1 Introduction

Recent experimental and numerical studies have shown that the load-bearing capacity and failure behaviour of fibrous composite materials are dependent on the local microstructure and in-situ constituent material properties within the heterogeneous material [1, 2]. Many researchers have attempted to simulate the microstructural behaviour of the material under load through the use of micromechanical modelling techniques. These models consider each constituent material as a distinct phase within the composite, and provide an interesting insight into the failure initiation and propagation of the composite under various types of loading. Of great importance, however, are the constituent mechanical properties which are used to define the materials in these micro-models.

The vast majority of micromechanical models of composite materials assume that the material properties of the constituent materials are the same as the material properties of the material in its bulk form. However, this may not be the case after the complex composite preparation and high-temperature curing processes [3]. Interactions between the constituents and their coupling agents may alter the constituent mechanical properties at the microscale, leading to error in the predicted response by the aforementioned micromechanical models. The matrix is the constituent most likely to be altered during the curing process as the material is in a molten state for a period of the cycle. The fibres are often coated with coupling agents in an attempt to improve the adhesion between the fibre and matrix constituents, and promote stress transfer across the interface between the constituents. These fibre treatments could interact with the matrix material while it is in a liquid state. It is also likely that any change in mechanical properties of the matrix material will be dependent on the matrix pocket size, and the location of the material relative to nearby fibre-matrix interfaces throughout the heterogeneous composite microstructure.

Nanoindentation is a technique which can be used to determine the hardness and Young’s modulus of extremely small localised regions. Although originally used to determine the properties of thin films on substrates, the technique has been used in recent years to determine the in-situ mechanical properties of fibrous composites. Gregory and Spearing [3] carried out nanoindentation experiments on in-situ matrix pockets of two separate fibrous composite systems, as well as neat polymer plaques of the same matrix material. The tests indicated that the elastic modulus and hardness of the in-situ resin was up to 30% greater than that of the neat resin. Several authors [4-7] also carried out lines of shallow indents across fibre-matrix interfaces. This resulted in a small number of indents close to the fibre-matrix interface which produced mechanical properties with intermediate values between those of the matrix and fibre constituents. This region of unique properties close to the fibre-matrix interface has been termed the “interphase” region.

The goal of this project is to outline a methodology to fully characterise the micromechanical properties of a fibrous composite material in-situ, using the nanoindentation technique. The potential issues and downfalls of using the nanoindentation technique for this purpose are being outlined and investigated to ensure that the methodology is as robust as possible.


2 Nanoindentation Theory

Nanoindentation tests involve pushing a diamond tipped indenter head into a bulk material under either load or displacement control. The displacement is monitored as a function of the load throughout the load-unload cycle. When determining material properties such as hardness and elastic modulus, a three-sided pyramid indenter known as Berkovich indenter is commonly used. The methods of interpreting nanoindentation data have been developed over a number of years with the Oliver and Pharr [8] method being the most extensively used method of determining modulus and hardness. Hardness (H) is defined as the contact pressure under the indenter:

\[ H = \frac{P}{A_c} \]  

(1)

where P is the load and A_c is the projected contact area. The initial slope of the unloading curve can be related to the elastic modulus of the material using Equation 2:

\[ S = \frac{dP}{dH} = \frac{2E_s \sqrt{A_c}}{\sqrt{\pi}} \]  

(2)

Where S is the initial slope of the unloading curve or contact stiffness, P is the applied load and E_s is the reduced modulus. When using the Oliver and Pharr model, the projected contact area is determined using an area function which expresses the area as a function of the contact depth (h_c). The area function for an ideally shaped Berkovich tip is given in Equation 3.

\[ A = F(h_c) = 24.56h_c^2 \]  

(3)

The contact depth (h_c) is estimated based on Sneddon’s expression for the shape of the surface outside of the area of contact for an elastic indentation by a paraboloid of revolution [9].

\[ h_c = h_{max} - \varepsilon \frac{P_{max}}{dh} \]  

(4)

Where \( h_{max} \) and \( P_{max} \) are the maximum displacement and load, respectively, and \( \varepsilon \) is equal to 0.75 for a paraboloid of revolution. As the measured displacement in a nanoindentation experiment is a combination of the displacement of the indenter tip as well as the specimen, the specimen modulus (\( E_s \)) can be related to the reduced modulus (\( E_r \)) using Equation 5, provided the indenter modulus (\( E_i \)) is known and the Poisson’s ratios of the specimen and indenter (\( \nu_s \) and \( \nu_i \) respectively) are known or can be estimated.

\[ \frac{1}{E_r} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_i^2}{E_i} \]  

(5)

For the finite element simulations in this paper, it is assumed that the indenter behaves rigidly, Equation 5 can be reduced down to Equation 6 by assuming the value for \( E_i \) is infinite.

\[ \frac{1}{E_r} = \frac{1-\nu_s^2}{E_s} \]  

(6)

3 Materials Description

The material under investigation in this research is HTA/6376, a high strength carbon fibre reinforced plastic (CFRP) used in the aerospace industry. The average diameter of the HTA fibres is 6.6µm and the fibre volume-fraction for the composite is in the region of 60% [12]. The material properties of the composite constituents, as well as the properties of the bulk composite material, are given in Table 1.

4 Finite Element Analysis

The theory on which the nanoindentation is based assumes that the indentations are being carried out into a monolithic material far from any interface with another material. For this reason a number of issues can arise when using the method on fibrous composite materials. When indenting the matrix constituent, care must be taken to ensure that no stress transfer occurs over nearby fibre-matrix interfaces, which would constrain the indentations
and lead to an overestimation of the matrix elastic modulus and hardness [3, 5, 6, 7, 10].

The elastic-plastic nanoindentation process was modelled using 3D finite element models. The commercial finite-element software ABAQUS v6.10 [17] was used to create the models and carry out the analyses. A large strain solution was used and both materials were defined using the elastic properties shown in Table 1. The HTA fibre was assumed to exhibit anisotropic linear elastic behaviour while the 6376 resin’s elastic-plastic behaviour was modelled using the pressure-sensitive Mohr-Coulomb yield criterion. This yield criterion is capable of taking into account the hydrostatic pressure sensitivity of the 6376 resin and has been previously used to predict yielding in polymers associated with fibrous composite materials [1, 2, 16]. The Mohr-Coulomb criterion induces yield in the material when the combined normal (σ_n) and shear (τ) stresses reach a critical level according to Equation 7.

\[ \tau_c = \tau + \sigma_n \tan \phi \]  \hspace{1cm} (7)

where \( \tau_c \) is the cohesion stress (yield stress in pure shear) and \( \phi \) is the angle of internal friction. The yield criterion can be expressed in terms of the maximum and minimum principal stresses, as shown in Equation 8.

\[ (\sigma_1 - \sigma_3) + (\sigma_1 + \sigma_3) \sin \phi - 2 \tau_c \cos \phi = 0 \]  \hspace{1cm} (8)

Experimental data from tension and compression tests carried out on specimens of 6376 epoxy resin [11] allow the friction angle (\( \phi \)) and cohesion stress (\( \tau_c \)) to be determined as 26° and 82 MPa respectively.

4.1 Fibre Constraint

In order to characterise the mechanical constraint effect caused by the surrounding fibres when indenting the matrix constituent, 3D finite element modelling was used. The models make use of the six-fold symmetry of the Berkovich indenter by making it necessary to only model one sixth of the substrate and indenter geometry. Eight node brick elements (of type C3D8) were used in ABAQUS to model the specimen geometry, while the indenter has been represented by an analytical rigid plane with an angular offset of 24.7° from the surface, as shown in Figure 1. This perfectly represents the Berkovich indenter geometry when the six-fold symmetry is taken into account.

The HTA fibres are represented by discrete cylindrical regions shown in Figure 1. These sections were added to the bulk specimen in order to realistically represent cylindrical fibres surrounding the indentation zone. The diameter of the HTA fibres measured 6.6µm while the spacing between them measured 0.5µm. These values were chosen based on average results determined in a previous study which characterised the fibre distribution of the HTA/6376 composite microstructure [12]. Beyond this first layer of surrounding fibres, the material has been assigned the homogenised properties of the HTA/6376 composite through an embedded cell approach. The homogenised properties of the composite are given in Table 1. The ‘constraint factor’ has been defined as the distance from the initial point of indentation to the closest point on the edge of the fibre. This constraint factor is then varied and the indentation depth held constant at 1µm in order to determine the change in indentation response closer to the fibre regions.

The values of Young’s modulus obtained for each constraint factor were compared with the unconstrained value of Young’s modulus obtained from the unconstrained model (i.e. with no fibre or homogenised composite regions). This gave an indication as to how much the constraints were affecting the value of indentation modulus calculated using the nanoindentation simulation’s load-displacement data. The ratio of Young’s Modulus to unconstrained Young’s modulus is plotted against constraint factor in Figure 2. This figure shows a gradient in modulus was apparent as fibres closed in around the indentation area. The models indicate that values of indentation modulus calculated can be up to 47% greater than the unconstrained value due to the mechanical constraint of the surrounding fibres. Note that there was no contact between the indenter tip and the fibre constituents for all the values of constraint factor used.
5 Experimental Preparation

A panel measuring 80 x 50 x 1 mm was laid up following a [0], lay-up sequence from a unidirectional prepreg roll of HTA/6376 composite material (supplied by Hexcel). Bulk uncured 6376 matrix material was also acquired to allow comparison between the neat and in-situ properties of the material. The bulk uncured resin was co-cured with the composite lay-up in order to ensure that the bulk and in-situ resin materials were both processed until identical curing conditions. This was achieved by laying approximately 2mm of bulk resin on top on the composite panel as illustrated in Figure 3.

The specimens were cured in a vacuum-assisted autoclave process. The “hybrid” panels were heated at 2°C/min and consolidated for two hours at 175°C and 7 bar pressure. The panels were then cooled down to room temperature at 2°C/min. Small pieces of the hybrid panel measuring roughly 15 x 10 x 3 mm were cut from the panel and mounted in 31.75mm (1.25”) diameter clear epoxy cylinders with the fibre direction facing toward the top face of the cylinder, as shown in Figure 14. Mounting the samples in this way facilitated semi-automatic grinding and polishing down to a final polishing suspension particle size of 0.05 µm.

A micrograph showing the microstructure of the hybrid samples near the composite-epoxy interface is shown in Figure 5. Interestingly, there are now three distinct regions within the microstructure. The high volume-fraction region of the HTA/6376 composite is shown at the top of Figure 5, where there are very few large resin pockets. At the bottom of Figure 5 there is the bulk 6376 resin region which contains no fibres and finally, in the middle region, at the composite-bulk epoxy interface, there is a region of matrix containing fibres that have migrated into the resin regions during the curing process. In this region there are many resin pockets of varying size and also a number of fibres which are completely isolated from any other surrounding fibres.

6 Experimental Nanoindentation of Matrix Constituent

Nanoindentation tests were carried out on the hybrid specimens described in Section 5 using a G200 Nanoindenter supplied by Agilent Technologies. Indentations into the bulk 6376 resin of the hybrid specimens were carried out, as well as indentations into the pockets of resin surrounded by fibres in the composite section. The work was carried out using the hybrid specimens rather than separately cured bulk 6376 resin plaques, as these specimens ensured that the bulk and in-situ resins had been cured under identical pressure and temperature conditions. The distance between the bulk and in-situ resin regions during curing was in the order of microns ensuring that conditions were very similar for both sets of bulk and in-situ indentations. Curing the samples separately could lead to slight deviations of temperature and pressure during the curing cycle for both materials, which would make comparison of nanoindentation between the two samples more prone to error.

6.1 Experimental Investigation of Fibre Constraint

The mechanical constraining effect that the surrounding fibres have on a nanoindentation test carried out into the matrix constituent was characterised using the finite element models in Section 4.1. In order to characterise the phenomenon experimentally, a number of indents have been carried out into matrix pockets of the hybrid specimens. The continuous stiffness measurement (CSM) technique was used when carrying out the indents. This technique applies a small oscillation to the indenter tip which allows the contact stiffness to be measured continuously as a function of indentation depth. This then allows mechanical properties, such as hardness and elastic modulus, to be calculated continuously throughout the indentation loading cycle and not just at the point of unloading.
The bulk matrix material was characterised by carrying out 30 CSM indents into the bulk 6376 resin region of the hybrid specimens. The maximum depth of the indents was set at 2µm. The variation of modulus with indentation depth for the bulk matrix indents is shown in Figure 6. There was initial scatter in the results for depths shallower than 100nm due to the indentation size effect (ISE) which is a feature of nanoindentation testing that has been well documented previously [13-15]. At larger indentation depths the data remains relatively consistent. The elastic modulus of the material has been calculated by averaging data from the 30 tests, using the data between the depths of 100nm and 2µm. The mean value of modulus for the bulk 6376 matrix material was calculated as 5.05 GPa with a standard deviation of 0.1 GPa.

In order to compare the nanoindentation response of the in-situ resin with that of the bulk resin, CSM nanoindentation experiments were carried out into 50 resin pockets of the hybrid specimen. The hybrid specimens contain a much wider range of matrix pocket sizes than the high volume-fraction bulk HTA/6376 composite. This allowed a wide range of resin pocket sizes to be characterised than would be possible with just a HTA/6376 composite sample. Resin pockets with a circular array of surrounding fibres were preferred in order to make the experimental indentations as comparable to the finite element models as possible. The pocket radii were measured using images of the indent taken from the optical microscope of the G200 Nanoindenter. An example of a residual indentation in a matrix pocket is shown in Figure 7.

The CSM modulus data for 2 of the 50 indentations are compared with the CSM data for the bulk composite in Figure 6. For the lower depths the values for modulus remain relatively consistent. This is followed by a region of gradual increase in modulus values, with increasing indentation depth. This is due to the mechanical constraining effect of the surrounding fibres which was evident in the finite element models of Section 4. At a certain point the modulus then starts to increase rapidly due to the indenter coming in contact with one or more of the fibres that surround the indentation area. These observations are consistent for all the matrix pocket indentations with the phenomena occurring at different indentation depths depending on the radius of the matrix pocket.

In order to characterise the fibre constraint from indentations carried out into a variety of different matrix pocket sizes, the concept of a ‘constraint factor’ has been used. The constraint factor (CF) at any point in the indentation has been defined as the radius of the matrix pocket being indented (R_p) divided by the instantaneous indentation depth (h) in Equation 9.

\[
CF = \frac{R_p}{h}
\] (9)

The modulus data from the CSM curves were normalised by dividing by the unconstrained value of modulus (E_{unconstrained}). The unconstrained modulus values were the values extracted from the CSM data at the unconstrained depth (h_{unconstrained}). From the finite element investigation carried out in Section 4.1, it was determined that the indentations remain relatively unconstrained when the constraint factor is 20 or greater. This implies that the unconstrained indentation depth is equal to the pocket radius divided by 20.

\[
h_{unconstrained} = \frac{R_p}{20}
\] (10)

By analysing the data in this way, the fibre constraint effect on CSM data from indentations carried out in matrix pockets of varying size could be investigated. Figure 8 shows the normalised modulus values plotted against the constraint size for all 50 indents carried out into the matrix pockets. The data for the 50 indents converges nicely when the data is analysed in this way, with three regions of interest. (i) For large values of constraint factor there is some scatter in the data. This is caused by the indentation size effect (ISE) becoming an issue for indenters carried out into the smaller-sized matrix pockets. As we expect little or no fibre constraint at these high values of constraint factor, this scatter is
not an issue. (ii) A gradual increase in the normalised modulus values is observed for all the indents as the constraint factor decreases. This is caused by mechanical constraint of the surrounding fibres which becomes more prevalent as the constraint factor decreases. (iii) Following this gradual increase in normalised modulus, a rapid increase in normalised modulus is observed for a number of the indents for the lower values of constraint factor. This is where the indenter tip has actually contacted one or more of the neighbouring fibres while indenting to the maximum depth of 2µm. This is observed at the top of the residual impression shown in Figure 7. The impression made by a Berkovich indenter at the maximum indentation depth of 2µm will extend 6-9µm out from the initial point of contact, depending on the orientation of the tip. Therefore any indents carried out into pockets this radius size or smaller are likely to have contact between the diamond indenter tip and the fibres. The scatter observed for values of constraint factor where this steep increase in normalised modulus is observed is most likely due to the matrix pockets not being perfectly circular, the initial point of the indentations not being directly at the centre of the pockets and the orientation of the Berkovich indenter tip relative to the closest neighbouring fibre.

The values of normalised modulus and constraint factor from the finite element investigation in Section 4.1 have also been superimposed onto Figure 8. The effect of the mechanical fibre constraint on the indentation modulus is similar for both the finite element models and the experimental CSM data. This is made evident in the middle portion of the figure where the gradual rate of increase in normalised modulus for the models and the experiments are very similar. The CSM experiments show that the indentation modulus of the matrix constituent can be increased by 40-50% by the neighbouring stiff fibre regions, and that care should be taken to avoid this phenomenon when attempting to determine the true properties in these regions.

6.2 Investigation of bulk versus in-situ matrix properties

Since the mechanical constraint has been characterised both experimentally and numerically through the use of finite element analysis, this knowledge can now be used to confidently investigate any real change in mechanical properties of the composite’s matrix constituent following the curing process. The CSM technique can be used to determine the unconstrained modulus value for indents constrained by, or contacted by fibres while approaching the maximum indentation depth. The unconstrained modulus (\(E^{\text{unconstrained}}\)) was determined from the CSM data at the unconstrained depth (\(h^{\text{unconstrained}}\)) which was defined using Equation 10. The lowest value of unconstrained depth for all the 50 pockets was 193nm. Indentations at this depth or deeper can be considered to be free from the indentation size effect (ISE) which may have added scatter or bias to the data.

Once the unconstrained depth is known, the unconstrained, true value of modulus for the matrix in the pocket can be determined. A preliminary examination of the results indicates the values of indentation modulus for the large pockets are similar to that of the bulk matrix material. However, for the smaller pockets, an increase in modulus is apparent, with an increase of up to 19% measured from the experiments. The results appear to indicate that the curing process has an effect of the in-situ properties of the composite’s matrix constituent, causing a distinct increase in modulus.

Conclusions

The nanoindentation of a fibrous composite microstructure has been investigated experimentally and numerically using finite element analysis. The finite element models were used to characterise the effect of the mechanical constraint of the surrounding fibres on the nanoindentation. The continuous stiffness measurement (CSM) experimental nanoindentation technique also allowed this phenomenon to be characterised
experimentally. A similar trend of increase in modulus versus ‘constraint factor’ was shown for both the finite element models and the experiments. The value of indentation modulus from experiment could potentially increase by 40-50% due to this constraint effect. Characterising this effect allowed the true unconstrained values of modulus to be compared with that of the bulk matrix material. It was found that the change in elastic modulus was dependant on the matrix pocket size and increased by up 19% on the bulk matrix material value.

References


Tables

Table 1: Constituent and composite material elastic properties [1, 18]

<table>
<thead>
<tr>
<th></th>
<th>Fibre (HTA)</th>
<th>Matrix (6376)</th>
<th>Composite (HTA/6376)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{11}$ (GPa)</td>
<td>238</td>
<td>3.63</td>
<td>139</td>
</tr>
<tr>
<td>$E_{22}/E_{33}$ (GPa)</td>
<td>28</td>
<td>3.63</td>
<td>10</td>
</tr>
<tr>
<td>$\nu_{12}$</td>
<td>0.28</td>
<td>0.34</td>
<td>0.32</td>
</tr>
<tr>
<td>$\nu_{23}$</td>
<td>0.33</td>
<td>0.34</td>
<td>0.5</td>
</tr>
<tr>
<td>$\nu_{31}$</td>
<td>0.02</td>
<td>0.34</td>
<td>0.32</td>
</tr>
<tr>
<td>$G_{12}$ (GPa)</td>
<td>24</td>
<td>1.35</td>
<td>5.2</td>
</tr>
<tr>
<td>$G_{23}$ (GPa)</td>
<td>7.2</td>
<td>1.35</td>
<td>3.6</td>
</tr>
<tr>
<td>$G_{31}$ (GPa)</td>
<td>24</td>
<td>1.35</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Figures

Fig 1: Finite element model used to determine effect of mechanical fibre constraint

Fig 2: Normalised Modulus plotted against Constraint Factor for the finite element models

Fig 3: Composite (HTA/6376) and bulk resin (6376) lay-up sequence
Fig. 4 'Hybrid' sample where bulk 6376 epoxy and HTA/6376 composite have been cured together and mounted in epoxy puck.

Fig. 5: Resulting microstructure of the 'hybrid' sample at the composite-epoxy interface.

Fig. 6: Modulus versus Depth data for indentations into bulk 6376 resin and two resin pockets determined using the CSM Nanoindentation technique.

Fig. 7: Optical microscope image of a residual impression from an indentation carried out into a matrix pocket with a radius of 5.71µm.
Fig. 8: Normalised Modulus plotted against Constraint Factor for all 50 pocket indents. The same data from the finite element investigation has also been superimposed.