires several small specimens and a transducer-coupling medium to be used. This method requires that both the transmitting and receiving ultrasonic transducers be attached directly to the specimen, on opposing faces, with the aid of the coupling medium (water-based gel). The electronic equipment required is identical to that employed for the immersion method. Since all the stiffness components of an orthotropic material cannot be deduced from a single specimen, several small specimens need to be cut to allow wave propagation in known planes and directions. Only small amounts of material are required for the tests, at high frequencies, a parallel beam of ultrasound may be propagated with a small cross-sectional area (typically at 5 MHz transducer can produce a plane wave 10 mm across). Commonly, ultrasonic transducer frequencies between 0.1 and 10 MHz are employed. In the vicinity of a surface, the wave velocity is lower than that in the bulk material. This causes a change in the shape of the pulse, introducing an error into the velocity measurement. It is therefore necessary to use a wavelength, which is sufficiently small compared with the dimensions of the sample to ensure true plane wave conditions exist. This condition is satisfied when sample dimensions are greater than a few wavelengths.

Other factors that can directly influence the accuracy and consistency of results include angle measurements (see Figure 3.13), sample density and homogeneity, sample dimensions, temperature and surface finish (tolerance of ± 0.01 mm, or better). The wave velocity in water varies with temperature. Discrepancies in the wave velocity measurements alter the stiffness matrix constants and, consequently, the engineering properties that are computed using these values. Small aberrations in velocity measurements can lead to dramatic changes in stiffness components. This occurs as a result of the dependence of these parameters on other stiffness components. A detailed description of the theory behind the technique can be obtained from references [68-70].

Unpublished work conducted at NPL has shown that accurate results can be achieved on good quality materials. Composite materials tested included unidirectional carbon-fibre/epoxy and glass-fibre/epoxy, and glass-fibre fabric/epoxy. The elastic modulus values agreed with both theoretical predictions, based on measured volume fractions and manufacturer's fibre and matrix property data, and with the mechanical test results. Shear moduli tended to be higher than both predictions and mechanical test values. This was expected as the non-linear, matrix dominated response of the material was being observed at high frequency and low strain. The Poisson's ratio values were the least accurate or consistent results, however, this is inherent with both ultrasonic measurements and mechanical testing.

It may be possible to invert micro-structural models for composites to extract stiffness information on the interphase from velocity measurements, but this would require the models to include an interfacial component that is an accurate representation of an actual composite [72]. As the interphase constitutes a region of non-uniform elastic properties, it is difficult to foresee ultrasonic measurements providing quantitative interphase elastic property data. However, ultrasonic measurements could possibly provide information for quality assurance purposes.

Ultrasonic Spectroscopy can be used to detect the damage caused to fibre-reinforced polymer materials due to hygrothermal ageing. Acoustic parameters, such as velocity and attenuation, are linked to the viscoelasticity and microstructure of the propagation medium [73]. The acoustic parameters can be measured by means of pulsed ultrasonic spectroscopy. It is possible to relate changes in ultrasonic properties to moisture content and the level of material degradation, and also identify damage mechanisms. Changes in frequency dependency of velocity and attenuation have been related to matrix cracking. The length of the ultrasonic pulse and the size of the sample limit the resolution of this technique.

Acoustic Emission Monitoring (AE) involves detection of sound waves (usually inaudible to the human ear) made by a structure under load. The technique, which can be used for monitoring the "state of health" of a structure, involves attaching one or more ultrasonic microphones to the object and analysing the sounds using computer based instrumentation. AE may arise from friction (including bearing wear), crack growth and material changes such as corrosion. Microscopic events can be detected if sufficient energy is released and source location is also possible using multiple sensors.

Large structures (e.g. pressure vessels) can be continuously monitored from a few locations, and proof and qualification tests for routine inspection purposes can be conducted whilst the structure is in service. Applications include testing pipelines and storage tanks (above and below the ground), fibreglass structures and weld monitoring. It can be used to monitor composite laminates for damage initiation and growth (e.g. fibrillar breaks, matrix microcracking and interfacial debonding) during mechanical testing. Detection of relevant signal from noise may be difficult. The technique relies on the operator having sufficient experience to be able to identify particular defect types from the AE data.

4 MODELLING INTERFACIAL AND INTERPHASE PROPERTIES

Analysis of composite materials can be considered in degrees of structural complexity building up from the micromechanics scale (i.e. ply or lamina level) to the formation of laminates from the properties, fibre orientation and distribution of individual laminae (i.e. macromechanics scale). The objective of micromechanics is to predict the behaviour of laminae as a function of the properties and volume fractions of the constituents, usually fibre and matrix. These properties are referred to the three principal material axes (see Figure 4.1) of the lamina (or ply). A lamina is modelled as a single layer of continuous or discontinuous reinforcement (or filler), unidirectional or random. Several laminae are bonded together to form a laminated structure. The lamina is treated as the smallest repeating volume element (RVE) of a laminate and is considered to be homogeneous and anisotropic.

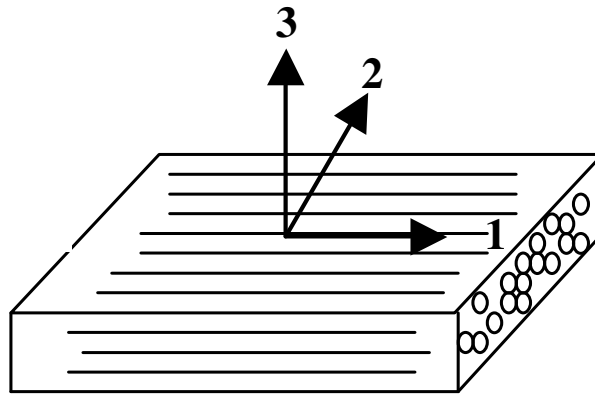


Figure 4.1: Principal material axes.

The ideal approach to modelling composite behaviour is to commence with the basic properties of the constituent materials (i.e. fibre and matrix) and be able to predict the elastic and strength properties and performance of the composite. The success of this approach relies primarily on the existence of a strong interfacial bond between the constituents that will ensure transfer of load from the matrix to reinforcement without causing interfacial failure. The interfacial bond and interphase region surrounding the reinforcement can influence composite strength, modes of failure and elastic properties.

In modelling composite properties, gross simplifications (i.e. perfect fibre/matrix interfacial bonding and uniformity of matrix properties surrounding the filler) are made in relation to the stress state arising in the interface. Most composite models make no allowance for the influence of interfacial or interphase properties on composite behaviour. The success of models that exclude these effects is dependent on the quality of the fibre/matrix interfacial bond and environmental test conditions with predictive reliability decreasing for poor quality material and hostile environments. When the fibres are strongly bonded to the matrix the strength and stiffness properties can be calculated with reasonable reliability. In order to achieve reliable prediction of composite properties, the micromechanics models need to accurately account for fibre and bulk matrix properties, as well as interfacial and interphase properties.

This section examines models for analysis of elastic and strength properties of composite systems in which the interface and/or interphase is included as one of the constituents. The models considered cover a wide range of length scales from the nanoscale (10^{-10} m) to the macroscale (10^0 m), and fibre formats (i.e. continuous and discontinuous, aligned and random). Both micromechanics and nanomechanic models (including molecular dynamics) are discussed.

4.1 MICROMECHANICAL MODELS

This section reviews the different micromechanical model approaches that have been developed in an attempt to accurately predict thermoelastic constants, strength and failure modes of conventional fibre-reinforced polymer composites. It concentrates essentially on lamina properties rather than laminated structures.

4.1.1 Concentric Cylinder Models

Multiple concentric cylinder assemblies have been used extensively in the literature as the basis for modelling thermoelastic properties of continuous unidirectional laminates, and for predicting the stress transfer that occurs following fibre fracture and transverse matrix cracking. In the concentric cylinder model, the fibre is represented by a cylinder, which is either singly embedded in a matrix cylinder or doubly embedded in concentric cylinders of increasing diameter representing the interphase and bulk matrix (Figure 4.2). The volume fractions of the composite in each cylinder remain constant.

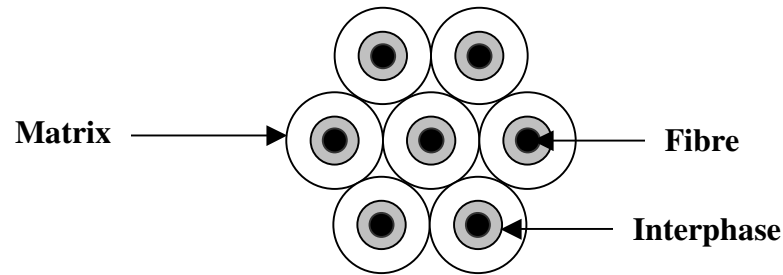


Figure 4.2: Hexagonal fibre array depicting fibres with interphase and matrix.

In earlier approaches, the RVE for a unidirectional laminate was considered to be a set of perfectly bonded coaxial cylinders. Hashin and Rosen [74-75] modelled a composite as an assembly of concentric cylinders, deriving lower and upper bounds for the elastic properties of unidirectional composites using extremum principles of minimum potential and minimum complementary energy, respectively. It was assumed that all constituents were linearly elastic, isotropic and homogeneous. Two fibre cases were considered. In the first case, the fibres were assumed to have identical cross-sectional area and form a hexagonal array in the transverse plane (Figure 4.2) and in the second, fibres were allowed to have different diameters and were randomly located in the transverse plane. In both cases, the ratio of inner to outer diameter was identical, and the composite was considered to be macroscopically homogeneous and transversely isotropic.

It was not obvious from the numerical study conducted by Hashin and Rosen [74], which of the two fibre arrays best represents a real composite. The random array is more representative of real composites, but insufficiently rigorous because of the geometric approximation of irregular fibre and interphase shapes by circles. However, good agreement between predicted and measured thermoelastic properties have been achieved using the random fibre array [76].

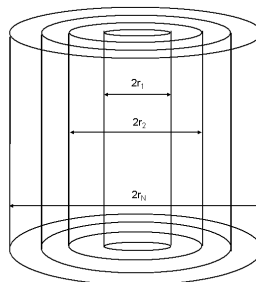


Figure 4.3: Diagram showing concentric cylinder model.

A new multiphase concentric cylinder model (Figure 4.3) has been developed at NPL by L N McCartney [77] in which the concentric cylinders consist of different transverse isotropic materials having the same axis of symmetry that coincides with the axis of the cylinders. The model enables the stress and displacement distributions to be calculated for a set of perfectly bonded concentric cylinders subject to biaxial, axial shear and transverse shear loading. The cylinders are assumed to form a hexagonal array. The stress and displacement solutions can be used to calculate the effective thermoelastic properties for a unidirectional fibre-reinforced laminate given the thermoelastic properties for each cylinder of the assembly. The model accounts for thermally induced residual stresses and provides exact elasticity solutions. Predictions for a carbon fibre-reinforced epoxy composite were in good agreement with corresponding FEA calculations.

4.1.2 Halpin-Tsai Method

Halpin-Tsai semi-empirical relationships have been used extensively for determining engineering properties of continuous and discontinuous fibre-reinforced systems. The following generalised form can be used to determine any thermoelastic property P of a composite [76, 79-80]:

$$P = P_m \left(\frac{1 + \xi \chi V_f}{1 - \chi V_f} \right) \quad (4.1)$$

where:

$$\chi = \left(\frac{P_f}{P_m} - 1 \right) / \left(\frac{P_f}{P_m} + \xi \right) \quad (4.2)$$

P_m and P_f are the associated matrix and fibre properties respectively and V_f is the fibre volume fraction. The reinforcing (or scaling) parameter, ξ , is dependent on fibre geometry, packing geometry and loading conditions. The dimensionless quantity χ may be viewed as the “reduced” properties of the constituents.

The central tenet of the Halpin-Tsai relationship is that properties P of a composite material must lie somewhere between the extremes of the Voigt upper bound and the Reuss lower bound. Voigt model corresponds to the mechanical analog of “springs in parallel” and the Reuss model is associated with “springs in series”. The arbitrary scaling parameter ξ serves to adjust the effective properties P between the upper and lower bounds, and can be treated as an adjustable parameter whose value can be obtained from experimental determination of the property of the composite at a specific fibre volume fraction. Values of $\xi = 1$ and $\xi = 2$ have been obtained for in-plane shear modulus G_{12} and transverse tensile modulus E_{22} , respectively. These values were obtained by comparing the calculated values obtained using the Halpin-Tsai Equations (4.1) and (4.2) with exact elasticity solutions through a curve fitting exercise [81]. Halpin and Tsai [78] have shown that equations agree well with more exact solutions. The Halpin-Tsai relationship has also been used successfully to determine elastic properties of unidirectional discontinuous fibre-reinforced laminae [79-80], and has been incorporated into NPL CoDA (Composite Design and Analysis) software with appropriate values of ξ for the different elastic properties and fibre formats.

Equations (4.1) and (4.2) assume that the fibre-matrix interface is a perfect continuum boundary and the matrix modulus in the vicinity of the fibre is identical to the bulk matrix modulus. In reality, the fibre surrounded by a complex environment, consisting of areas of imperfect bonding, residual thermal stresses and high stress gradients produced by localised stress concentrators (i.e. voids, micro-cracks and inclusions), with the fibre-matrix interface being an homogeneous layer of variable thickness and distinct physio-chemical properties.

The scaling parameter ξ can be determined for an unknown system (or a poorly bonded system) from experimental determination of the property P_{exp} by:

$$P = \frac{P_f(P_{exp} - P_m) - V_f P_{exp}(P_f - P_m)}{P_m[(P_f - P_{exp}) - (1 - V_f)(P_f - P_m)]} \quad (4.3)$$

Once a value of ξ has been determined for one set of experimental values (P_{exp} , V_f), the property P may be determined for other fibre volume fractions; provided ξ does not change with fibre volume fraction.

4.1.3 Interphase Model

Using classical elasticity theory, Sideridis [82] developed the following approximation for determining G_{12} , which accounts for the shear modulus of the fibre G_f , matrix G_m , and interphase G_i components:

$$\frac{G_{12}}{G_m} = \frac{4G_m \left(G_f V_f + \frac{2V_f}{r_f^2} \int_{r_f}^{r_i} G_i(r) r dr + [(G_i^2 + G_m^2)(2 - V_m) + 2G_i G_m V_m] V_m \right)}{[G_i V_m + G_m (2 - V_m)^2]} \quad (4.4)$$

Parameters r_f and r_i represent the outer radii of the fibre and inter-phase cylindrical elements, respectively (see Figure 4.1). The model considers the interphase to be inhomogeneous in nature with mechanical properties varying across the interphase region. Different laws of variation of its elastic modulus and Poisson's ratio were taken into account in order to define the overall modulus of the composite.

Although this complex relationship shows reasonable agreement with experimental data and other theoretical predictions, it still requires accurate experimental data on both G_i and the physical dimensions of the interphase, which is a difficult task. A similar relationship has been derived by Sideridis [83] for transverse tensile modulus E_{22} .

4.1.4 Interfacial Shear Strength

Micromechanics modelling of in-plane shear strength, S_{12} , has not developed to the stage where a reliable prediction based on constituent material properties is possible. The simplest method of estimating shear strength is to assume that a "rule of mixtures" applies:

$$S_{12} = \tau_i^u A_i + \tau_m^u (1 - A_i) \quad (4.5)$$

A_i is the fraction of the fracture area occupied by interfacial failure, and τ_i^u and τ_m^u are the interfacial and matrix shear strengths, respectively. This approach assumes that the fracture path bisects a regular square array. Fracture, however usually propagates preferentially through the matrix in a non-linear manner without disturbing the fibres, and not conveniently along the fibre-matrix interface for Equation (4.5) to apply.

Shu and Rosen [84] performed a more rigorous analysis of the unidirectional laminae and obtained “lower” and “upper” bounds to S_{I2} . It was assumed that the fibres were elastic-brittle and rigid, and the matrix was elastic-perfectly plastic, which obeys the von Mises yield criterion. An upper shear strength limit of $4\tau_m^u/\pi$ was predicted for V_f approaching unity, which is a 27% increase on the lower bound value τ_m^u . Hancox [85] showed that for a well bonded carbon fibre-reinforced epoxy material, the predicted and experimental values are in tolerable agreement for $V_f \leq 0.6$.

In the case where the fibre-matrix interface is the weakest link, it has been suggested that [86]:

$$S_{I2} = \frac{\tau_m^u}{(1 + V_f)^2} \quad (4.6)$$

This approach ignores the presence of stress concentrations within the lamina, which increase in magnitude as $V_f \rightarrow 1$.

Relating in-plane shear strength to the mechanical properties of the constituents and simultaneously accounting for non-uniform fibre distribution, interfacial bonding, stress concentrators and residual thermal stresses is exceedingly complex. However, it is possible to obtain reasonable agreement between the experimental data and the following empirical relationship [87-88]:

$$S_{I2} = [1 - (\sqrt{V_f} - V_f)(1 - G_m / G_{I2f})]\tau_m^u \quad (4.7)$$

For laminae with a brittle matrix, the stress concentration effect will cause the strength of the composite to be lower than that of the unreinforced matrix material. If the matrix is able to relieve these stress concentrations through local deformation processes then $S_{I2} \approx \tau_m^u$.

If $G_{I2f} \gg G_m$, as in the case of unidirectional carbon fibre-reinforced epoxy, then Equation (4.7) reduces to:

$$S_{I2} = [1 - (\sqrt{V_f} - V_f)]\tau_m^u \quad (4.8)$$

Applying a “law of mixtures” rule, shear strength can be approximated by the following relationship:

$$S_{I2} = [1 - (\sqrt{V_f} - V_f)]\tau_m^u + (\sqrt{V_f} - V_f)\tau_i^u \quad (4.8)$$

τ'' is not in the strictest sense “true” interfacial shear strength, but is the average shear stress necessary to separate the fibre from the matrix under shear loading. Similar relationships can be derived for transverse tensile strength.

4.2 MODELLING NANOCOMPOSITES

The modelling of nanocomposites is of considerable interest, in order to characterise their mechanical properties for potential engineering applications. Due to the small length scale of the nanofiller in relation to the bulk material, modelling the nanocomposites can be complex. There are two main approaches for modelling nanocomposites. Molecular modelling can be used to analyse the local load transfers, interface properties or failure modes at the nanoscale. Continuum models based on micromechanics can be used to analyse the global properties of the nanocomposites at the micro- or macro-scale.

4.2.1 Molecular Modelling

Molecular modelling techniques are important in the prediction of physical material properties, such as elastic response, binding energies and atomic structure. As the technique models the discrete molecular structure, it is ideal for studying the atomic interactions at the nanoscale. However, these techniques can be computationally expensive, and therefore limited to small length and timescales. The three main molecular modelling techniques for the prediction of nanocomposites properties are molecular dynamics (MD), Monte Carlo and ab initio simulation. Of these, molecular dynamics is the most widely used technique.

A combination of modelling techniques is usually required to simulate the bulk behaviour of nanocomposites. To scale up predictions from a molecular dynamic simulation the Equivalent-Continuum Method (ECM) can be used [89]. An equivalent continuum, identical to the MD model geometry, is developed and a constitutive law is used to describe the mechanical behaviour of the continuum. The energies of deformation of the MD and equivalent-continuum models are derived for identical loading conditions. The unknown mechanical properties of the equivalent-continuum are determined by equation from the energies of deformation. The properties of a larger-scale material are then determined using the equivalent-continuum volume element properties.

4.2.2 Continuum Based-Modelling

Continuum-based methods assume the existence of continuum for all calculations and generally don't include the chemical interactions between constituent phases. The continuum-based techniques primarily include computational methods, such as FEA and boundary element methods (BEM), and the micromechanics approaches developed for composites.

Micromechanics Approach

For fibre-like materials, load is transferred to the reinforcement through shear stresses at the fibre/matrix interface. In nanocomposites the structure of the filler (e.g. a nanotube) can be taken into account, and the properties of an effective fibre can be defined. This can then be used to determine the elastic properties of a composite using a micromechanics approach. Micromechanics approaches typically assume perfect adhesion (perfect load transfer) and ignore interfacial phenomena.

One micromechanics approach commonly used is the Halpin-Tsai method. Thostenson and Chou [90] used an approach based on Halpin-Tsai to determine the effective elastic modulus of a nanocomposite consisting of aligned multi-walled carbon nanotubes embedded in a polystyrene matrix. The elastic modulus of the multi-walled nanotube was modelled by assuming that the outer wall acts as an effective solid fibre with the same diameter and length. An applied external force on the nanotube and fibre results in an iso-strain condition, which can be used to relate the elastic properties of the nanotube to the effective fibre. The Halpin-Tsai equation can then be used to predict the overall elastic properties of the polymer matrix with nanotube reinforcement. For multi-walled nanotubes there is typically a distribution of nanotube diameters in a sample.

Thostenson and Chou [90] have looked at double Lorentz and Gauss distributions as probability density functions for the nanotube diameter distribution. This model has been used to show that the properties of nanotube composites are strongly influenced by the nanotube diameter. Modelling the diameter distribution of the reinforcement is essential for accurate modelling of the overall nanotube composite elastic properties. Experimental elastic modulus data were obtained for model composite systems, aligned nanocomposite films with 5 and 10 wt% nanotubes. These data were compared with elastic modulus predictions using the micromechanics model. Predictions using the Lorentz distribution compare well while the Gauss distribution overestimates the composite modulus especially at higher loading fractions.

Micromechanics models can be used to model different aspects of nanocomposite morphology. Brune and Bicerano [91] used the Halpin-Tsai equation to predict the modulus of a nanocomposite containing incompletely exfoliated stacks of clay platelets. In this case, pseudo-particles were used to represent the incompletely exfoliated stacks and included the inter-platelet spacing. The model was used to demonstrate the reduction of reinforcement efficiency of clay platelets of high aspect ratio in a polymer matrix as a result of incomplete exfoliation.

Li et al [92] also used the Halpin-Tsai method to model the distribution of clay platelets. The average dimensions of platelet stacks required for the model were determined from TEM observations. A two-step approach was used – first the platelet stack was treated as a localised composite. Solutions from this analysis were then used with the Halpin-Tsai equation to obtain the elastic modulus of the overall composite. There was good correlation between predictions and experimental data from tensile and bend tests, although the model was only suitable for clay concentrations up to 30 wt%, which is considerably greater than concentrations usually used in nanocomposites.

Micromechanics methods such as Halpin-Tsai do not include interface properties. In nanocomposites there are nanoscale interactions between the embedded nanotube and adjacent polymer chain leading to the formation of an interphase region. Experimentally it is very difficult to measure the mechanical properties of this interphase region due to the small length scale. Fisher et al [93] used a three phase (fibre/nanotube – annular interphase – matrix) Mori-Tanaka micromechanics model to predict the properties of the interphase region from macroscale viscoelastic data. The Eshelby tensor was used as the dilute strain concentration tensor for ellipsoidal inclusions, the limiting case of which is an infinitely long cylindrical inclusion. If the Eshelby tensor were calculated for each of the three phases, this would represent a system where the interphase is separate to the fibre. Therefore the analytical solution was reformulated to produce a tensor for the case of an annular interphase surrounding the nanotube. An elastic analysis was used to predict the effective composite modulus for two cases - aligned fibres and randomly oriented fibres. The authors suggest this model could be extended to predict viscoelastic properties. This method could then be used with experimental data to infer the viscoelastic properties of the interphase.

An alternative approach, which takes account of the interface, is to use equivalent-continuum modelling (ECM, Section 4.2.1) to model the nanotube, local polymer adjacent to the nanotube and the nanotube/polymer interface as an equivalent-continuum fibre. The mechanical properties of this RVE can be calculated through molecular modelling. This RVE can then be used as an effective fibre in a micromechanics analysis.

Odegard et al [94] used equivalent-continuum modelling to obtain a representative volume element for a polyimide/single-walled nanotube composite. The authors then used the Mori-Tanaka approach to predict the elastic properties of the composite at various lengths, orientations and volume fractions of nanotubes. The predicted values were larger than measured values. The difference between experimental data and the model was thought to be due to the fact that the model assumes fibres are perfectly dispersed in the polymer matrix, while in reality a significant proportion of nanotubes remain in bundles in the composite material.

Buryachenko and Roy [95] used the ECM approach in conjunction with a one-particle approximation of the multiple-particle effective field method (MEFM) to predict elastic properties. This method allows for the interaction of particles within a nanocomposite and is based on homogeneous ellipsoidal inclusions. The method models the inclusion shape and the ellipsoidal spatial correlation of inclusion location (known as correlation holes). The authors used an orientation distribution function to represent the distribution of fibres.

The model allowed consideration of both isotropic and transversely anisotropic fibres and was used to predict the effective longitudinal and transverse modulus of the composite as a function of volume concentration of fibres for 1-D, 2-D and 3-D random cases. Predictions were compared to those obtained using the Mori-Tanaka method. The MEFM estimations were found to agree well with the Mori-Tanaka predictions for the 1-D and 3-D cases.

Computational Methods

The computational methods available to model nanocomposites are FEA and BEM. These methods provide numerical computation of bulk properties based on geometry, properties and volume fraction of constituent phases. The material RVE is discretized into elements for which the elastic solution leads to the determination of stress and strain fields. In FE analyses, the whole RVE is meshed with elements and the level of mesh refinement determines the predictive accuracy - ideally a fine mesh should be used to be able to capture the stress fields accurately. Whereas in the boundary element method, elements are only used along the boundaries. The boundary integral equations (BIE's) are solved to evaluate the stress and strain fields. Hence, this method is less computationally expensive than FE methods.

Liu and Chen [96] have used both methods to model a carbon nanotube composite, although BEM was the main focus of the work. For BEM, the equation used was a weakly-singular form of the conventional boundary integration equation and so did not involve computation of any singular integrals. This BIE can be applied to thin shell-like materials or structures, as long as the nearly-singular integrals can be computed accurately and efficiently. The BIE is applied to the carbon nanotube and matrix separately and the resulting two equations are coupled at the interface. Perfect bonding is assumed between the nanotube and matrix. A square RVE with a single fibre was modelled as a BEM mesh and also an FE mesh. The BEM model was much smaller than the FE model. Two load cases were considered: bending loading to study deformation and axial loading to study the load transfer mechanisms. Good correlation was found between methods for both cases, although the BEM was more efficient.

When modelling a large number of nanotubes, the size of the FE and BEM models becomes more of an issue. A recent development in this area is fast multipole BEM, which further improves the efficiency of the BEM. This method has been used by Liu et al [97] to obtain the effective modulus of a carbon nanotube composite. In this analysis, the nanotube was treated as a rigid fibre in an elastic matrix, with the assumption of perfect interfacial bonding. The fast-multipole BEM elements of integration are grouped together according to distance between the element and the source point. The integrations on elements in one cluster are computed together using multipole expansion therefore reducing computing time. Triangular elements were used to discretize the interface between the fibre and matrix. Two fibre orientations were studied; uniformly aligned and randomly aligned (fibres still aligned in x-direction but with no regular pattern). True random orientation couldn't be considered due to problems generating RVE models without causing contact of the fibres.

The authors used BEM to calculate the effective longitudinal modulus and compared results to those from the Halpin-Tsai method. The two methods compared well at low volume fractions. The effect of volume fraction of larger aspect ratio fibres on the effective modulus was studied using a refined mesh. The authors compared results with predictions obtained in earlier work using molecular dynamics combined with an equivalent continuum model, and to results from the Halpin-Tsai method. There was good correlation with the molecular dynamics method while the Halpin-Tsai method underestimates the effective modulus (probably due to the large aspect ratio of the fibres). The authors suggest more realistic interface conditions based on molecular dynamics simulations could be incorporated into fast-multipole BEM.

Computational methods can also be utilised for studying different aspects of a nanocomposite, such as nanotube properties and interphase regions. Meo and Rossi [98] used an FE model based on molecular mechanics to obtain the Young's modulus of the nanotube itself. The authors used a combination of non-linear springs and torsional elastic springs to create a mesh of the nanotube based on the carbon-carbon model. Predicted nanotube modulus values were in good agreement with numerical and experimental data presented by other researchers.

Bogetti et al [99] used AFM to demonstrate that there is a property gradient throughout the interphase region between the nanofiller and the bulk matrix. Interphase properties of both an unsized and a sized carbon fibre were investigated. AFM measurements found that the interphase region for the unsized fibre was too small (relative to the size of the indentation probe) to characterise accurately. A 3-D FE model of the sized fibre composite was constructed. This incorporated the property gradient across the interphase through the use of a user-defined UMAT subroutine within the ABAQUS FE software package. The analysis was used to predict the indentation response along a radial line from the centre of a fibre. Good agreement was found between the FE predictions and the AFM measured values of stiffness at an ambient temperature.

5 DISCUSSION AND CONCLUSIONS

The review highlights the limitations of micromechanical interface test methods in providing reliable quantitative interfacial data; as summarised below (see also [4]):

- No single ideal or universally applicable interfacial measurement method exists that can provide quantitative data for engineering or design purposes.
- There is a lack of consensus and understanding regarding failure processes occurring at the interface and the data reduction analyses, which best provide useful and reliable data.
- There are no test standards currently in existence for evaluating interfacial properties, although efforts have been initiated in ASTM to develop a guide for single fibre push-in /push-out tests for ceramic composites.
- Data analysis methods are oversimplified, assuming constant shear assumptions when non-uniform stress and strain distributions and mixed mode failures occur in all cases.
- Generally, there is a high degree of scatter in the data generated due to the intrinsic random nature of the interface, small interfacial area involved and the sensitivity to specimen geometry and loading conditions.
- Results differ significantly between tests due to differences in specimen geometry and loading methods, stress and strain distributions, thermal expansion and stiffness mismatch between constituents, cure shrinkage, friction and Poisson's effects.

An inherent problem associated with micromechanical interfacial test methods is the determination of an interfacial property that is independent from the specific test arrangement, and the fact that none of the methods are suitable for characterising interphase properties. Despite these problems, it is possible that by tightening controls on specimen preparation, specimen dimensions and test parameters, and formalising the analysis methods that improved consistency and reliability can be achieved.

The fragmentation and pull-out tests are the most favourable in achieving these aims, giving the best balance between testing and modelling aspects. However, interest in micromechanical interfacial techniques seems to have diminished due to the inherent problems associated with testing and data analyses, and by the lack of progress in developing standards for the different interfacial test methods. Attention now has begun to focus on a new generation of techniques, such as SPM, nanoindentation and nanoscratch. SPM consists of a powerful set of techniques, which could potentially provide in-situ quantitative mechanical and chemical measurements for characterising interfacial and interphase properties for conventional composites and nanocomposites. Combined with atomic force, acoustic, thermal and electrochemical probes, as well as nanoindentation and nanoscratch facilities, SPM could provide a comprehensive set of data sufficient to fully characterise the interface and interphase properties. It is not limited to ambient conditions, and thus could be used for sub-zero and elevated temperature studies.

These techniques should enable the direct measurement of *in-situ* interfacial and interphase properties, such as hardness, elastic properties, yield stress, true stress/strain curves, interfacial adhesion strength and fracture toughness, as well as feature dimensions and mapping facilities for determining uniformity of interphase properties. Additional information includes strain hardening, surface residual stress and glass transition temperature. The techniques are applicable to most fibre-matrix combinations, providing information on actual composite systems. Specimen preparation and handling, and data analyses are straightforward.

There are a number of issues still to be resolved with SPM, nanoindentation and nanoscratch in order to provide the necessary confidence in the use of these techniques in providing reliable engineering and modelling data. As with the micromechanical test methods, there is a high degree of uncertainty in the measured data, which can be attributed to a number of factors, such as load frame compliance correction, calibration errors, difficulty in establishing true zero for load and displacement, variability in probe tip geometry, wear and deformation of indenter tip, surface roughness effects, thermal drift and vibration effects. All these issues need to be addressed in rigorous and controlled manner in order to formalise methods based on these surface techniques for characterising mechanical and chemical properties of the interface and interphase. This will involve identifying suitable indenter tips for inducing interfacial fracture in a controlled and known manner.

Various models of differing complexity are available for modelling conventional and nanocomposites. These range from the more basic micromechanical models, such as Halpin-Tsai and concentric cylinder methods used routinely for conventional composites up to the complex molecular modelling approaches applied to nanocomposites. Both Halpin-Tsai and concentric cylinder methods are able to accommodate interphase properties. The Halpin-Tsai method is a semi-empirical approach relying on experimental data in order to generate the reinforcing (or scaling) parameter, which could be modified to allow for different degrees of interfacial strength.

The concentric cylinder method developed by L N McCartney, although limited to transversely isotropic continuous unidirectional fibre-reinforced composites can be used to estimate thermoelastic properties in which the interphase properties are included. The issue arises as to validation of the model for partially or poorly bonded systems and the ability of the model to accommodate non-uniformity of properties across the interphase region as observed in actual composites. It may be possible to provide the necessary input data using the novel techniques discussed previously in order to verify the applicability of the model for these systems. This is particularly pertinent for qualifying different sizings for fibres and evaluating environmental resistance.

If the behaviour of this interphase region in nanocomposites is to be considered then the molecular modelling approach is the most accurate. But this approach is complex, computationally very expensive and is hence limited to small length scales. An alternative approach is to use an equivalent-continuum model based on molecular modelling predictions to obtain a representative volume element, which can be used in a micromechanics analysis. Alternatively, micromechanics models such as Mori-Tanaka can be reformulated to include an interphase region, which removes the molecular modelling requirement. As computing power becomes cheaper, computational methods are becoming more attractive. If the interphase region can be characterised a FE mesh can be created with a defined interphase region, and appropriate material properties. The use of a user subroutine even allows for the variation of properties across an interphase.

Recommendations for Future Work for DTI funded Measurements for Materials Characterisation project SM10 “Characterising Micro- and Nano-Scale Interfaces in Advanced Composites” are summarised below.

Test Methods

- New/novel test methods - AFM, nanoindentation and nanoscratch
 - Thermo-elastic properties of interphase
 - Fracture toughness and interfacial strength
 - Dimensions of interphase (fibre sizing)
- Mechanical/coupon test methods
 - Fracture toughness, flexure and tensile properties
- Thermal properties
 - Thermal conductivity and thermal expansion
- Environmental stress corrosion (ESC)

Predictive Analysis

- NPL Concentric Cylinder Model - continuous aligned composites
 - Thermo-elastic properties of interphase
 - Sizing effect - varying degrees of fibre/matrix adhesion
- Halpin-Tsai Method - continuous aligned, flake and nanoparticulate reinforced composites
 - Thermo-elastic and strength properties
- Molecular modelling - nanoparticulate reinforced composites
 - Thermo-elastic properties

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