polymer

Nano-indentation and nano-scratch of polymer/glass interfaces. II: model of interphases in water aged composite materials

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Abstract

The interphase region in dry and water aged polymer/glass fibre composite materials was investigated by means of the nano-indentation and the nano-scratch techniques. The indentations as small as 30 nm in depth were produced along 14 μm path starting from the matrix and ending on the fibre. This was done in order to detect water degradation of material properties in the transition region between the fibre and the matrix. The distinct properties of the interphase region were revealed by a sequence of two to three indents in dry materials and up to 15 indents in water aged, degraded materials. These results indicated interdiffusion of water into the interphase regions. The nano-scratch test results showed that the interphase region width increased and the material properties degraded during water aging. Doubts about the presence of the interphase, raised over the hardness results in the vicinity of the harder glass region, were refuted with the results showing the expansion of the interphase region during water aging. These two experimental techniques showed to be a useful tool in the investigation of the size and the character of the interphase region in the fibre/polymer matrix composite materials. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The interphase in composite materials is defined as a region which is formed as a result of bonding and reactions between the fibre and the matrix. In all complex materials, the degree of contact and the cohesive forces at the interface are of considerable importance. As an example of this, stress is transmitted from one phase to another across the interface, and the extent to which this take place depends on these factors. With two phases A and B, phase A may be in direct contact with phase B, or there may be an intervening phase between them. The intervening phase may be deliberately added to improve adhesion, or it may be the result of a chemical reaction between A and B [1]. Silane coupling agents, utilized so as to improve the fibre–matrix bond in polymer/glass fibre composites, chemically react with matrix polymers, creating interphase regions of significant thickness [2]. Material properties of the interphase region have not been fully determined yet, and the influence on the bulk composite properties is not well understood. Therefore, it is also not well understood how the interphase region, and the composite material, can be affected by environmental aging.

Basically, there have been two approaches to the science of interphase: (i) one that involved techniques of FTIR and NMR spectroscopy in the investigation of the presence of silane on chemical level [3–5]; and (ii) standard bulk testing of composite materials involving different coupling agents [6]. The gap between these distant areas of research has decreased with single fibre studies [7] giving information on the fibre–matrix bond in conjunction with finite element analysis (FEA) [8], and Raman spectroscopy [9,10]. However, the above techniques still cannot provide the information on the material properties of the interphase, that have the critical influence on the stress distribution at the fibre/matrix interface [11]. Without knowing the interphase properties, the stress analysis is incomplete, and in the best case approximate. The interphase properties have been successfully detected in some recent works with nano-hardness tests [12–15], originally designed for hardness/property measurement of thin films and surfaces. Pioneering these techniques into the polymer/glass composite interphases, Sham et al. [16] have detected the interphase region properties of vinylester/glass system with different silane

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agents and their applied concentrations. A similar method is used in this work with a modified mechanical analysis, involving several polymer/glass composite systems under different environmental conditions.

In the first part of this work [17] we presented the nano-indentation and the nano-scratch measurements of the interphase regions in polymer/glass composite systems. The results of both techniques have shown the presence of an interphase region. The nano-indentation hardness test detected the variation of material properties in the interphase region, while the nano-scratch test defined the size of the interphase region by the change in the coefficient of friction. In the second part reported here, we use the same experimental techniques in order to investigate degradation of the interphase region after aging in water. The nano-indentation and the nano-scratch tests successfully indicate subtle degradation of material properties along the interphase region in phenolic/glass and polyester/glass systems.

2. Experimental

2.1. Preparation of test materials

Three composite panels were made using:

1. phenolic resin Resinox CL1916 mixed with 7 wt% AH1964F hardener;
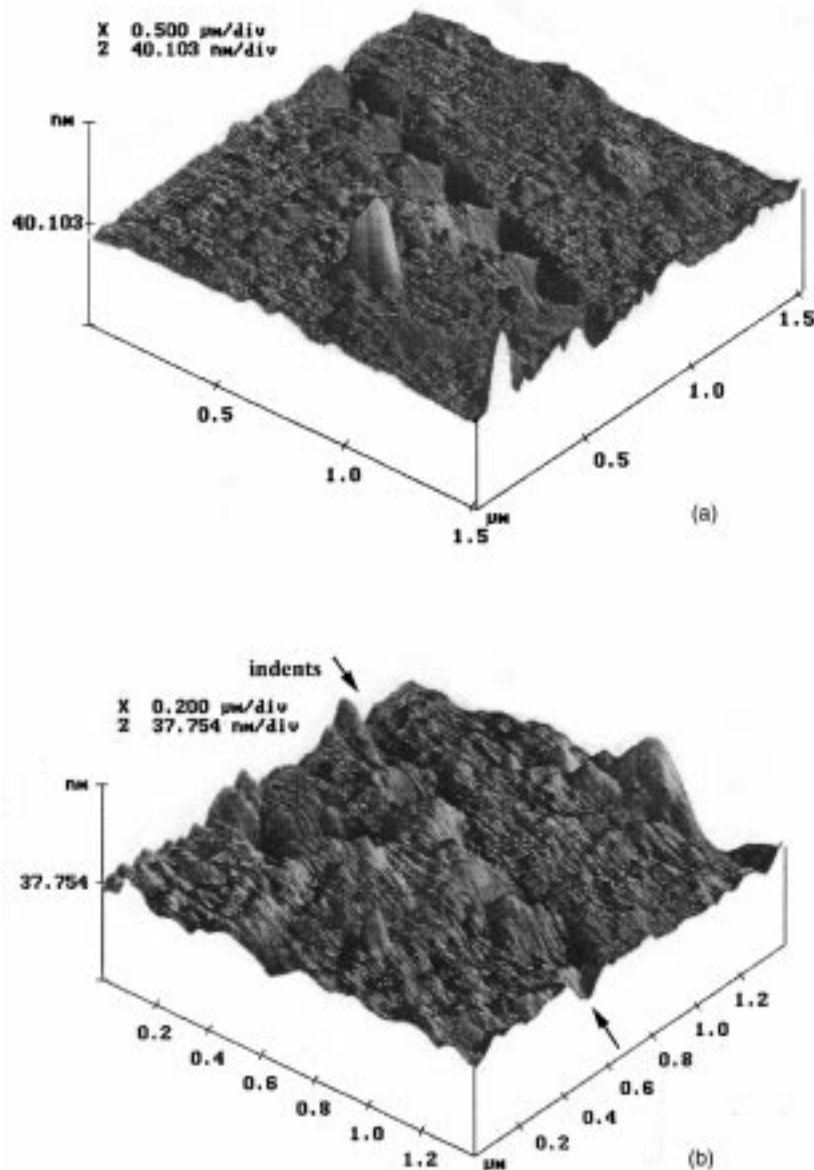2. phenolic resin Resinox CL1880 mixed with 7 wt% H1196 hardener;

Fig. 1. AFM image of (a) glass fibre surface, and (b) polyester matrix with a line of indents. Vertical scale is 40 nm per division.
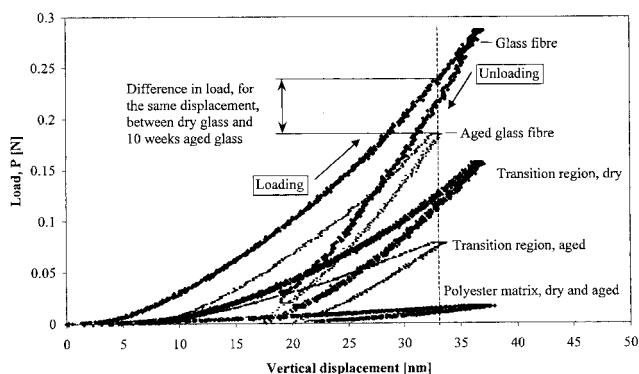
Fig. 2. A typical recording of load versus displacement during indentation test, for dry and 10 weeks aged polyester/glass system. The glass fibre and the transition region are very affected by water degradation.

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,[1] 20 μm in diameter. Several cubes were cut from each composite material using a diamond saw. The silane coupling agent used in this work is not specified, as the materials were made and supplied by DSTO (Defence Science and Technology Organisation, AMRL division). Dimensions of the cubes were $10 \times 5 \times 5$ mm³. The surface of each cube in the direction perpendicular to glass fibres consisted of perfectly cross-sectioned glass circles embedded in the resin. The polishing process involved wet 600 and 800 Emery paper followed by 0.3 μm and finally 0.05 μm wet polishing alumina pastes.

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

2.2. Nano-indentation test

The apparatus used in this work was Nano Indenter II, made by Nano Instruments, Inc. A detailed description of the instrument is available elsewhere [18,19]. Depths of indents were programmed to have a constant value of 30 nm. Displacements of indentation depths were consistent with +10 nm tolerance in glass. 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 neighbouring indents. The time employed for the loading–unloading cycle was 200 s and the holding time was 10 s. The indents were made along a path of 7 μm in the matrix

and 7 μm in the fibre, a total length of approximately 14 μm. Parts of the line of indents in glass and polyester matrix in dry condition are shown in Fig. 1(a) and (b). 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).

2.3. Nano-scratch test

The nano-scratch test involves moving a sample while being in contact with the diamond tip. A detailed information about the test is explained in the first part of this work [17]. 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. Hence, 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.)

3. Experimental results

3.1. Indentation results

A typical load-displacements curves for indents in the matrix, interphase and glass, in the dry and 10 weeks aged conditions, are shown in Fig. 2. The indents 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 [17]. The modulus of the indented material is obtained from the following equation:

$$E_r = \left(\frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_s^2}{E_s} \right)^{-1} \qquad (1)$$

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 [20]. Hardness of material calculated from an indent produced by Berkovich tip is calculated from the equation below

$$H = \frac{P}{24.5 h_c^2} \qquad (2)$$

where P is the load and h_c is the contact depth of the indent [19]. Hardness values, calculated using Eq. (2) for all the three conditions of polyester/glass, CL1880/glass and CL1916/glass systems, are shown in Fig. 3(a)–(c). No corrections were made for the indenter tip defect [21]. 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

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[1] The size of glass fibres reported in our previous publication [17], was incorrectly given as 450 g/m². It should be 900 g/m².
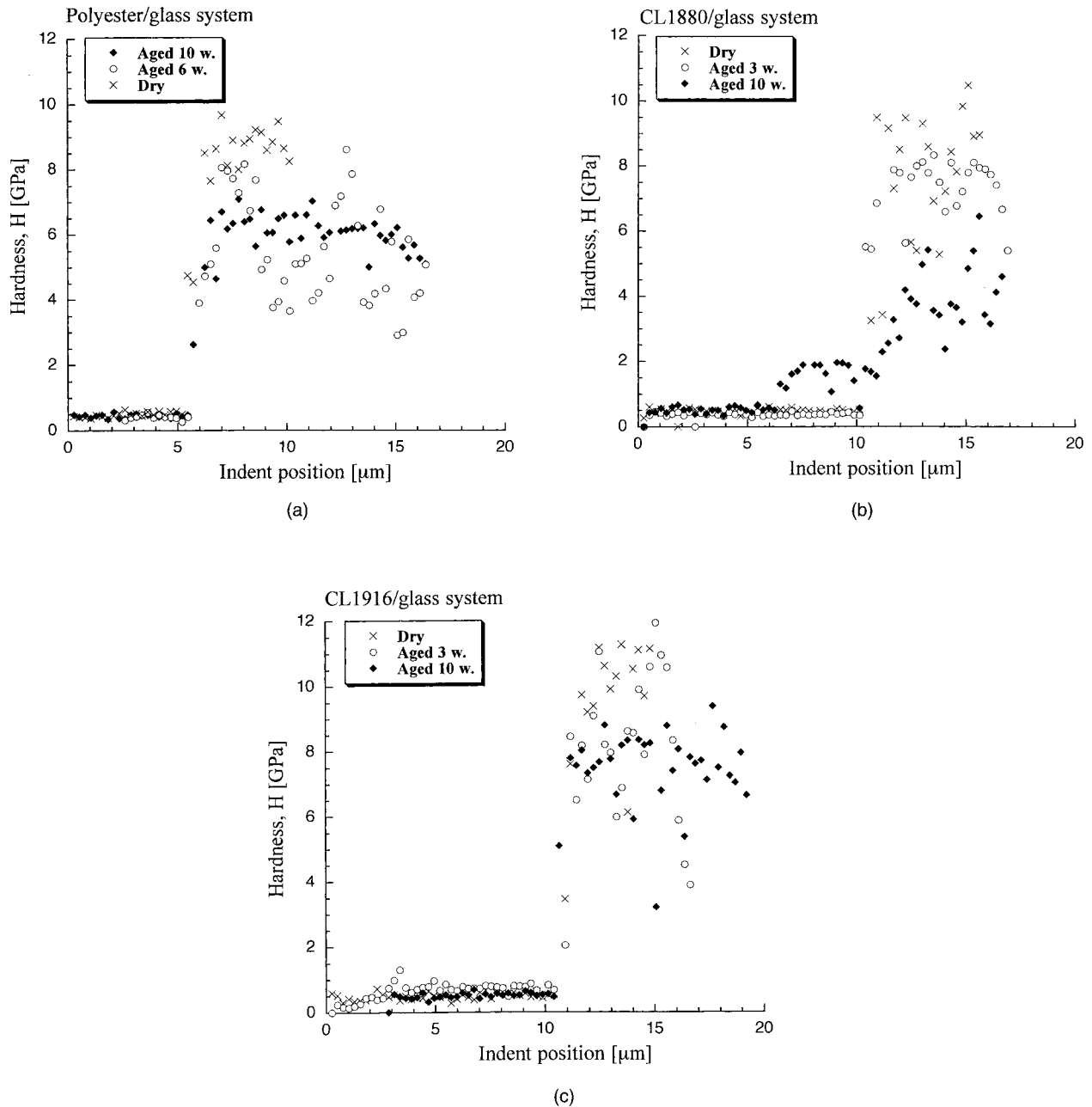
Fig. 3. Hardness calculated according to Eq. (2) for (a) polyester/glass, (b) phenolic CL1880/glass, and (c) phenolic CL1916/glass systems in dry and aged conditions. Note the transition zone from the matrix (on the left) to the glass fibre (on the right).

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 after water degradation, calculated from the nano-indentation test results, are presented in Fig. 4.

3.2. Nano-scratch results

A typical scratch recordings, including the profile depth and the coefficient of friction for dry and 10 weeks aged surfaces, are shown in Fig. 5(a). The profile depth is the penetrating depth of the tip, influenced by the hardness of the scratched material. The coefficient of friction is determined from the ratio of the lateral to the normal force. Therefore, the coefficient of friction indicates the resistance of the material to the tip penetration in the tangential direction. More details on the scratch morphology and interphase measurement can be found elsewhere [17,22]. The corresponding diagram for the Phenolic CL1880/glass system is shown in Fig. 5(b). The test results, i.e. the profile depth and
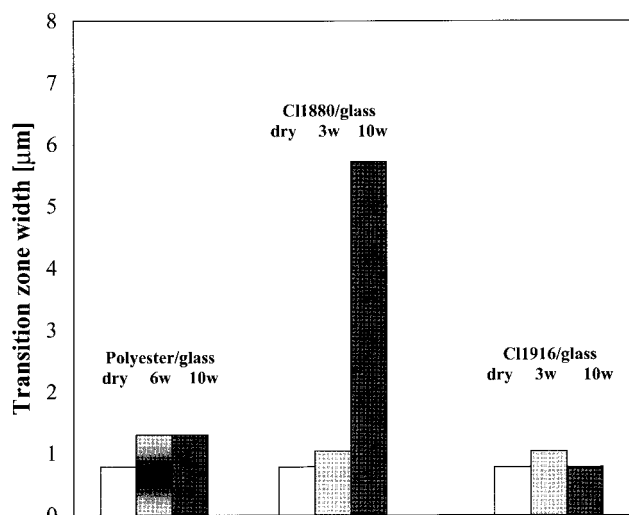
Fig. 4. The widths of the fibre/matrix transition zone for (a) polyester/glass, (b) phenolic CL1880/glass, and (c) phenolic CL1916/glass systems in dry and aged conditions. The transition zone widths are calculated from the hardness results as distances between the indents in that zone.

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 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 from the nano-scratch test for the dry and aged conditions, are plotted in Fig. 6(a)–(c).

4. Discussion

4.1. Nano-indentation results

In previous work that involved the nano-indentation results [14], some doubts about the material properties of the interphase were raised over the hardness results in the vicinity of the hardener 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 after 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 trends obtained from the nano-indentation test are a genuine character of the interphase region. The interphase regions in the three systems

presented in this work are harder than the matrix, as shown in Fig. 3(a)–(c).

4.2. Nano-scratch results

The profile depth and coefficient of friction have similar patterns in dry condition and water aged materials, for two systems (CL1880/glass and polyester/glass) widths of interphase regions expanding during water aging, as shown in Fig. 5(a) and (b). The results indicate the increasing process of interdiffusion [23] during water aging, that will be discussed later.

4.3. Interphase region

The interphase region was strongly affected by water degradation in each system. Here we discuss each system separately. All materials were made using the same glass fibres with the same 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.

4.3.1. Polyester/glass system

Being a very stable system, the Polyester Synolite 0288-T-1/glass composite (Fig. 7(a)) preserved smooth surface morphology during aging in water. The size of interphase region steadily increased during aging, as seen from Figs. 4(a) and 6(a). The interphase region reached its saturation after three weeks and remained at about the same size after 10 weeks of aging. Trends of the nano-indentation and the nano-scratch tests are very consistent.

4.3.2. Phenolic CL1880/glass system

Phenolic CL1880/glass system exhibited catastrophic changes during aging in water, involving multiple debonding between the matrix and the fibres, as shown in Fig. 7(b). The interphase region of this system was investigated on areas where the fibres were still bonded to the matrix. The results presented in Figs. 4(b) and 6(b) show a completely changed character and width of this interphase region, with the material properties stronger than that of the matrix. As the size of the interphase region expanded several times after 10 weeks water aging, we can conclude that the results indicate a genuine character of this interphase region. The 'harder' part of the interphase region basically disappeared in phenolic/glass systems after 10 weeks of aging, while the 'softer' part expanded far beyond its previous size. The nano-indentation and the nano-scratch results for the two normal forces are very consistent for this system, for both dry and water aged conditions.

4.3.3. Phenolic CL1916/glass system

Phenolic CL1916/glass system also suffered debonding during water degradation (Fig. 7(c)), although not as severe as CL1880/glass. The nano-indentation results (Fig. 4(c)) and the nano-scratch results for the normal load of 0.4 mN
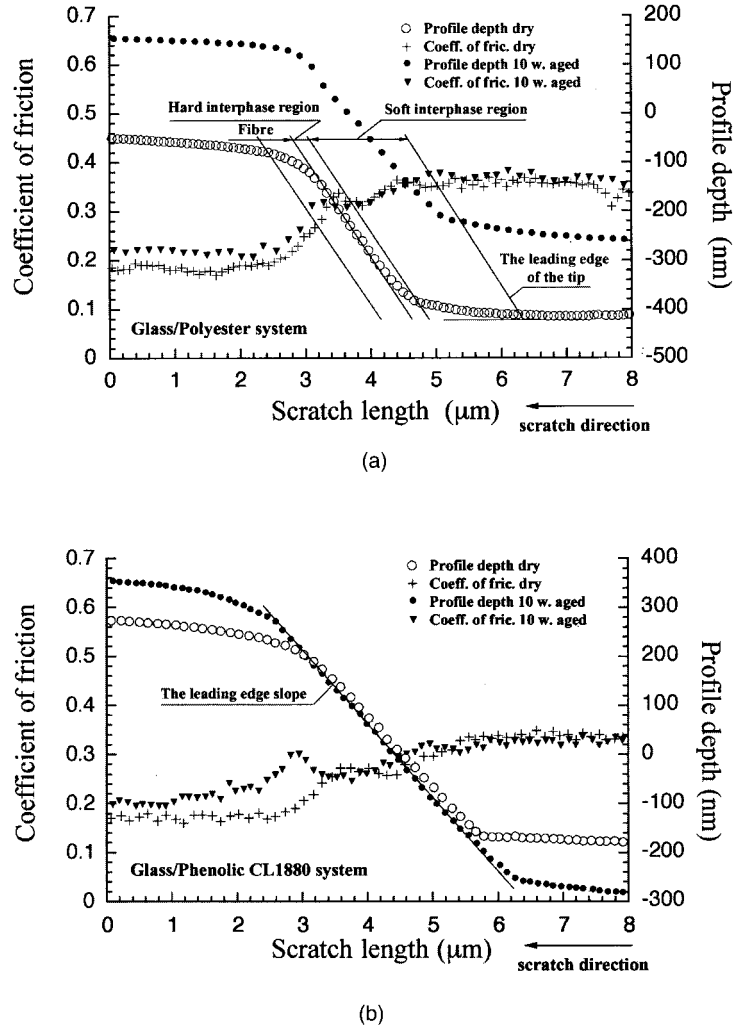
Fig. 5. (a) A typical scratch recording for polyester/glass, including the profile depth and the coefficient of friction. The results are presented for polyester/glass system in dry and 10 weeks aged conditions. The vertical distance in profile depth between the fibre and the matrix has increased with aging, the coefficient of friction of the interphase is lower and the interphase region is larger after aging. The parts of the interphase region are measured as distances between the leading edge positions (slopes). (b) The corresponding results for Phenolic CL1880/glass system in dry and 10 week water aged conditions.

indicate that the interphase region for this system remained the same size during water degradation. The nano-scratch test results for the normal load of 1 mN show that there is a significant change in the size of the interphase region, the result which can be explained by SEM observation of this material (Fig. 7(c)). Phenolic CL1916 resin contains 'bumps' of different structure and material properties than that of the resin. If the indenter tip in the scratch mode comes across these unstable regions, the profile depth will behave as with a harder interphase region. It is quite possible that one of these bumps happened to be close to the fibre investigated in the mode with the normal force of 1 mN, thus increasing 'interphase' zone in the test results. This is a reasonable assumption, since several of the nano-indentation and the most of the nano-scratch results confirmed the unchanged size of the interphase region for this system.

4.4. Interdiffusion

The glass fibre–silane–polymer matrix link is formed by (i) chemical bonding, and (ii) the interpenetrating network (IPN) as schematically shown in Fig. 8(a), by Plueddemann [23]. In the chemical bonding theory, the bifunctional silane molecules act as a link between the resin and the glass by forming a chemical bond with the surface of the glass through a siloxane bridge, while its organofunctional group bonds to the polymer resin [24]. In addition, the resin penetrates into the chemically reacted silane layer and intermixing of silane and matrix molecules takes place, according to the IPN theory. As previously discussed, the interphase region of the systems used here was found to consist of two parts, the hard (closer to the fibre) and the soft (closer to the matrix) interphase region, both of them having
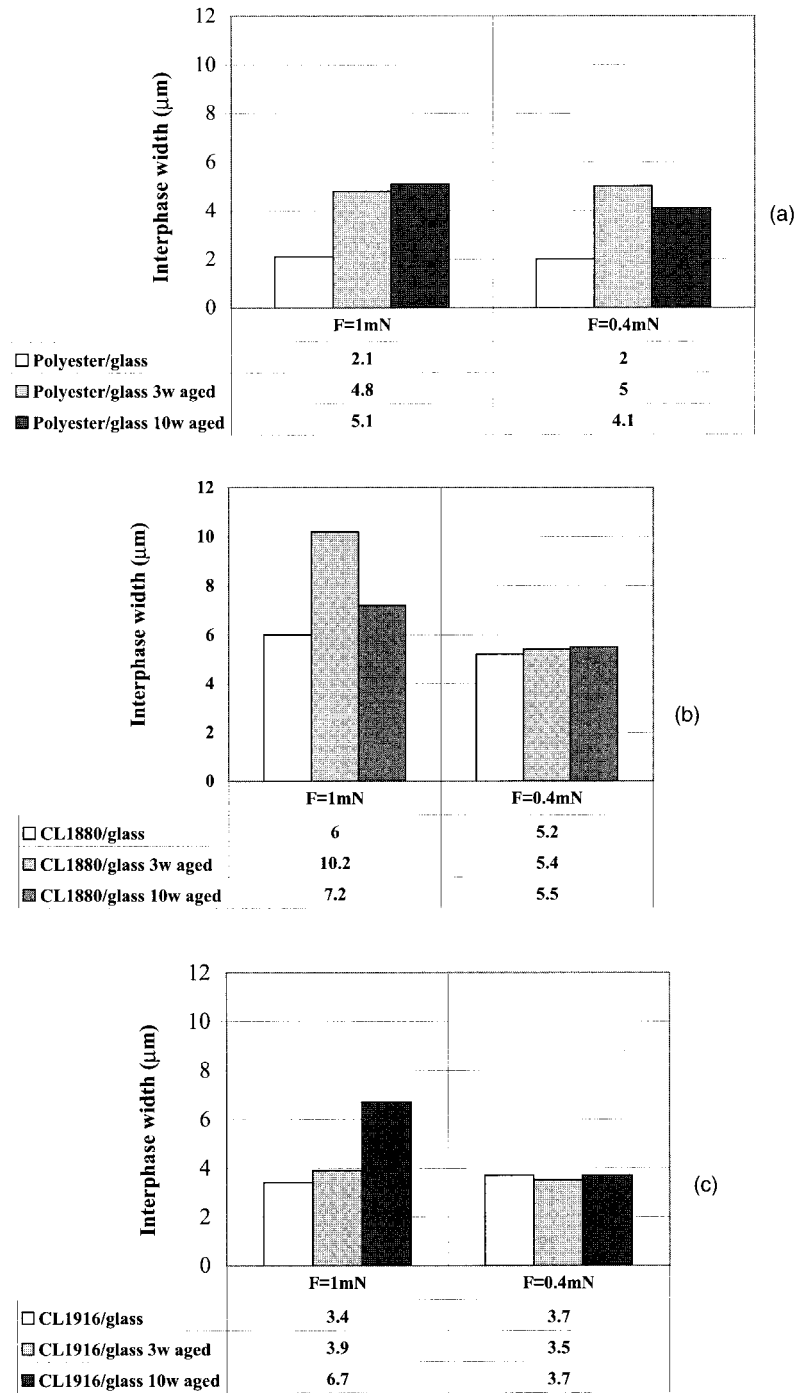
Fig. 6. The actual lengths of he characteristic parts of the scratch path, measured between the characteristic positions of the leading edge of the indenter for (a) polyester/glass, (b) phenolic CL1880/glass, and (c) phenolic CL1916/glass systems.

stronger material properties than that of the polymer matrix. After aging in water, the hard interphase region dissolved into softer thus increasing the size of the interphase zone (Fig. 8(b)). This phenomenon needs to be discussed on a molecular level.

The well established theory of the fibre/silane/matrix interface, proposed by Schrader [25], explains three differ-

ent structural regions in the deposited layer of the silane coupling agent: (i) physisorbed region, the outermost layer that consists mainly of the bulk of the deposited silane (Fraction One); (ii) chemisorbed region, the next layer that possesses better resistance to hydrolysis than physisorbed region (Fraction Two); and (iii) chemically reacted region, the innermost region next to the glass surface,
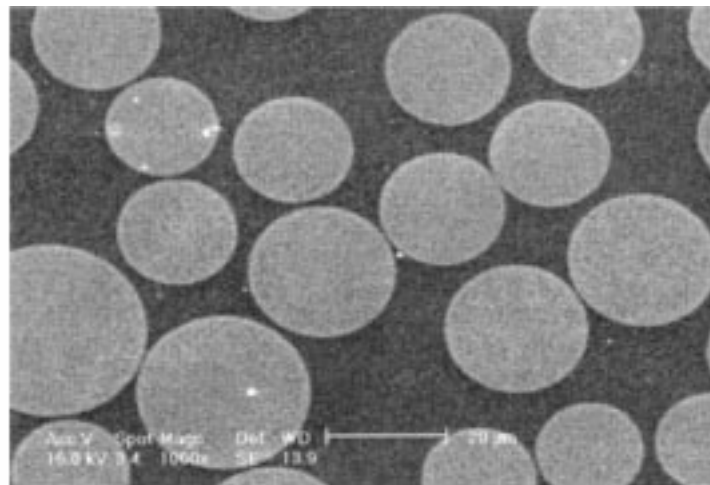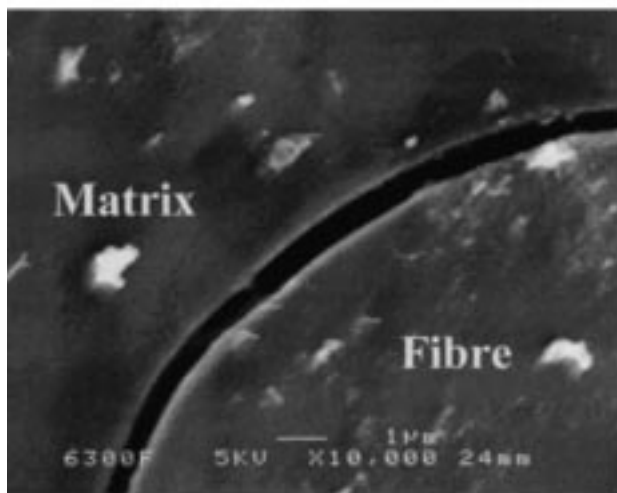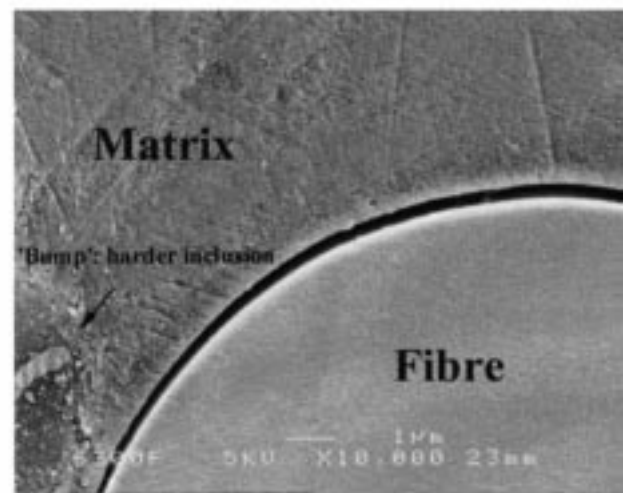
Fig. 7. SEM images showing surface morphology after 10 week aging for (a) polyester/glass, (b) phenolic CL1880/glass, and (c) phenolic CL1916/glass systems.

consists of a three-dimensional network of siloxane (Fraction Three). The physisorbed region (Fraction One) comprises the major fraction (as much as 98% of the total deposited silane) consisting of the hydrolyzate of silane physically adsorbed to the glass surface. Fraction One can be rapidly removed by cold water rinse. Fraction Two, a chemisorbed layer of the coupling agent, requires about 3–4 h extraction in boiling water for essentially complete removal. After the extraction of Fraction Two, Fraction Three — a monolayer of silane permanently bonded to the glass surface — remains intact. It appears that in this work only Fraction One could be affected with water aging. The influence of hydrothermal condition on the above layers of silane is explained in detail elsewhere [26]. In this work, silane coupling agent was applied on the glass fibres without involving subsequent rinsing in water or other hydrothermal condition.

It is postulated here that the rich multilayer of silane comprising the three fractions reacted incompletely with the matrix polymer. The innermost layer, Fraction Three, chemically reacted with the glass surface and bonded with adjacent layers of deposited silane. The outmost layer, Fraction One, reacted with the polymer matrix. During aging in cold water, the non-reacted portion of Fraction One dissolved deeper into the matrix with molecules of the matrix polymer. Thus, in dry conditions the results from both the nano-techniques showed a significant hard portion of the interphase region, which we assume to be the result of the thick deposit of Fraction One and bonded matrix polymer. After water aging the two nano-hardness techniques showed degradation in hardness and a significant expansion of the interphase region. Such results strongly indicate that water dissolved the physisorbed portion of the silane multilayer, and that the unreacted silane chains were bonded to
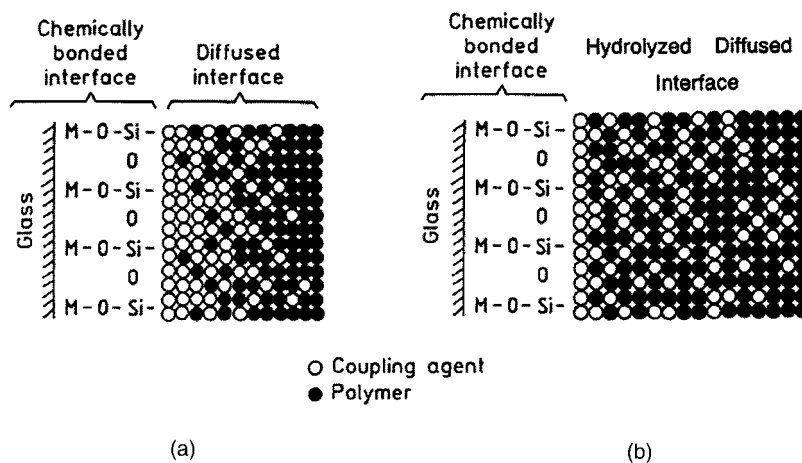
Fig. 8. A schematic model for (a) interdiffusion and IPN in a silane-treated glass fibre/polymer matrix composite, after Porter [20]; and (b) an extended model, after aging in water. Note the hard interface dissolving and increasing the size of the interphase.

the matrix polymer while moving deeper into the matrix. Therefore, the initially harder part of the interphase region expanded after aging in water, forming the extended soft region of reacted silane molecules.

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

As shown in the previous discussion, the polyester–silane chemical bond was strong and remained so during the environmental aging while the size of the interphase region increased. This indicates that water hydrolyzed the interphase region (Fraction One) degrading its properties, and increased the size of the interphase by moving molecules of silane deeper into the matrix. The chemical bond, however, remained undamaged and the model for this system after aging in water is presented in Fig. 8(b).

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 model for this system would also correlate to Fig. 8(b) but without the chemical bond.

The Phenolic CL1916/glass system had also suffered debonding prior to water aging but not to such a large extent 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 for the previous two systems.

5. Conclusions

The width of the interphase region between the fibre and the matrix was detected by both techniques in the first part of this work [17]. The results were consistent although materials had different surface morphologies, with phenolics being more inhomogeneous than polyester. It was noticed that the interphase region of dry materials consisted of the hard and soft parts. These parts were formed from a high concentration of silane applied on the fibre and the interdiffusion of silane into the matrix, respectively.

In the second part reported here, it was found that the interphase region increased with water aging for CL1880/glass and polyester/glass, up to several times its original size, revealing the material properties stronger than that of the matrix for all the three systems. The results were confirmed by both experimental techniques. The nano-indentation test detected degradation of the material properties and the extension of this region deeper into the matrix, while the nano-scratch test detected sensitive changes in the size of the interphase region. It was noticed from the scratch-test that hard interphase part, related to as the physisorbed portion of the silane multilayer deposited on the fibres, was dissolved and diffused deeper into the matrix during water aging, thus increasing the size of the interphase region. These results show that the nano-indentation and the nano-scratch tests can be employed as a useful tool in the investigation of the transitional material properties in multiphase materials.

Acknowledgements

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