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ACIDIC DEGRADATION OF FRP COMPOSITES

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Abstract: Fibre-reinforced polymers (FRPs) are increasingly being used as reinforcement in new concrete structures and as strengthening materials for the rehabilitation of existing concrete structures. The main advantages of FRPs are their light weight, high strength, and non-corrosive features. The research presented in this paper is an effort to understand the interlaminar fracture behaviour of glass/epoxy composite laminates after acid treatment of varying dilution. This study uses 3-point flexural test to qualitatively assess such behaviour for 50 weight percentage of E-glass fibres reinforced epoxy composites after acid treatment. The specimens were tested at 2 mm/min and 500 mm/min crosshead speed to evaluate the sensitivity of mechanical response during loading at these conditions. The mechanical performances of the laminated specimens treated in acid solution of different concentration were compared by using SEM photographs. Phenomenological behaviour of these materials may be attributed by degradation of matrix and fibre caused due to acid attack, water diffusion and generation of residual stresses in the composite laminates.

Keywords: glass/epoxy composites, acid attack, interlaminar shear strength, water diffusion and residual stress.

1. INTRODUCTION

In recent years, glass fibre-reinforced polymers (GFRPs) have received considerable attention as alternatives to steel and aluminium as structural materials in the construction, automotive, and aerospace industries due to their high specific strength, high stiffness to weight ratio, corrosion and fatigue resistance, ease of handling, and ease of fabrication. In the construction field, GFRPs have been employed as reinforcing elements in Portland cement concrete environment, as structural shapes for non-corrosive environments such as bridge decks, building columns, and sewage treatment plants. Glass fibre reinforced polymers (GFRPs) were selected and used to build the bridge deck for O’Fallon Park Bridge in Denver, Colorado [1].

A major advantage of GFRPs is that composite properties can be optimized for a specific application by varying the design factors, such as fibre volume content, fibre architecture, type of resin, and the chemical nature of the sizing applied to the surface of the fibre. It can be anticipated that GFRPs will come into contact with atmospheric humidity, acid rain, chemicals, and an alkaline environment in the proximity of Portland cement concrete [2]. This may lead to some micro-structural and morphological transformations during its service life, leading to property changes due to physical and chemical aging. It is possible that the presence of moisture in the composite, whether by itself or in combination with other chemicals, can initiate undesirable structural changes within the fibre reinforcement and the matrix or the interface, and this can potentially reduce the durability of the GFRP [3]. It is well known that the polymer composites are prone to the absorption of surrounding media either of a liquid or gaseous nature and this may include a reduction in mechanical properties. Even the epoxy resins, regarded to be

reasonably resistant to attack, can have strength lowered by the pick up of aggressive environments such as water [4]. The absorbed, moisture promotes a gradual degradation of fibre interfaces, extensive internal damage in the form of micro-cracks, and blisters. Changes in mechanical properties of the composite material as a consequence of fluid ingress may be reversible, partially reversible, irreversible or a combination of these types depending on the exposure time and conditions [5]. The extent of damage depends on the fluid type, fluid concentration as well as the composition of the fibres under attack. Use of coupling agents tends to delay the corrosion process and minimize loss in mechanical properties [6]. The detrimental effects due to fluid absorption on the matrix of composites are secondary compared to the damage in the fibres and the fibre/matrix interphase.

The glass/epoxy composites are susceptible to rapid stress corrosion in acidic environment because of the loss of integrity of the fibre/resin interface [7]. The main objective of this paper is to study the mechanical performance of glass/epoxy composite laminates after acid treatment of varying dilution.

2. EXPERIMENTAL

2.1 Material

Araldite LY-556, an unmodified epoxy resin based on Bisphenol-A and hardener (Ciba-Geigy, India) HY-951, aliphatic primary amine were used with woven roving E-glass fibres treated with silane based sizing system (Saint-Gobain Vetrotex) to fabricate the laminated composites.

2.2 Fabrication of Composites

The glass fibre/epoxy composite laminates were fabricated by wet lay-up method; the glass fibre woven cloth of required dimension was laid over a mould and then catalyzed epoxy resin was poured absorbed over the reinforcement. The wet composite was rolled, to distribute the resin and to remove the air pockets. The sequence was repeated until the desired thickness was obtained. The layered structure was allowed to harden on cure. It was cured at room temperature for 48 hours. After curing, the laminate was cut into the required size for 3-point bend (Short-Beam Shear) test by diamond cutter. Then stability test was done for the composite laminates. Here the laminates were weighed and then heated in an oven at 50 °C. The weight is intermittently checked till we get a stable weight, that is, with further heating there is no change in the weight of the composite.

2.3 Acid Treatment

After the stability test the samples were allowed to come back to the ambient temperature. Then they were kept in the desiccators so that there is no further absorption of moisture. The cured specimens were exposed to 0% HCl, 5% HCl, and 40 % HCl concentrated acid solution for 7 days. After the exposure all the samples were taken out and were tested in 3-point bend test machine.

2.4 3-point bend test

All the mechanical flexural tests were performed at 2 and 500 mm/min crosshead speeds. The interlaminar shear strength (ILSS) was measured as follows,

$$\text{ILSS} = 0.75p/bt$$

Where,

'p' is the breaking load, 'b' the width, and 't' the thickness of the specimen.

An Instron1195 tensile testing machine was used to perform SBS tests in accordance with ASTM D 2344-84 standard. Multiple samples were tested at each point of experiment and the average value was reported. The mechanical performances of the laminated specimens after acid treatment were compared by using SEM photographs.

3. RESULTS AND DISCUSSION

Figure 1 shows the effect of concentration of 1M HCl acid solution on the interlaminar Shear Strength (ILSS) of glass/epoxy composites at crosshead speed of 2 mm/min (◆) and 500 mm/min (■). There is a reduction in interlaminar Shear Strength to about 16-18% after treating with 5 % HCl concentrated acid solution and the reduction increases to 29-30% in 40% HCl concentrated acid solution at both the crosshead speeds. This decrease in ILSS may be attributed to the degradation caused due to stress corrosion cracking (SCC) of the laminates [8] and micro cracks developed in the matrix. It was observed that the amount of water absorbed by the laminates is maximum in 0% HCl concentrated solution and decreases with increase in the concentration of the acid solution. This can be attributed to the bulky nature of HCl molecule, which slows down the rate of ingress of water and thus decreasing the diffusion [9]. Here the amount of liquid that can diffuse in to a polymer depends on the size of the diffusion molecule relative to free volume available within the polymer. The ILSS values are found to be loading rate sensitive. The lower values at higher speed may be due to the unavailability of sufficient time to transfer load properly and the stress induced cracks may grow without blunting [10]. At lower speed time available for redistribution of load is more so that stress induced cracks are less.

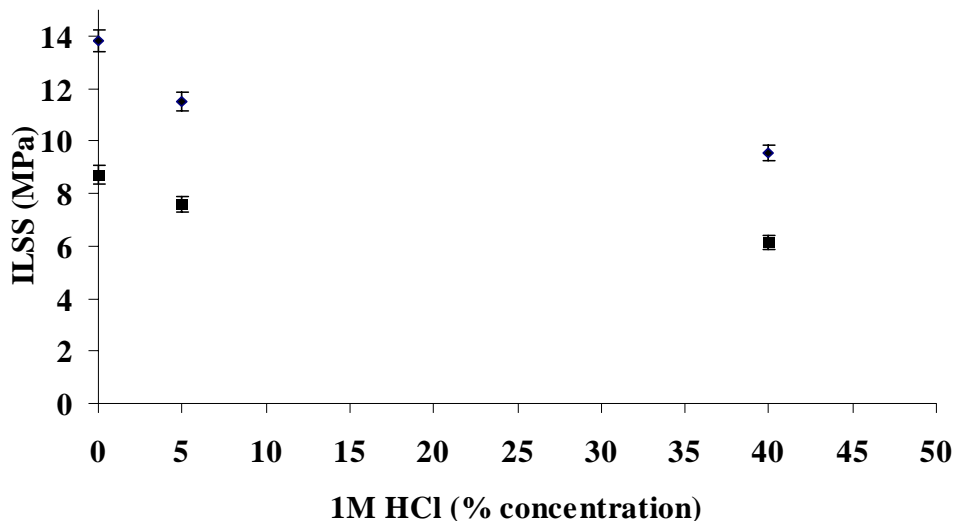


Figure 1: Variation of Interlaminar Shear Stress (ILSS) with the concentration of 1 M HCl acid solution at crosshead speeds of 2 mm/min (◆) and 500 mm/min (■)

Stress corrosion cracking depends mainly on the amount of glass fibres exposed which depends on the polymer matrix [8]. Here the stress corrosion cracking occurs in presence of residual thermal stresses or external applied stress and hydrogen ions. These residual thermal stresses are generated while fabrication which is controlled by the cooling rate. This causes a temperature gradient across the radius of the fibre having lowest temperature at the surface and highest at the centre. These stresses affect the fracture morphology of the glass fibres (figure 2). SCC involves planar fracture with three stage process when the stress applied externally in which first stage refers to single fibre transverse crack initiation, second stage refers to crack growth spreading to neighbouring fibres through the matrix and the third stage is the stable propagation of the crack across the specimen resulting in failure. The number of nucleation sites will be more when the applied stress is more [11].

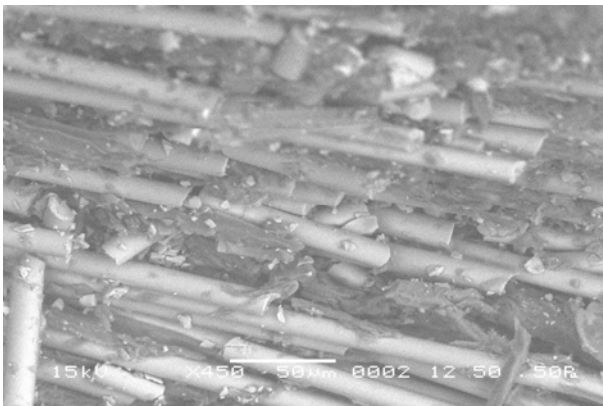


Figure 2: SEM micrograph showing transverse cracks in glass fibres

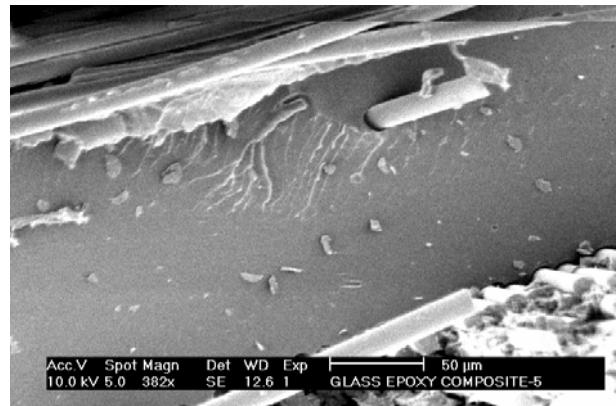


Figure 3: SEM micrograph of as-cured sample showing no degradation of matrix

The acid is believed to reach the fibres by flowing through microcracks, crazes or similar voids in the polymer matrix, which occur as a consequence of the stress intensification ahead of the crack tip of a growing stress-corrosion crack. Once a crack has started through the fibres then cracks appear in the matrix (figure 5).

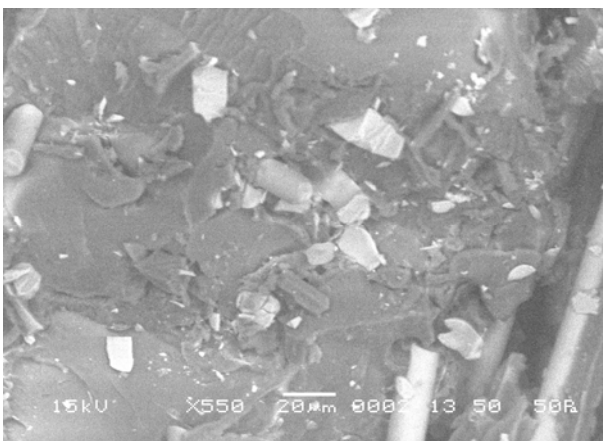


Figure 4: SEM micrograph of glass/epoxy sample after treating with 0% HCl acid showing very less degradation due to water ingress

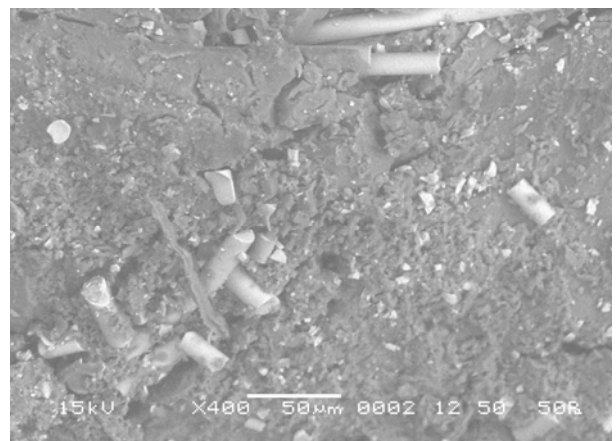


Figure 5: SEM micrograph of glass/epoxy sample after treating with 5% HCl acid showing microcrackings and crazes due to acid attack

Figure 3 and figure 4 shows no presence of severe microcrackings while the figure 5 shows small microcrackings and crazes which forms a network path in the polymer matrix through which the acid flows. This results in rapid transport of acid to the surfaces of the unbroken fibres. Diffusion of acid through the matrix then becomes a second order transport process, as acid is directly

introduced to the surface of intact fibres. Cracks can then grow more quickly and the strength decreases. Cracking also accelerates because the decreasing cross section raises the mean stress on the intact fibres.

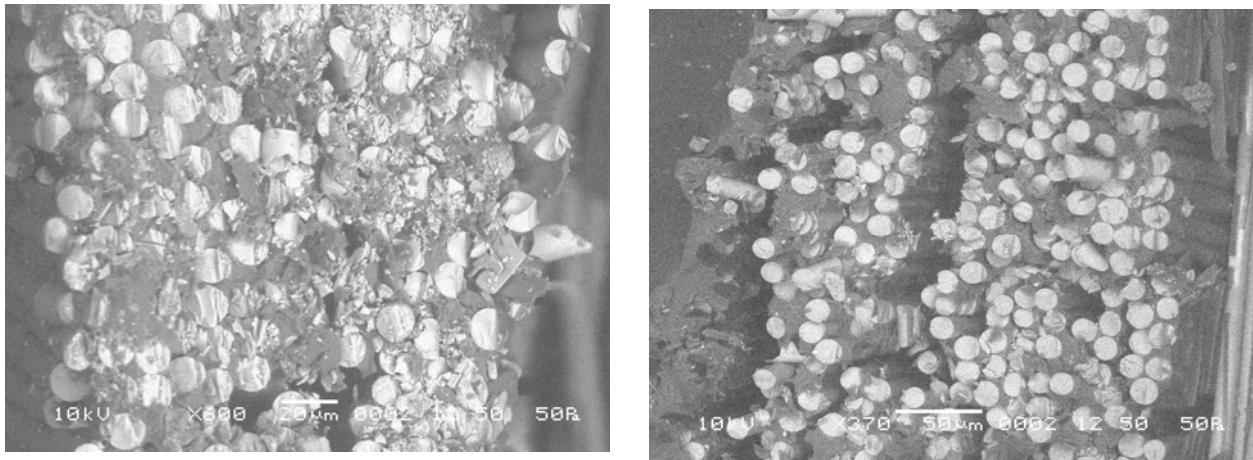
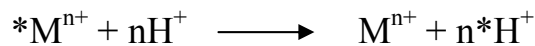


Figure 6: SEM micrographs of samples treated with (a) 5% HCl (b) 40% HCl concentrated solution showing increase in amount of matrix crackings and debonding at fibre/resin interface with increase in concentration

Figure 6 shows that as the concentration increase the amount of microcrackings and crazes increases which makes easier acid flow through more available paths in the polymer matrix and hence degradation of glass fibres will be more. HCl acid would digest the binder materials and debond the fibre from the matrix. This effect decreases as the concentration decreases. The glass fibres were reported to be chemically deteriorated which is related to an ion exchange process or leaching process wherein the cations, such as sodium, calcium and aluminium, in the glass are replaced by hydrogen ions in the acid [12]



Where the ions denoted by an asterisk are associated with the glass phase and M^{n+} is a cation. So the glass fibres having more of these ions in their chemical constitute are more susceptible to degradation. Hence, E-glass fibres are more prone to acid damage as they contain nonsiliceous oxides of calcium, aluminium (CaO , Al_2O_3) in major amount [13]. The smaller size of the hydrogen ion relative to the cations that are replaced results in tensile stresses in the glass fibre, and it is these stresses that lead to the propagation of cracks to the interior and failure of the specimen results. The Cl^- ions released after the leaching process diffuses quickly where the matrix has voids and reacts with the various components in the polymer, weakening the bond strength [14]. This leads to microcracking and fracturing which adversely affects the matrix and fibre/matrix interfacial bond.

4. CONCLUSIONS

It can be concluded that the glass/epoxy composites are prone to acid damage. It was reported that the ILSS values decreases as the concentration of acid increases. This can be attributed to the degradation of glass fibres by leaching and generation of microcracks in the matrix due to the diffusion of Cl^- ions which weakens the interfacial bond. Also the laminates are observed to be

loading rate sensitive and the moisture ingress into the laminates decreases as the concentration of acid increases due to the bulky nature of HCl which impedes the diffusion of water.

5. ACKNOWLEDGEMENTS

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