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APPLICATION OF NANO-INDENTATION, NANO- SCRATCH AND SINGLE FIBRE TESTS IN MICRO- INVESTIGATION OF INTERPHASES IN COMPOSITE MATERIALS

Running head: A. Hodzic et al, Nano-Hardness tests in polymer-glass interphases

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Abstract

Three novel experimental techniques were employed in this work in order to investigate the influence of the interphase region in polymer-glass composites on the bulk material properties: (i) the microdroplet test, the single fibre test designed to characterize the fibre-matrix bond (interface region) and to determine the interfacial shear stress in composite material; (ii) the nano-indentation test, a novel nano-hardness technique with ability to produce an indent as low as a few nanometers, thus employed in order to measure nano-hardness of the fibre-matrix interphase region; and (iii) the nano-scratch test, used in conjunction with the nano-indentation test for measurement of the interphase region width.

The microdroplet test (MDT) has been used to characterize the interfacial bond in fibrous composite materials. The specimen consists of a fibre with a drop of cured resin pulled out while the drop is being supported by a platinum disc with a hole. A properly tested specimen fails at the droplet's tip-fibre interface, revealing the ultimate interfacial shear strength. In this study, finite element analysis (FEA) of the MDT has been focused toward simulation of the fibre-matrix interphase region. The influence of a several functional variations of the material properties across the interphase layer on the stress distribution at the droplet's tip was analyzed. The results showed that the variation of the interphase properties significantly affects the stress distribution at the fibre-droplet interface, and therefore the stress redistribution in composite material. These results led to further experimental investigation of the interphase region, in order to obtain the material properties essential for the interfacial stress analysis.

The interphase region in dry and water aged polymer/glass composite materials was investigated by means of the nano-indentation and the nano-scratch techniques. The nano-indentation test involved indentation as small as 30 nm in depth, produced along 14 μm path between the fibre and the matrix. The distinct properties of the interphase region were revealed by 2-3 indents in dry materials and up to 15 indents in water aged, degraded materials. These results indicated interdiffusion in water aged interphase regions.

The nano-scratch test involves moving a sample while being in contact with a diamond tip. The nano-scratch test, used in conjunction with the nano-indentation test, accurately

measured the width of the interphase region. The results showed that the harder interphase region dissolved into the softer interphase region (both regions being harder/stronger than the matrix) expanding its width after aging in water.

Keywords: composites, interface, interphase, interfacial shear stress, micro-hardness.

I. Introduction

The interphase is defined as a region which is formed as a result of bonding and reactions between the fibre and the matrix. Designed to enhance the bond between fibres and matrix in polymer/glass composite materials, silane coupling agents react to varying degrees with different matrix polymers extending interphase regions deeper in the matrix. It is not yet clearly understood how the matrix properties are affected in the interphase region, where the silane physically and chemically interacts with the matrix polymer. This region is the factor of synergy in composite materials, as the stress redistribution from the matrix to the fibres takes place through their bond/interphase. Therefore, although the interphase region appears to have insignificant volume fraction, its influence to overall material properties is prevalent (Kim and Mai, 1998). In order to better understand the interfacial mechanisms in composite materials and the role of coupling agents, several experimental techniques have been designed and employed to test local regions in the composite materials:

(i) the single fibre tests have been developed to minimize the influence of complicated stress transfer mechanisms in composites and to observe a test specimen containing a single bond (Drzal and Herrera-Franco, 1991).

(ii) the Raman spectroscopy that has been approved as a successful technique, showing that the stress distribution at the interface was far from linear and dependent on a surface treatment of the fibres (Robinson et al, 1987, Young et al, 1995).

(iii) other techniques such as Fourier transform infrared spectroscopy and NMR spectroscopy have been focussed on the chemical aspects of the interphase region (Ishida and Koenig, 1979, Hoh et al, 1988)

(iv) various finite element analyses of fibre-matrix bond (Hodzic et al, 1999 a).

Although providing important and otherwise unavailable information on the local characteristics in the composite materials, these tests could not provide the information on the material properties of the interphase region. Recently, the nano-indentation and the nano-scratch tests, originally designed to investigate the material properties of thin films and surfaces, have been employed in this direction. In the work reported here, and previously (Sham et al, 1999) the nano-indentation tests were employed in order to investigate the material properties of the interphase region in polymer-glass systems. The nano-scratch test was used in conjunction with the nano-indentation test, in order to detect the total width of the interphase region.

In predicting the mechanical behavior, important parts of a composite material are regions with different material properties. Hence, the nano-indentation and the nano-scratch techniques are an important step toward a better understanding of the multiphase materials.

II. FEA

Finite element analysis of the microdroplet test was carried out using STRAND6 software and the model was treated as a linear axisymmetric problem. The model comprised approximately 8-10 000 plate elements and the interphase region was modelled as seven layers of functional change in material properties such as elastic modulus and Poisson's ratio. The mesh is shown in Fig. 1. Fig. 2 shows an enlarged image of the epoxy droplet

and glass fibre, where the central part of the droplet is in a shape of a ball and two sides in a shape of a conus each with a small radius ending on the fibre. 2D section of a ball with a conus at each end has been the basic model for the droplet in the FEA. Also, the bonding radius (the radius between the droplet's conus and the fibre) has been included in the FEA model in order to make it close to the shape of the real specimen. In this work, the accent was placed on interphase modelling. More details on geometric analysis is available elsewhere (Hodzic et al, 1999 a).

Interphase is a chemically affected region around the fibre in the fibre-matrix bond, due to the presence of the silane coupling agent. The interphase was modelled as seven adjacent layers with functional changes in material properties, starting from the fibre in radial direction. Eight different functions were varied through the interphase properties as shown in Table 1. The layers were modelled as plates having dimensions of 1 μm each in radial direction, forming the layers along the full length of the specimen in the axial direction, as shown in Fig. 1.

The interphase properties were varied whilst the geometric conditions and the applied load of 160 mN were kept constant. The eight functions that were used for the simulation of different properties of the interphase region could be separated in two groups as shown in Table 1: the strong and the weak interphase region. The strong interphase region included stronger material properties than the epoxy resin and vice versa.

The analysis of the stress distribution along the interface region showed significantly different behavior between the weak and the strong interphase group, as shown in Fig. 3. At the droplet's tip, the stresses of the weak interphase group had approximately the same value while the stresses of the strong interphase group significantly differed. As the material properties of the interphase were stronger, the stress at the droplet's tip had a higher value.

These results indicated that the quality of the interphase region has a strong influence on the stress distribution in the microdroplet test, designed to establish the interfacial shear stress at the fibre-matrix bond. Therefore, this result reflects the quality of overall properties of composite materials, the stress redistribution between the fibres and the matrix. The material properties of the interphase region need to be established in order to obtain the accurate stress value at the droplet's tip region. Qualitatively different interphase properties resulted in various stress distributions for the given applied load. The stresses at the droplet's tip of the weak interphase regions exhibited consistent results, while the functional decay in material properties of the strong interphase group had a major role in the stress values of that region. This phenomenon indicated that the change in material properties of the interphase should be established prior to testing of the microdroplet specimen. The novel nano-hardness techniques, rarely employed in composite materials, were used as the next step in the characterization of the glass fibre – polymer matrix interphase region.

III. Experimental

A. Preparation of test materials

Three composite panels were made using:

- (1) Phenolic resin Resinox CL1916 mixed with 7 wt% AH1964F hardener,
- (2) Phenolic resin Resinox CL1880 mixed with 7 wt% H1196 hardener; and

(3) Polyester resin Synolite 0288-T-1 mixed with 2.4 wt% methyl ethyl ketone peroxide as a catalyst.

The fibres were unidirectional 900 g/m² E-type glass, 20 µm in diameter. The panels were made and supplied by the Aeronautical and Maritime Research Laboratory (AMRL) in Melbourne. Several cubes were cut from each composite material using a diamond saw. Dimensions of the cubes were 10x5x5 mm. The surface of each cube in direction perpendicular to unidirectional glass fibres, consisted of perfectly cross-sectioned glass circles embedded in resin. The polishing process involved wet 600 and 800 Emery paper followed by 0.3 mm and finally 0.05 mm wet polishing alumina pastes.

The cubes were immersed in water during the periods of three, six and ten weeks at the room temperature. In this way, polishing was not required after the water aging. Therefore the polished and aged surface was investigated in situ. The tested areas, as observed by the optical microscope attached to the nanoindenter, were carefully chosen to be parts of surfaces without fibre - matrix debonding or other surface damages.

B. Nano-Indentation test

The nano-indentation test was originally designed for investigation of materials properties of thin films and surfaces (Oliver et al, 1986). This experimental technique is advantageous due to its capability to produce an indent as low as a few nanometers. The apparatus used in this work was Nano Indenter II, made by Nano Instruments, Inc. A detailed description of the instrument is available elsewhere (Bharat, 1995). Depths of indents were programmed to have a constant value of 30 nm, the lowest value carried out in polymer-glass composites. Displacements of indentation depths were consistent with +10 nm tolerance in glass. Part of the line of indents in glass fibre is shown in Fig. 4. From the shape of the Berkovich indenter, the resulting indents were 210 nm wide. Each successive indent was displaced by 260 nm in order to avoid overlapping of plastic deformation zone onto neighboring indents. The indents were made along a path of 7 mm in the matrix and 7 mm in the fibre, a total length of approximately 14 mm.

The image of the surface after the nano-indentation experiment was produced by Atomic Force Microscope operated in contact mode (Multi Mode Scanning Probe Microscope with Nano Scope E controller, by Digital Instrument).

Hardness of material calculated from an indent produced by Berkovich tip is calculated from the equation below:

$$H = P/(24.5 h_c^2) \quad (1)$$

where: P is the load and h_c is the contact depth of the indent (Anonymous, 1995). Hardness is chosen as the representative material property due to its simple definition, illustrating the raw trend of the experimental results. However, it is important to mention that the trend of the modulus of elasticity data for each system is very similar to that of the hardness data.

C. Nano-scratch test

The nano-scratch test was used in order to investigate the width of the fibre-matrix interphase region. This novel technique involves moving a sample while being in contact with diamond tip. The coefficient of friction is determined from the fraction of the lateral and the normal force. Therefore, the coefficient of friction indicates the resistance of the material to the tip penetration in the tangential direction. In this work, the normal force was kept constant during the experiment. The tip was moving from the matrix to the fibre gradually decreasing its penetration (profile) depth after contacting the harder interphase region. A detailed information about the test is available elsewhere (Hodzic et al, 1999 b). The scratch length was about 60 μm starting from the matrix and crossing two fibres in this range that were found on the surface of each sample. Two matrix/fibre interphase regions were investigated in one run. (The part of the scratch path from the fibre to the matrix could not be analyzed due to the loss of balance in the system when the tip suddenly drops to softer material). The experiments were carried out with two values of the normal force, 0.4 mN and 1 mN, in order to investigate the influence of the penetration depth to the final measurement of the interphase width.

IV. Experimental Results

A. Indentation Results

A typical load-displacement curves for indents in matrix, interphase and glass, in dry and ten weeks aged condition, are shown schematically in Fig. 5. The indents of each condition were chosen to have the same displacement, in order to enable a better visual comparison. More details about the test results analysis are given elsewhere (Hodzic et al, 1999 c).

The modulus of the indented material is obtained from the following equation:

$$E_r = [(1-\nu_i^2)/E_i + (1-\nu_s^2)/E_s]^{-1} \quad (2)$$

where E_i , ν_i are the elastic modulus and Poisson's ratio of the indenter tip (diamond) and E_s , ν_s are the equivalent properties of the indented material.

The modulus of elasticity for each indent is calculated with Poisson's ratio of the material obtained from the technical literature. The Poisson's ratios for each matrix and glass material were 0.38 and 0.22 respectively. Hardness values, calculated using equation (1) for the polyester/glass system, are shown in Fig. 6. The results for the other two systems are not presented due to their similarity. The transition region observed between the matrix and the fibre has a similar character for the polyester and the phenolic systems in dry conditions. This region shows material properties distinct from those of the matrix and the fibre. In the results for dry materials there is a gradual change of properties from the matrix to the fibre. During water aging, the properties of the interphase regions in the three composite systems involve different patterns of degradation. The widths of the interphase

regions during water degradation, calculated from the nano-indentation test results, are presented in Fig. 7.

B. Nano-scratch results

A typical scratch recordings, including the profile depth and the coefficient of friction for dry and ten weeks aged polyester/glass surfaces, are shown in Fig. 8.

The actual lengths of the characteristic parts of the scratch path are schematically presented in Fig. 9. More details on the scratch morphology and interphase measurement can be found elsewhere (Hodzic et al, 1999 b). The test results, i.e. the profile depth and the coefficient of friction, include both the motion of the tip and the scratch path. In order to get the scratch path only, the lines parallel to the edge of the tip are drawn at the characteristic points of the scratch graph. These lines represent different positions of the edge of the tip, placed at the points where different material properties were detected along the scratch.

Relative positions between these lines represent genuine lengths of the scratch stages in the scratch direction, excluding the vertical displacement. The interphase region visually comprises the "soft" (closer to the matrix) and the "hard" (closer to the fibre) regions, parts of the same exponential function. The widths of the interphase regions, derived from the nano scratch test for the dry and aged conditions, are shown in Fig. 10 (a, b, c).

V. Discussion

A. Experimental results

The microdroplet test FEA results revealed the influence of the material properties along the interphase region on the fibre-matrix stress redistribution. For the weak fibre-matrix bond, defined as the interphase modulus lesser or equal than that of the matrix, the functional variation of E and ν in radial direction insignificantly affected the stress distribution at the droplet's tip/interface. However, in the case of the interphase properties stronger than that of the matrix, the functional variations of E and ν resulted in different stress values at the droplet's tip, where the crack propagation is being initiated in a properly tested specimen. In light of this result, further experimental nano-hardness investigation of the material properties at the fibre-matrix bond was carried out.

In some previous work that involved the nano-indentation results (Williams et al, 1990), some doubts on the material properties of the interphase were raised over the hardness results in the vicinity of the harder glass region. If the results of the interphase region were merely there because of the fibre's influence, the hardness results would have been the same for any material and any condition. However, the hardness results vary for different materials and different conditions, with the interphase region expanding several times during water aging, far beyond the region of the fibre's influence. From the results of the work presented here, it can be concluded that the hardness results obtained from the nano-indentation test are a genuine information on the character of the interphase region.

The interphase regions in the three systems presented in this work have stronger material properties than that of the matrix, as shown in Fig. 5 (a, b, c). The nano-scratch test, employed in conjunction with the nano-indentation test, was found to be more effective in measurement of the interphase width. The nano-indentation test was able to detect significant changes in materials properties, whereas the nano-scratch test also revealed the parts of the interphase region that were slightly different from the matrix. The profile depth and coefficient of friction had similar patterns in dry condition and water aged materials, with the widths of interphase regions expanding during water aging. The "harder" part of the interphase region basically disappeared in phenolic/glass systems after 10 weeks of aging, while the "softer" part was expanded far beyond its previous size. The results indicate the increasing process of interdiffusion (Plueddemann, 1988) during water aging, more discussed elsewhere (Hodzic et al, 1999 d).

The interphase region was strongly affected by water degradation in each system. All the materials were made using the same glass fibres and the silane coupling agent. Therefore, differences in the interphase region degradation are due to different chemical bonds between the three matrix materials and the silane agent applied on the fibres.

The three polymer/glass systems used in this work exhibited different characteristics during aging in water.

B. Materials

The polyester - silane chemical bond was strong and remained during the environmental aging while the size of the interphase region was increased. This indicates that water hydrolyzed the interphase region degrading its properties, and increased the size of the interphase by moving molecules of silane deeper in the matrix. The chemical bond, however, remained undamaged.

The Phenolic CL1880 - glass system had suffered debonding prior to water aging as observed by SEM. The gaps between the fibres and the matrix increased during aging with the interphase region drastically expanding. This indicates very weak chemical bond and high level of hydrolysis of the interphase during immersion in water.

The Phenolic CL1916 - glass system had also suffered debonding prior to water aging but not in such great percentage as CL1880. During aging in water the fibre - matrix gaps were widened but the interphase region remained about the same size. The chemical bond was weak and even more damaged during aging in water while the interphase was not affected by hydrolysis as the previous two systems.

VI. Conclusion

1. The material properties of the interphase region in polymer-glass composite materials play an important role in the fibre-matrix stress redistribution. It was shown in this work, by means of FEA, that the crack initiation along the fibre-matrix interface region

was strongly affected from the functional variation of material properties if $E_{\text{interphase}} > E_{\text{matrix}}$.

2. The nano-indentation test results clearly showed that $E_{\text{interphase}} > E_{\text{matrix}}$ in three polymer-glass systems, for dry and water aged conditions. The results showed far-expanding interphase region after water aging, proving to be a genuine phenomenon, not a mere influence of the fibre's presence on the test results.
3. The nano-scratch test, used in conjunction with the nano-indentation test, accurately measured the width of the interphase region. The results showed that the harder interphase region dissolved into the softer interphase region (both regions being harder/stronger than the matrix) expanding its width after aging in water.
4. From the above conclusions, it is clear that the material properties of the interphase region are to be investigated for every composite system prior to establishing the stress analysis.

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

X 0.500 $\mu\text{m}/\text{div}$
Z 40.103 nm/div

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10 (a)

☐ CL1880/glass	6	5.2
☒ CL1880/glass 3w aged	10.2	5.4
☒ CL1880/glass 10w aged	7.2	5.5

Fig. 10(6)

Fig. 10 (c)

Legend	Function	Description	Group
int = mat	$E, v = \text{const}$	Interphase props. = matrix props.	weak
lindec	$E, v = A - B(x)$	Linear decay of props. of interphase	strong
step	$E, v = \text{const}$	Interphase props. = const. middle value > matrix	strong
pit	$E, v = \text{const}$	Interphase props. = const. < matrix props.	weak
expup	$E, v = A + Be^x$	Exponential increase in props. of interphase	weak
hill	$E, v = A + Be^{1/x}$	Exponential increase in props. of interphase	weak
fall	$E, v = A - Be^x$	Exponential decay in props. of interphase	strong

Table 1