Published in Polymers and Polymer Composites, 2006 (Accepted Post-print version)
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Effects of Changing Seawater Temperature on Mechanical Properties of GRP Composites

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SUMMARY

Glass fibres were used to fabricate epoxy and unsaturated polyester laminated composites, which were then immersed in seawater. The specimens were immediately transferred from one seawater bath to another one at a different temperature to induce thermal shock, with concurrent hydrothermal ageing. Thermal shocks of two types, up-cycle (lower to higher temperature immersion) and down-cycle (higher to lower temperature immersion) were applied and their repetition induced thermal fatigue. The aged samples were subjected to 3-point short beam shear tests. The tests were performed at room temperature with 2 mm/min and 50 mm/min crosshead speeds. The weakening effects were sensitive to loading rate. The effect of fibre volume fraction was also investigated. The maximum interlaminar shear strength fell by 35% in glass/epoxy composites (in 55 and 65 weight % fibres) and by 33% in glass/polyester composites (in 60 weight % fibres) as a result of the most severe conditioning cycles. It was also observed that the reduction in shear strength in general was less at high crosshead speeds. This may have been linked to a reduction in matrix ductility.

1. INTRODUCTION

Many applications of glass fibre reinforced polymers (GRP) expose the materials to a wide range of temperatures. The effect of temperature on moisture diffusion and environmental ageing is a complex phenomenon and not very well established. Moisture absorption at high temperatures may induce irreversible damage to polymers and their composites, such as chemical degradation, cracking and interfacial debonding. The use of GRP composites in critical marine components has usually been accompanied by conservative design safety factors because of limited durability data. Seawater ageing still remains an uncertain factor[1].

Polyester and epoxy resins are permeable to water but impermeable to the ions present in a number of aqueous solutions. Unsaturated polyester resins are precluded from high performance applications because of their poor wet/hot mechanical properties and high curing shrinkage. But their reasonably good corrosion resistance at moderate temperatures is very attractive in many areas of use. Unfortunately, high cure shrinkage and large differences in the coefficient of thermal expansion between glass fibres and polyester resin can induce additional residual stresses. Unsaturated polyester matrix composites can also be degraded in hydrothermal ageing by blistering/ cracking because of an osmotic process. The osmotic pressure is less of a problem in saline solutions than in pure water [2].

Hydrothermal ageing can promote thermo-oxidative degradation in epoxy networks. It is generally believed that a major mechanism of shear strength reduction in composites by environmental exposure is weakening of the interfacial bond. A remarkable reduction in shear strength has been observed within a short time upon hydrothermal ageing[3]. The rapid bond strength reduction implies that it is primarily due to short-term processes. It is thus imperative to evaluate the effect of changing and harsh aqueous environments on the mechanical properties of composites. The loss of microstructural integrity by interfacial degradation upon environmental ageing is a major concern for the wider use of GRP composites as critical marine components.

A change in temperature can alter the relative rates of the diffusion and relaxation processes in the polymer matrix. Furthermore, moisture absorption at elevated temperatures may induce irreversible changes to polymer composites, such as cracking, blistering, chemical degradation and debonding, hydrolysis, oxidation and the leaching of small molecules[4]. Increasing the volume fraction of fibres in a composite means more fibre/matrix interfacial area for the same fibre diameter. Thus more energy can be dissipated by the interface. The interfacial damping factor is proportional to the volume fraction of fibres[5]. Reports of the effect of the interface on diffusivity are inconclusive. But the interface is known to be susceptible to damage by environmental ageing.

A need exists for an evaluation of reliable environmental resistance data for fibrous composites under cyclic hydrothermal treatment, especially in seawater. They have the potential to become even more successful materials in marine applications,

where moisture induced mechanical performance has to be assessed over a period of as long as 20 to 30 years. Glass fibres are generally attacked and weakened by prolonged immersion in aqueous solutions. The mechanism is believed to involve hydroxyl or hydrogen ion penetration into the fibres and these ions progressively replace the sodium ions originally present. The misfit strain due to the replacement of ions may introduce cracks into the fibre surfaces. The aqueous solutions may hydrolyse the siloxane groups of the glass and accelerate flaw growth [6].

The mechanical properties of FRP composites are strongly influenced by the fibre/polymer matrix interface. Failure may occur in the interfacial region due to chemical reactions or to plasticisation when water penetrates the interfaces. Differences between the thermal coefficient of expansion of the reinforcement and that of the matrix phase, together with the cure shrinkage associated with thermosetting resins can often induce stress concentrations at the interface. The present experiment was designed to study the effects of changing the seawater immersion temperature on the matrix-dominated short beam shear (SBS) strength of glass/epoxy and glass/polyester composites at different strain rates. The effect of volume fraction on delamination was also taken into account.

Thermal shock and thermal fatigue are very common in many applications of GRP composites. Thermal loading is produced in structural components by the aerodynamic design of modern marine objects. The invincibility of composites has been their biggest myth. A reported premature failure of E-glass composite wraps applied to circular highway-supporting columns, under sustained stresses of approximately a third of the strength, is not an isolated incident. Such loss of

strength is generally accelerated in adverse wet environments. There is a small possibility of a steep rise in seawater temperature because of accidental fire due to lightning, electrical faults or high speed collisions. This can give rise to intense thermal stresses in the components around manufacturing and in-service defects or cracks. The concentration of thermal stresses around these defects can result in catastrophic failure[7]. The loss of adhesion and microstructural integrity at the fibre/matrix interface because of cyclic treatment may be reflected in the interlaminar shear strength (ILSS). SBS test results can be used to indicate the bond strength if the bonding level is the only variable[8]. Little, if any, durability data regarding the effects of seawater ageing combined with thermal shock on interfacial debonding in polymer composites at different loading speeds has been cited in the open literature to date.

2. EXPERIMENTAL

An unsaturated orthophthalic polyester resin (Saint-Gobain Vetrotex) and an unmodified epoxy resin based on bisphenol-A (Ciba-Geigy, India) were used with woven roving E-glass fibres (Saint-Gobain) to fabricate composite laminates by hand lay-up. The laminates were fabricated with several glass layers to acquire the thickness required for ASTM D 2344-84. Three fibre weight percentages (55, 60 and 65) were targeted in the laminate preparation. The laminates were cut to the required dimensions for the 3-point SBS test using a diamond cutter.

The SBS test specimens were conditioned in desiccators for several days under ambient conditions until their weights stabilised. The samples were first immersed in a seawater bath in an oven at 50˚ C for 30 minutes. After that, they were

immediately plunged into another seawater bath at 100˚ C for a further 30 minutes. This procedure was defined as one shock cycle. Then some specimens were taken out from the 100˚ C temperature bath and put immediately into the 50˚ C temperature bath for 30 minutes. Then they were immersed again in the seawater bath at 100˚ C temperature bath for the same time. Thermal shock treatments were carried out concurrently in that order by exposing the samples in baths at different temperatures in quick succession for different environmental cycles. The weathered specimens were wrapped in aluminium foil to minimise further environmental interactions before mechanical testing. Three-point bend tests were performed within the shortest possible time after conditioning. The off-times were kept the same for all the aged specimens to eliminate/minimise the possibility of a recovery process by relaxation at ambient conditions.

The aged specimens were tested in a 3-point flexural mode to determine the ILSS. The tests were conducted at room temperature using an Instron machine. The experiments were carried out in accordance with ASTM D 2344-84 at crosshead speeds of 2 and 50 mm/min for each stage of cyclic treatment of the specimens. About 10 samples were tested at each point of the conditioning cycle to calculate a reasonable standard deviation limit. The data that were within the acceptable limit were accepted, and any others were rejected. The ILSS value was determined by the equation:

$$\text{ILSS} = 0.75p_b/bd$$

where p_b was the breaking load, b the width and d the thickness of the specimens.

4. RESULTS AND DISCUSSION

The variations in the ILSS values of glass/epoxy composites with the number of conditioning cycles are shown in Figs. 1(a), 1(b) and 1(c) for the three fibre weight percentages. The ILSS values were recorded at crosshead speeds of 2 and 50 mm/min for each fibre volume fraction in the same figure. The curves showed continuous falls in shear strength with increasing numbers of cycles. The shear strength is a function of the volume fraction of the constituents of a composite, which is not considered in the calculation of SBS strength[9]. (That is why figures have been drawn separately for the different volume fractions). All the figures indicate that the ILSS values were higher at higher loading speeds.

Figs. 2(a), 2(b) and 2(c) show the change in shear strength with the number of cycles for 55, 60 and 65% w/w glass contents. Here also, shear strength is plotted for 2 and 50 mm/min crosshead speeds. All plots indicated slow declines in ILSS with increasing numbers of conditioning cycles.

Scanning electron micrographs (Figs.3 and 4) show extensive matrix cracking and interfacial cracking in the conditioned specimens. The presence of these cracks can often lead to interfacial debonding, matrix fracture and post-debonding friction. Fracture behaviour in GRP composites is seldom conclusive because of their microstructural inhomogeneity. Thermal shock and thermal fatigue during ageing can induce matrix and interfacial cracking in glass/epoxy and glass/polyester composites. Cracks and debonded areas, nucleated by high residual stresses as a result of the changing aqueous environment, can easily propagate at the weaker interface. The continuous fall in ILSS values for all cases can be attributed here to

matrix cracking and/or interfacial debonding. The differential change in the condition of constituent phases (fibre, matrix resin and interphase) of fibrous polymer composites in such harsh and hostile environments can result in a significant mismatch among constituents and this eventually leads to the evolution of localised stress and strain fields in composites. The situations could easily result in the nucleation of delaminating microcracks in the composites. The cracks would be expected to propagate preferentially along the fibre/matrix and laminar interfaces.

CONCLUSIONS

The effect of changing seawater temperature during immersion ageing of glass/epoxy and glass/polyester composites on ILSS has been shown. The variation in loading rate was taken into consideration for the assessment of the mechanical behaviour of aged specimens. The shear strength was higher at all points of the cyclic environment at higher crosshead speeds. A fall in ILSS was noticed for both the composite systems. It was also observed that the reduction in shear strength was dependent on the volume fraction of fibres. A reduction in ILSS values was observed for both the lowest and highest fibre volume fractions in the present experiments. This could be attributed either to matrix damage or to interfacial damage. A greater amount of matrix phase was obviously present in the laminates with low fibre volume fractions. A higher fibre content means a greater interfacial area. The cumulative effect of thermal shock, thermal fatigue and aqueous environment was observed to be deleterious for the mechanical properties of

polymer composites. The behaviour of GRP composites in such environments was sensitive to the variations of constituent phases and also to the loading speed.

ACKNOWLEDGEMENT

The author is pleased to record the support and cooperation of NIT, Rourkela. I remain grateful to Anisha Ray for the continuous inspiration.

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Figure Captions

FIG. 1 Variation of ILSS with number of thermal fatigue cycles for glass/epoxy composite at 2 mm/min (●) and 50 mm/min (♦) crosshead speeds with (a) 55 % w/w (b) 60% w/w (c) 65 % w/w glass fibres.

.**FIG. 2** Variation of ILSS with number of thermal fatigue cycles for glass/polyester composite at 2 mm/min (●) and 50 mm/min (♦) crosshead speeds with (a) 55% w/w (b)60% w/w (c) 65% w/w glass fibres.

FIG. **3** Matrix micro-crack and interlaminar micro-crack in conditioned specimen.

FIG. 4 Matrix macro-crack in the treated sample.

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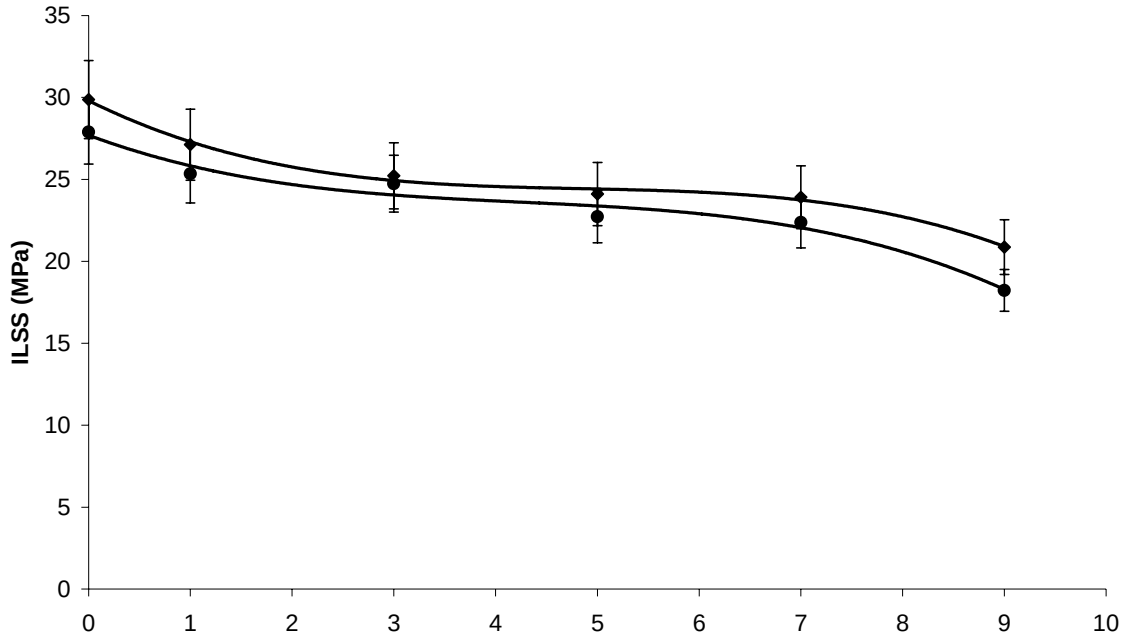
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ILSS (MPa)
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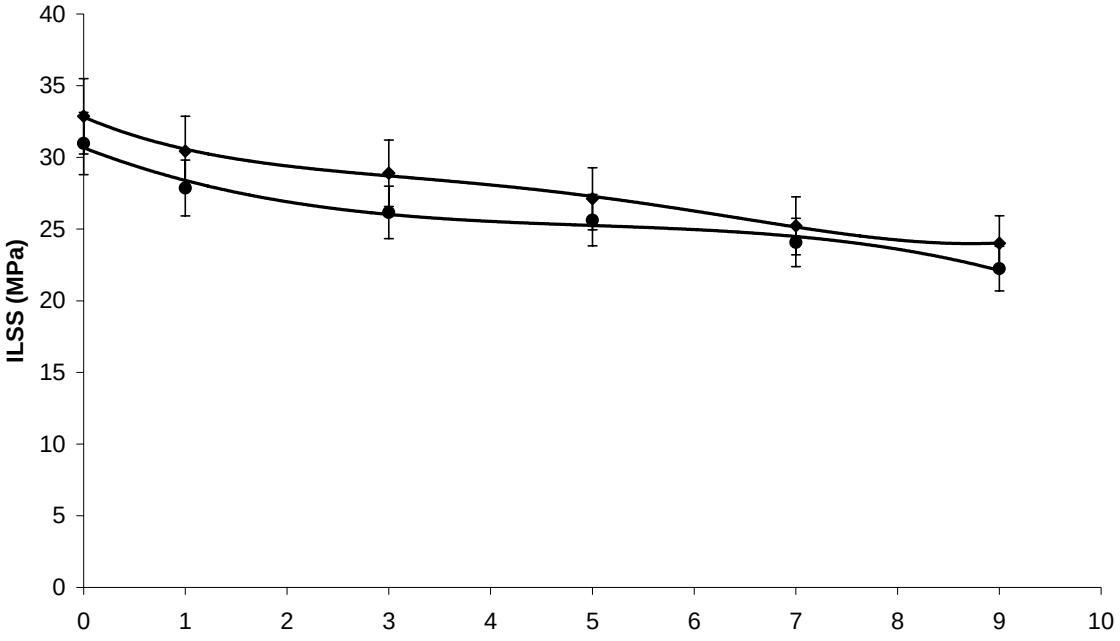
Number of thermal fatigue cycles in seawater immersion ageing

Fig. 1(a)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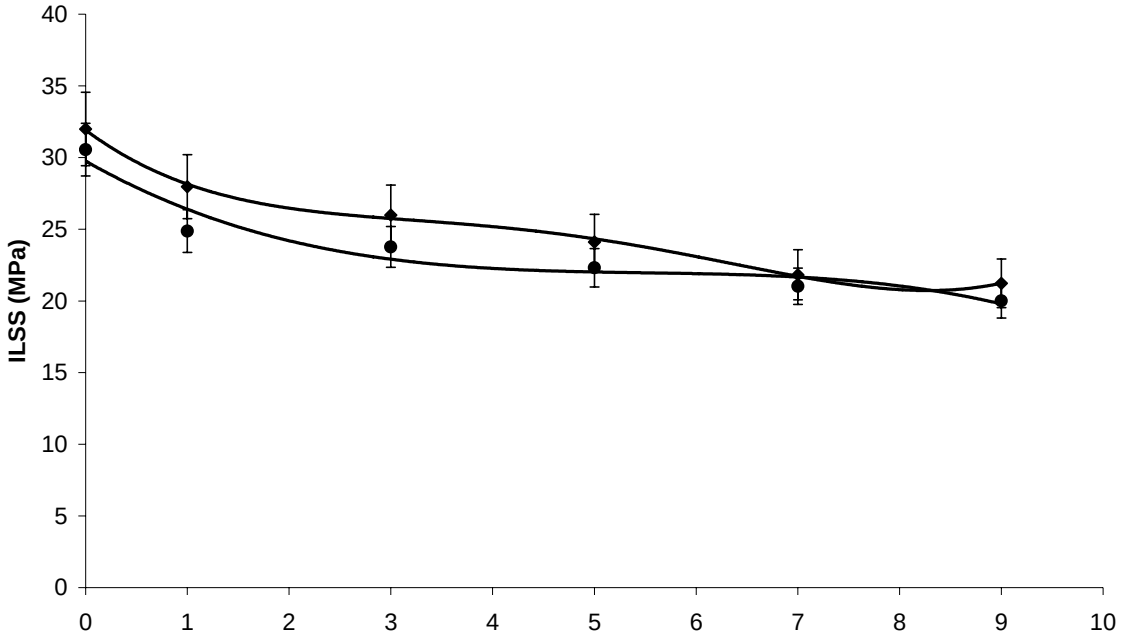
Number of thermal fatigue cycles in seawater immersion ageing

Fig. 1(b)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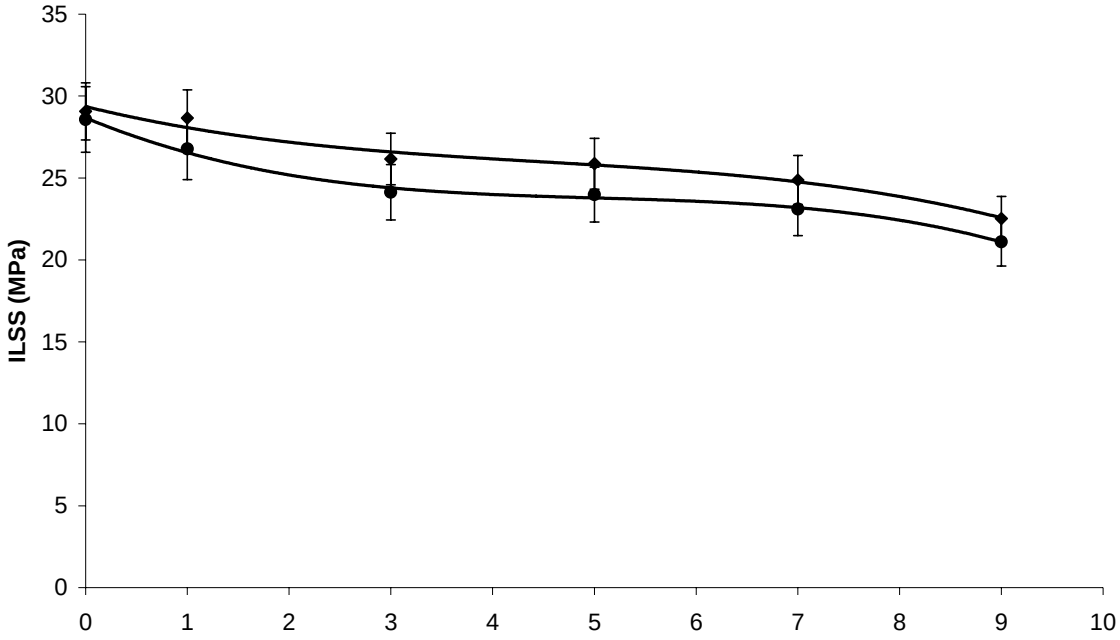
Number of thermal fatigue cycles in seawater immersion ageing

Fig. 1(c)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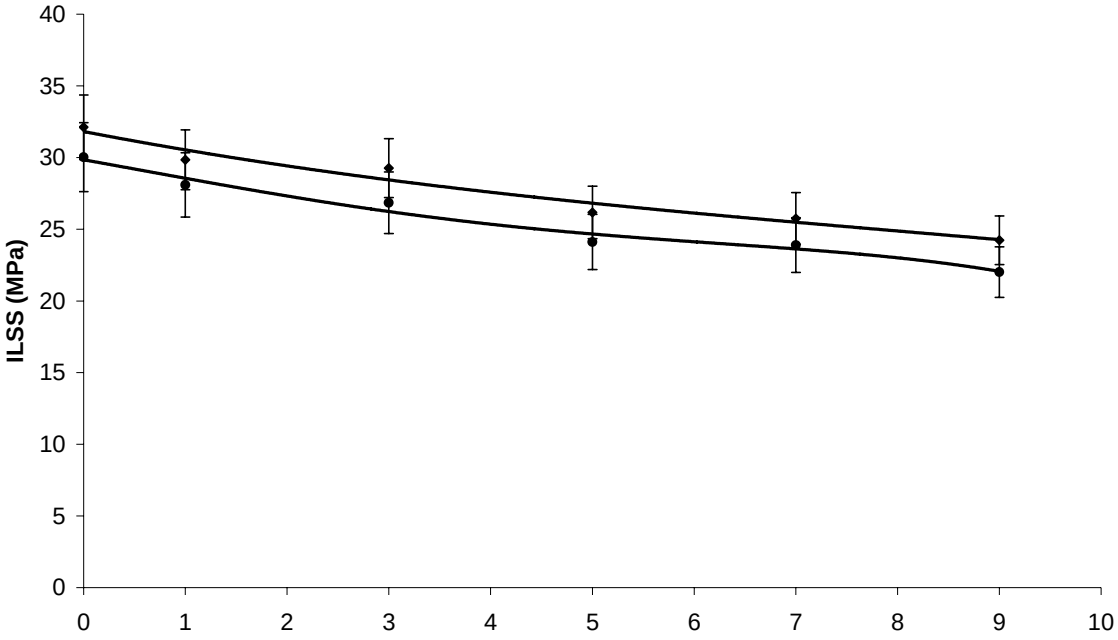
Number of thermal fatigue cycles in seawater immersion ageing

Fig. 2(a)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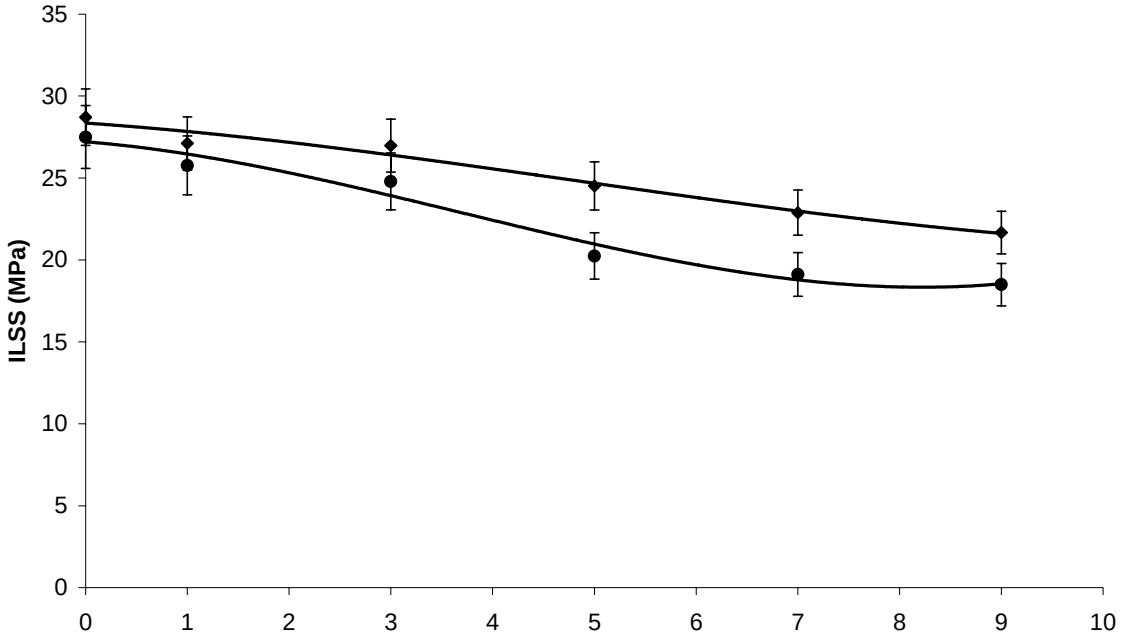
Number of thermal fatigue cycles in seawater immersion ageing

Fig. 2(b)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Number of thermal fatigue cycles in seawater immersion ageing

Fig. 2(c)

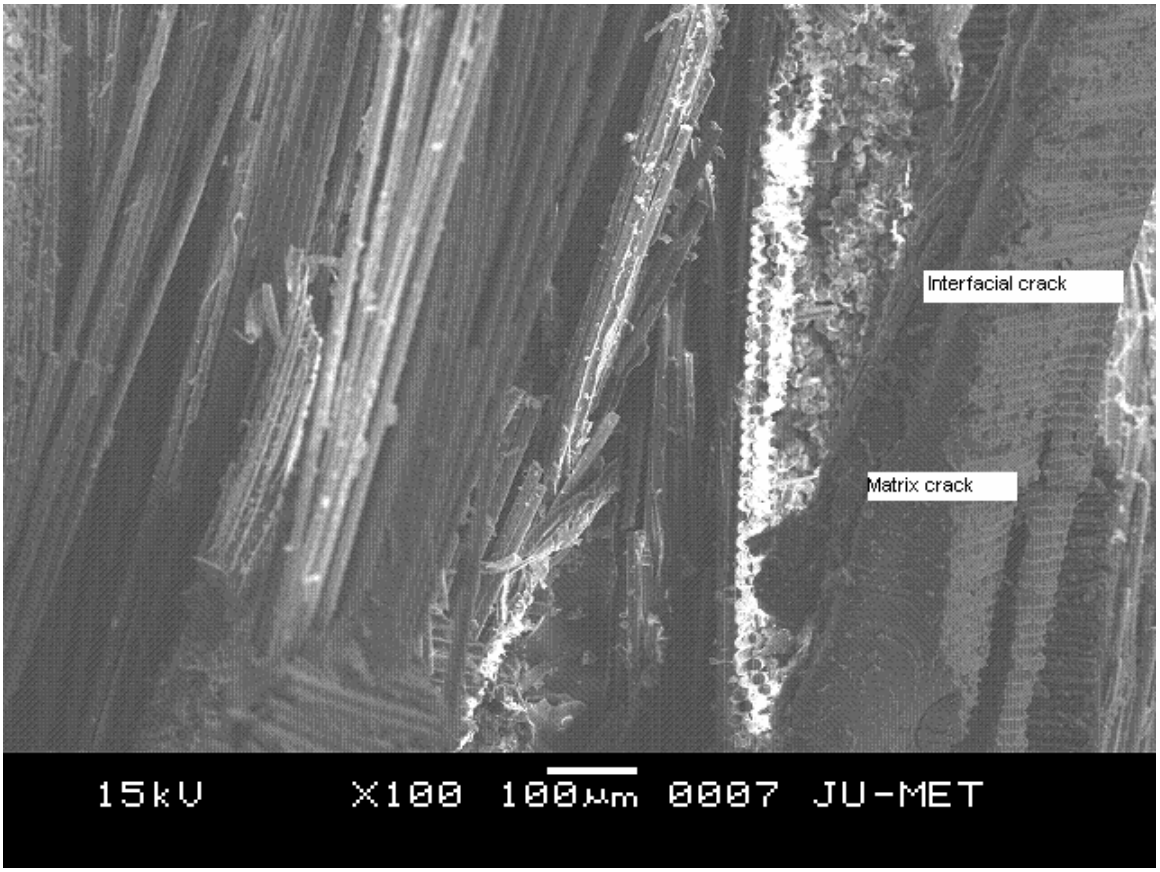

Fig. 3

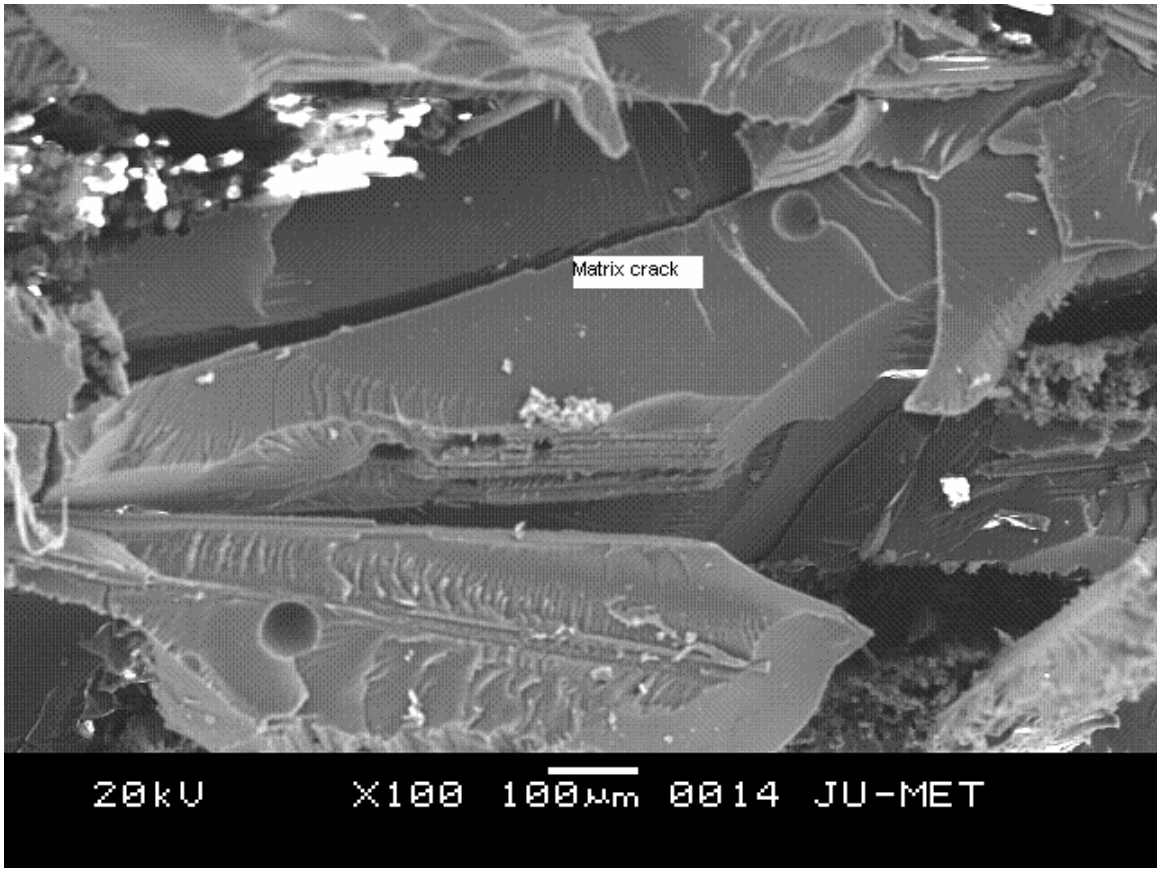

Fig. 4