

Environmental Durability of Fibre-Reinforced Composites

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ABSTRACT

The durability of the composites has been assessed in terms of the shear-lag parameter, n through the use of Raman spectroscopy. The decrease of the shear-lag parameter indicates damage due to hygrothermal ageing. The stability of the specimens subjected to the wet and dry conditions has been compared by the determined n . The n values for the wet composites have been found to decrease faster than those of the dry ones. The composites exposed to water vapour and liquid water environments were also investigated in terms of the moisture content, the mid-fibre strain and the debond length. There was no interfacial debonding for the specimen exposed to water vapour whilst the ones aged in the liquid water experienced such failure.

Key words: Raman spectroscopy - Shear-lag parameter – Durability
- Interfacial failure - Hygrothermal effects

INTRODUCTION

The durability of polymer composites in outdoor environments is the primary concern limiting the acceptance of these materials in some marine and aerospace applications. The polymer matrix in a composite binds reinforcing fibres that carry the service loads, preventing them from being directly exposed to an environment as well as providing all of the interlaminar shear strength of the composite (1). The matrix, however, is often considered to be the weak link in a composite system, since it may undergo physical damage and chemical degradation during environmental exposure and mechanical loading (2,3).

The long-term durability of composite materials has been cited as a major concern when these are expected to act as structural elements over a long period of time (4,5,6). At present, there are several unresolved issues involving the hygrothermal effects on the stability of composite materials. It is, therefore, necessary to conduct investigations in order to be able to predict service life and other aspects of performance.

Hygrothermal effects in single-fibre model composites were first investigated using Raman spectroscopy by Bannister and co-workers (5,7). The interfacial failure behaviour with respect to the fibre surface treatment during hygrothermal ageing has been reported. The investigation was conducted on aramid/epoxy composites. In the present study, the environmental durability of

composite is being assessed considering micromechanical parameters such as the shear-lag parameter n , the debond length and the mid-fibre strain. Definitions of these parameters are shown in **Figure 1**.

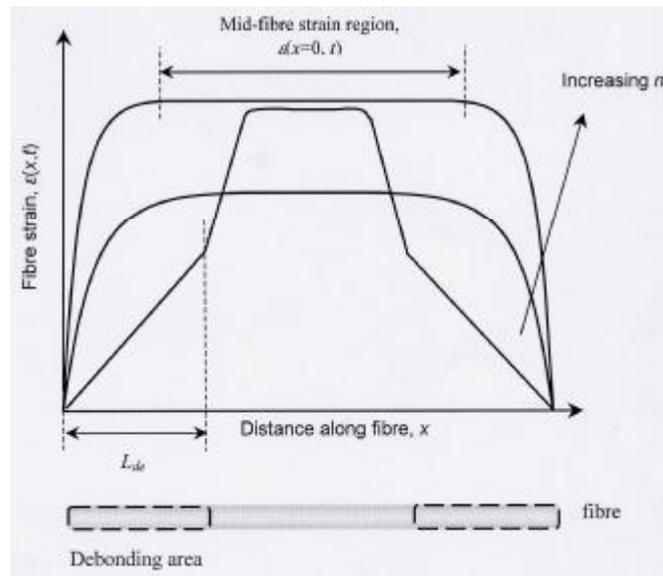


Figure 1. Schematic diagram of fibre strain profiles presenting the definitions of the mid-fibre strain ($\epsilon(x=0, t)$), the debond length (L_{de}) and the profile characteristics when the shear-lag parameter, n is increased

The objective of this study was to examine the durability of composites subjected to mechanical loading in dry conditions and non-mechanical loading due to hygrothermal effects. For the latter case, the composites were exposed to two environments: liquid water and water vapour (100% humidity) at various immersion times. The composites were made of different fibre types due to fibre surface treatment.

The first part of this work encompassed the dependence of the shear-lag parameter on the exposure time and the mid-fibre strain. A comparison between the composites subjected either to the mechanical loading using fragmentation test under dry conditions or exposed to the water environment for up to two years was made.

MATERIALS AND METHODS

Materials

The matrix was an epoxy resin composed of an Araldite resin, 50 g of LY5052 mixed with an Araldite hardener, 19 g of HY5052. The resin and hardener were supplied by Ciba Geigy, UK. A series of Twaron (poly(p -

phenylene terephthalamide)) aramid and PIPD (polypyridobisimidazole) fibres supplied by Akzo Nobel Research and PBO (poly(p-phenylene benzobisoxazole)) fibres produced by Toyobo Ltd, Japan, were used to prepare the composites. The Twaron fibre series consisted of the untreated TNHMF fibre, the surface finished TNHMF fibre, and the adhesion-activated TNHMA fibre (8).

Specimen Types

Three specimen configurations were used throughout this study:

a) a dumbbell specimen for the fragmentation test in the dry conditions depicted in **Figure 2**.

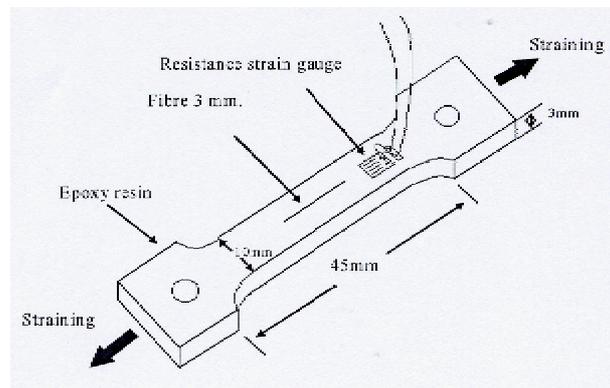


Figure 2. A schematic diagram of a dumbbell specimen

b) a 'diffusion slab (DS)' for the determination of the shear-lag parameter under the wet condition, illustrated in **Figure 3**.

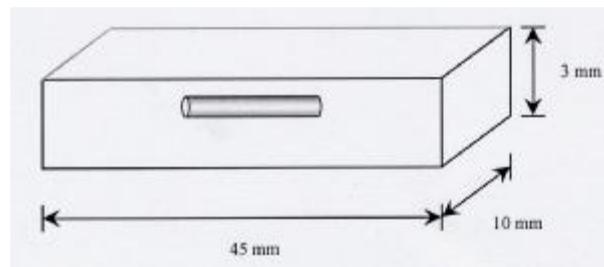


Figure 3. A schematic diagram of 'Diffusion slab' (DS) specimen geometry.

c) a 'double fibre pull-out (DFPO)' for exposing to water vapour and liquid water environments, depicted in **Figure 4**.

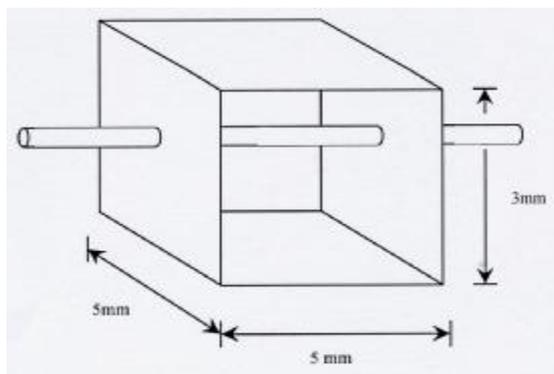


Figure 4. A schematic diagram of ‘Double fibre pull-out’ (DFPO) specimen geometry

All specimen configurations were prepared by a cold-curing process to avoid residual thermal stresses. The composite specimens were left to cure for at least 7 days at room temperature. For the fragmentation test specimen, a composite sheet was shaped into dumbbell specimens after curing using a routing machine. A resistance strain gauge was attached to each specimen in the test region using a cold-curing epoxy resin adhesive. The DS and DFPO specimens were fabricated in silicone rubber moulds. Single fibres were placed beneath the top surface of both the DFPO and DS specimens approximately 400 μm deep. The dimensions of the DS specimens were deliberately made to be identical to those of the dumbbell samples (Figures 2 and 3).

Fragmentation Test

The 1610 cm^{-1} aramid Raman band obtained from the Renishaw 1000 system was recorded from the left end to the right end moving along a single fibre using an exposure time of 4 seconds. The model composite was deformed in air to different strain levels at 0.1% intervals to 2.4% matrix strain. The measurements were performed every 20 μm along the individual fibres.

Raman Spectroscopy of the Aged Specimens

The DS and DFPO specimens were immersed in distilled water at room temperature. Only a DFPO (TNHM/epoxy) specimen was exposed to humid air at 100% relative humidity at room temperature in the desiccator. Once the samples had been removed from the moist environment, their surfaces were dried with absorbent paper. The specimens were thereafter weighed with an electronic balance with an accuracy of the order of ± 0.0003 g. The Raman spectra were obtained immediately using the Renishaw 1000 system after weighing to avoid the desorption effect of the specimens. Samples were placed freely on the microscope stage of the Raman system. Spectra were obtained by scanning the full fibre length typically in 50 mm steps. Subsequent Raman strain profiles were

recorded in equidistant time steps with respect to the logarithm of the variable. The initial immersion time was 24 hours.

RESULTS AND DISCUSSION

Dependence of the Shear-lag Parameter on the Exposure Time

It is well known that the shear-lag parameter, n reflects the bonding quality at the fibre/matrix interface (9). A high value of n indicates a nearly perfect bond at the interface as well as high stress transfer efficiency. If the interface is aged, the time dependence of the n parameter is likely to reflect deterioration in the stress transfer. **Figure 5** shows the fibre strain built up due to matrix swelling for a Twaron/epoxy composite DS specimen aged in water for up to 151 days. The shear lag parameter, n , can be obtained from curve fitting of the experimental data as shown in **Figure 5** by the shear-lag theory (*Equation 1*) (10,11). This was accomplished by using the 'Goal Seek' tool in Microsoft Excel. **Figure 6** shows the experimental data of the n at various exposure times for the TNHMA composite, the DS geometry. Where e_f is the fibre strain, e is the remote composite strain which is close to the matrix strain, r is the fibre radius, and s is the fibre aspect ratio.

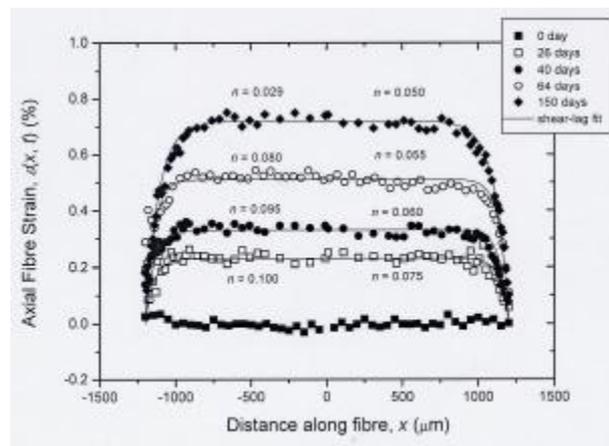


Figure 5. Fibre strain profiles of a TNHMA/epoxy aged in liquid water for up to 151 days, experimental data (symbol) and the analytical data (line)

A comparison of the n magnitude as a function of the square root of time for the five composite systems is shown in **Figure 7**. Curves in the **Figure 7** were obtained by grouping the experimental data from at least two specimens for each fibre type and fitting them with a gaussian function. The maximum (0.162) and minimum (0.097) n values derived using *Equation 2* (12) for the Twaron and the PIPD systems are illustrated by the 'theoretical n zone' in **Figures 6 and 7**. The

theoretical n values were calculated using: $E_m = 3$ GPa, $E_f = 102$ GPa (Twaron) and 282 (PIPD) GPa, $R/r = 4$, $V_m = 0.25$, where E_m and E_f is the Young's modulus of the matrix and the fibre, respectively. The term in (R/r) is a volume fraction parameter, and ν_m is the matrix Poisson ratio.

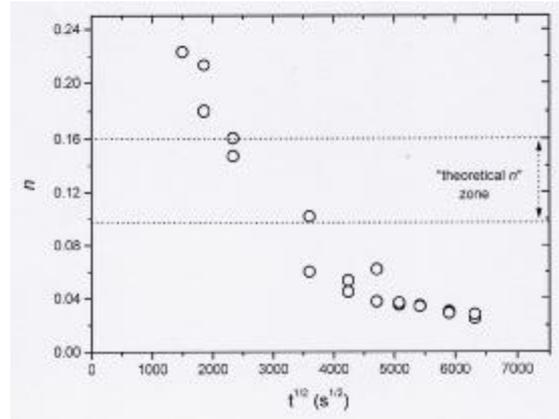


Figure 6. Variation of the shear-lag parameter, n with exposure times, the TNHMA-DS geometry

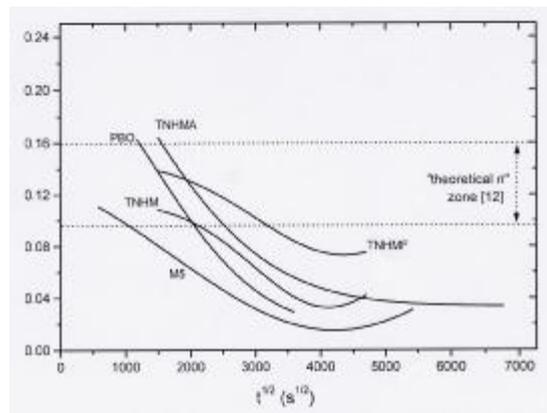


Figure 7. Variation of the shear-lag parameter, n with exposure times for all fibre types, the DS geometry

It can be seen that the n values for all specimens decrease as the time elapses. The reduction in the n values during exposure is attributed to the softening or the weakening of the fibre/matrix interface due to water ingress. The Twaron composites appear to have the greater n compared to the PBO and the PIPD composites. This is because the PIPD fibres have the highest modulus,

while Twaron fibres have the lowest considering the relationship between the mid-fibre strain and the n in Equation 2. On the other hand, it can be stated clearly that the higher the modulus, the lower the n value. Among the series of the Twaron fibres, the TNHM composite has the lowest n value, whilst the TNHMA curve shows the highest n initially and decays to the lower level than that of the TNHMF after 46 ($2000 \text{ s}^{1/2}$) days of exposure.

A more pronounced reduction in n for the PBO and the PIPD specimens implies that the Twaron composites maintain a better stress transfer efficiency in the wet environments. For the PBO composites, the rate of reduction in n was more pronounced than that of the Twaron and the PIPD composites (Figure 7). This indicates that the fibre/matrix interface of the PBO composites deteriorates due to ageing.

Durability of Wet and Dry Interfaces

Figure 8 shows a variation of the fibre strain obtained from the dumbbell specimen of the single-fibre model composite under the dry conditions, with the distance along the TNHM fibre embedded in epoxy matrix, at various matrix strain levels. The n values for the dry specimen were determined using the same procedure as that for the wet specimens described earlier. The durability of the wet and dry interfaces was then assessed and compared by correlating the shear lag parameter, n with the mid-fibre strain.

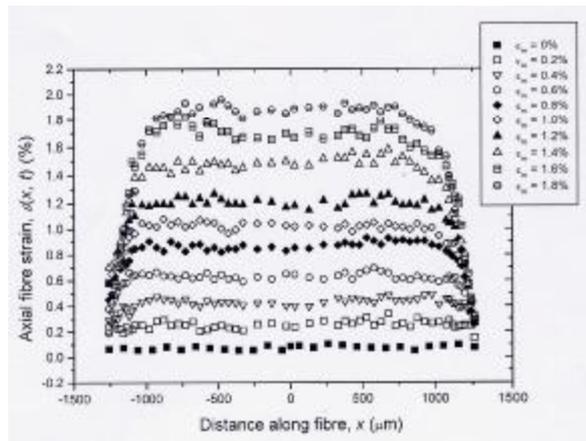


Figure 8. Fibre strain profiles of a TNHM/epoxy (dumbbell specimen) subjected to the mechanical loading in dry conditions, at various levels of matrix strain

Figure 9 demonstrates the dependence of the shear-lag parameter n on the mid-fibre strain for the Twaron/epoxy composites investigated by the mechanical loading (dry) and non-mechanical loading (wet) experiments. Figure 10 shows a comparison of the variation of the mid-fibre strain for the dry TNHM composite and the wet Twaron composites (TNHM, TNHMF and

TNHMA), the curves being obtained from fitting the experimental data (average of two specimens for each system) with the gaussian function. It can be seen that the n decreases when the mid-fibre strain increases. This is an indication of the decrease in the strength of the composite interfaces caused by water ingress for the wet specimens (13).

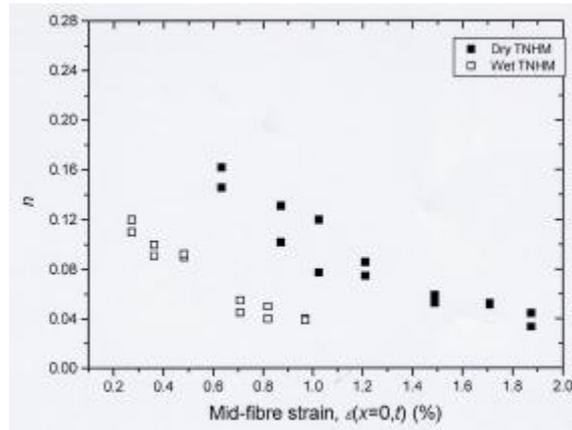


Figure 9. Dependence of the shear-lag n parameter with the mid-fibre strain for the TNHM composite specimens exposed to wet (DS geometry) and dry conditions

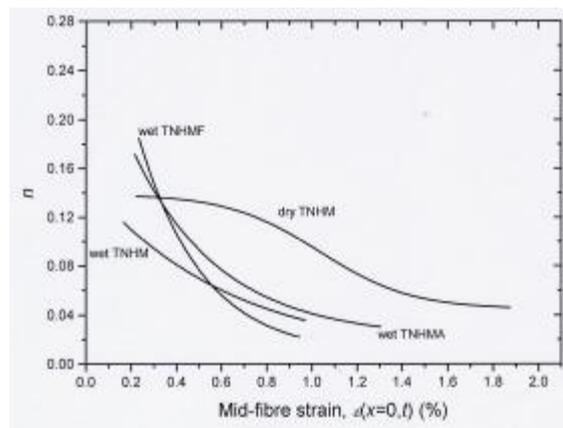


Figure 10. A comparison, n for Twaron composites under wet (DS geometry) and dry conditions

The n parameter for the tensile loaded specimens does not appear to be constant as originally assumed (14), and our investigation indicates that it also decays (**Figures 9 and 10**). This might be due to non-linear matrix deformation when the secant modulus decreases with the increasing strain (8). The n values of

hygrothermally aged samples appear to fall faster than those of the tensile loaded specimens in the dry conditions. This implies that, at a given mid-fibre strain level, the interfacial adhesion of the aged composites is impaired to a greater extent than that of the dry composites.

Durability of Composites Exposed to Water Vapour and Liquid Water

For this study, only the Twaron composite was selected to experience the two types of wet conditions: water vapour and liquid water. The purposes of this experiment were to study the moisture absorption rates and to compare the level of damage under two different wet conditions. The DFPO specimens were chosen since its geometry allows the fibre/matrix interface to be exposed directly to the penetrant. The following time dependent parameters between the two systems were compared and discussed: the moisture content, the mid-fibre strain, and the debond length. An example of the fibre strain built up due to the water ingress for a Twaron/epoxy DFPO specimen aged in water is shown in **Figure 11**. The mid-fibre strain and the debond length were determined based on the data from such fibre strain profiles.

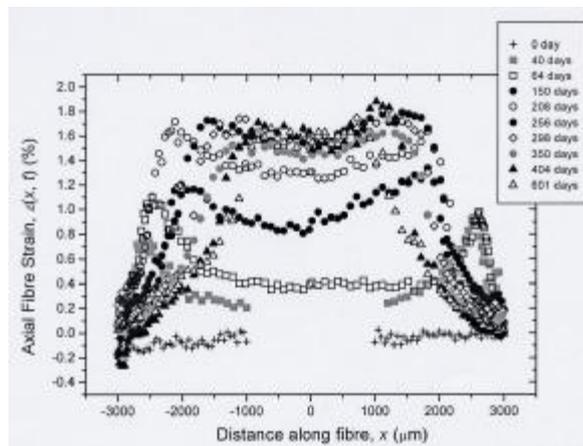


Figure 11. Fibre strain profiles of a TNHM/epoxy aged in liquid water for up to 601 days, DFPO geometry

Figure 12 represents the moisture content as a function of the square root of the exposure time for the composites exposed to water vapour and liquid water. There are data of three specimens shown in **Figures 12-14** which are TNHM (Vapour) representing TNHM composites, DFPO geometry aged in water vapour, TNHM1(Water) representing TNHM composite specimen number 1 exposed to liquid water, and TNHM2 (Water) representing TNHM composite specimen number 2 exposed to liquid water. It can be seen that all specimens absorb moisture at a comparable rate at the exposure time of up to 150 days

($3600 \text{ s}^{1/2}$). Nevertheless, after that the absorption rate of the TNHM/epoxy exposed to water vapour is significantly lower than the one exposed to liquid water. In addition, the moisture content appears to remain constant after an exposure time of 150 days, while the moisture content of the specimens exposed to the liquid phase is still increasing.

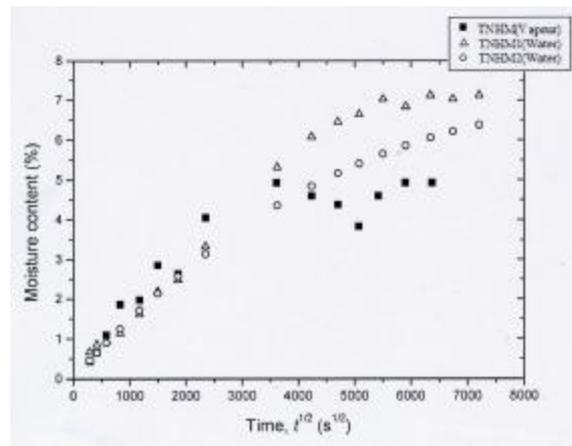


Figure 12. Moisture content of the TNHM/epoxy composites exposed to water vapour (TNHM (Vapour)) and liquid water (TNHM1(Water) and TNHM2 (Water)), DFPO geometry

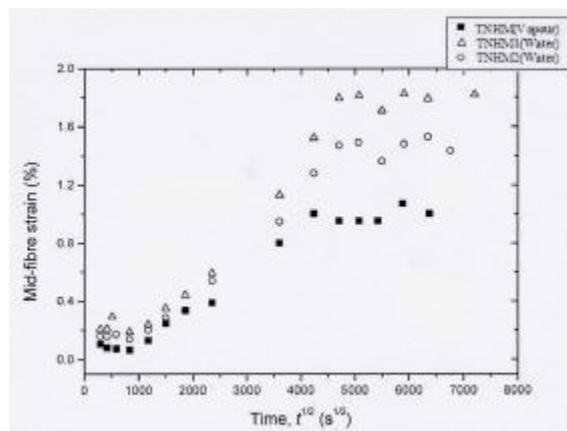


Figure 13. Mid-fibre strain of the TNHM/epoxy composites exposed to vapour water and liquid water, DFPO geometry

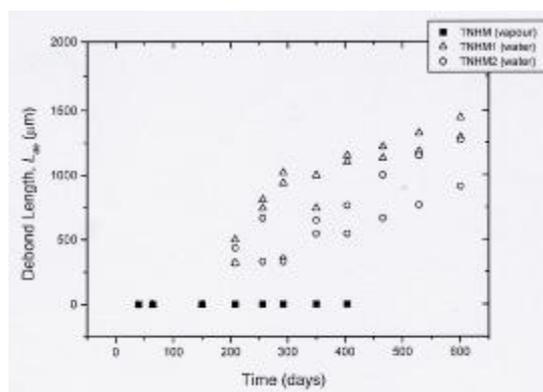


Figure 14. Variation of the debond length with time of the TNHM/epoxy composites exposed to water vapour and liquid water, DFPO geometry

With regard to the dependence of the mid-fibre strain on the exposure time (**Figure 13**), a similar trend to that observed for the moisture content (**Figure 12**) has been noted. It can be seen that both the moisture content and the mid-fibre strain of the system exposed to humid air increase at a rate similar to that for the system exposed to liquid water. However, after the exposure time of $4000 \text{ s}^{1/2}$, both rates (for the weight gain and the mid-fibre strain) decreased dramatically.

Identical fibre strain profiles showing no interfacial debonding were observed for the TNHM/epoxy subjected both to liquid water environment and to water vapour at least for the short exposure times (8). The debond length of the system exposed to the liquid water propagated to $1490 \mu\text{m}$ within 600 days of exposure, **Figure 14**. It can be seen, however, in **Figure 14** that the debond length for the TNHM exposed to water vapour remains zero at all time indicating no interfacial debonding.

At this stage, there are three following distinctive phenomena observed for the specimen exposed to water vapour: 1) a lower extent of the moisture content at the long exposure time (**Figure 12**); 2) a lower extent of the mid-fibre strain at the long exposure time (**Figure 13**); and 3) absence of the interfacial debonding (**Figure 14**). Considering these three items of evidence, it is likely that a combination of the lower moisture content and the associated lower mid-fibre strain at the long exposure time is responsible for the interfacial debonding not taking place.

CONCLUSIONS

The Raman technique has been successfully applied to assess the composite durability. The shear-lag parameter was found to decrease dramatically with the exposure time. This caused the reduction of the stress transfer efficiency of the composite systems. The stability of the interfaces for the Twaron composites is better than those for the PBO and PIPD systems. The shear-lag

parameter, n of the hygrothermally aged composites, was reduced to a greater extent than that for tensile loaded samples in the dry condition. Ageing caused the weakening of the bonding at the interface. Furthermore, it was found that the n values for the aged composites decayed faster than those of the dry composites due to interface degradation.

No debonding for the Twaron composite was observed after a long exposure to the water vapour. Furthermore, the total moisture content and the mid-fibre strain after a certain time were lower than those for the composite aged in the liquid water. It is believed that the interfacial debonding was not due to the low moisture content and was responsible for the low mid-fibre strain.

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REFERENCES

- 1) Chin JW Nguyen T Aouadi K. Effects of environmental exposure on fiber-reinforced plastic (FRP) materials used in construction. *J Composites Tech Res* 1997; 19: 205-13.
- 2) Harris B. Engineering Composites Materials. Cambridge University Press, Cambridge, 1999.
- 3) Fried N. Degradation of composite materials: The effect of water on glass-reinforced plastics. In: Wendt FW Liebowitz H and Perrone N (eds). Mechanics of Composite Materials. Pergamon Press, Pennsylvania, 1967.
- 4) Sala G. Composite degradation due to fluid absorption. *Composites Part B* 2000; 31: 357-73.
- 5) Cervenka AJ Bannister DJ Young RJ. Moisture absorption and interfacial failure in aramid/epoxy composites. *Composites Part A* 1998; 29A: 1137-44.
- 6) Varelidis PC Papakostopoulos DG Pandazis CI Papaspyrides CD. Polyamine coated Kevlar fabric in epoxy resin: mechanical properties and moisture absorption studies. *Composites Part A* 2000; 31(6): 549.
- 7) Bannister DJ. Micromechanical and Hygrothermal Behaviour of Single-fibre Epoxy Resin Composites. PhD Thesis, University of Manchester Institute of Science and Technology, Manchester Materials Science Centre, 1996.
- 8) Kueseng K. Hygrothermal Effects on Composite Micromechanics. PhD Thesis, University of Manchester Institute of Science and Technology, Manchester Materials Science Centre, 2001.
- 9) Peelamedu MS Yunhe Y Molyet KE Naganathan NG Dukkkipati RV. Investigation of Strain Transfer in an Induced Strain Actuator. In: 6th International Conference on Composites Engineering, Florida, June, 1999.
- 10) Andrews MC Bannister DJ Young RJ. Review - The interfacial behaviour of aramid/epoxy model composites. *J Materials Sci* 1996; 31: 3893.
- 11) Galiotis C. Interfacial studies on model composites by laser Raman spectroscopy. *Composites Sci Tech* 1990; 42: 125-50.

- 12) Hull D. An Introduction to Composite Materials. Cambridge University Press, 1996.
- 13) Kueseng K Hussain A Cervenka AJ Young RJ. Moisture absorption and interfacial failure in Twaron/Epoxy composites. *In: Proceedings of ECCM-9 conference, Brighton. June, 2000.*
- 14) Chau PS Piggott MR. Load Bearing Fibre Composites. Piggott MR (ed). Pergamon Press, Toronto, 1980.

บทคัดย่อ

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ความคงทนต่อสิ่งแวดล้อมของคอมโพสิตแบบเสริมเส้นใย

การวิจัยนี้ได้มีการใช้ตัวแปรจากทฤษฎี shear-lag คือค่า n มาใช้ในการประเมินสภาพความคงทนของวัสดุคอมโพสิต โดยค่า n ได้มาจาก เทคนิครามานสเปกโตรโกปี พบว่าค่า n ที่ลดลงของคอมโพสิตบ่งชี้ถึงการที่วัสดุถูกทำลายโดยความชื้น ค่า n ยังนำมาใช้ในการเปรียบเทียบความเสถียรของวัสดุตัวอย่างที่ศึกษาในสภาวะเปียกและแห้ง พบว่าค่า n ของคอมโพสิตในสภาวะเปียกลดลงเร็วกว่าในสถานะแห้ง นอกจากนี้ ยังมีข้อมูลของคอมโพสิตที่อยู่ในสิ่งแวดล้อมของไอน้ำกับที่อยู่ในน้ำสถานะของเหลว โดยได้รายงานถึง 1) ปริมาณความชื้นของวัสดุ 2) ค่าความเค้นที่บริเวณตรงกลางของเส้นใย และ 3) ค่าความยาวของการแตกหักของเส้นใย ในกรณีของตัวอย่างที่ถูกเก็บอยู่ในสภาวะไอน้ำจากการทดลองพบว่า วัสดุไม่ถูกทำลายที่บริเวณรอยต่อของเส้นใยกับเรซินเมตริกซ์ แต่ตัวอย่างที่แช่ในน้ำกลับถูกทำลายแทน

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