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Performance of externally bonded GFRP sheets on concrete in tropical environments. Part II: Microstructural tests

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Abstract

In the first part of the paper the structural scale tests on the synergistic effects of moisture, temperature, alkalinity and stress level on the performance and durability of GFRP sheet bonded externally on concrete have been discussed. This part describes the microstructural studies to find out the nature, quantum and mechanism of deterioration in the conditioned sheets. Micrographic investigations were carried out using a scanning electron microscope (SEM) to visualize the changes in the microstructure. The other tests are energy dispersive X-ray analysis (EDX) and inductively coupled plasma mass spectrometry (ICP-MS) to determine the chemical changes in the composite.

Keywords: Glass fiber reinforced polymer; Bonded sheets; Degradation; Microstructural tests

1. Introduction

In the first part of the paper the structural scale test of GFRP sheets bonded to concrete under tropical environment was discussed. The structural tests revealed that although the conditioned beams failed at higher loads than the fresh beams the mode of failure shifted to sheet rupture from sheet debonding. The loss in tensile strength of conditioned sheets was as high as 36% in nine months. Another interesting point was that the strength of the sheets increased due to outdoor conditioning. In this part, the microstructural tests done to investigate the reasons for such behavior are reported.

At present no standard durability test method exists and this makes the results obtained by different researchers difficult to compare. As a result, researchers report degradation of the GFRP rebars or sheets varying from 10% to 53% depending upon the parameters selected for durability tests viz. alkalinity, moisture, temperature, stress and duration of the tests [1–18]. The investigators, however, agree on the susceptibility of the glass fibers to alkali attack and this mechanism has been highlighted in all durability tests. The chemical composition of E-glass is SiO_2 54.3%, Al_2O_3 & Fe_2O_3 15.2%, CaO 17.3%, Na_2O/K_2O 0.6%., B_2O_3 8% to 10% [19–21]. In an alkaline environment glass fiber is known to be attacked by hydroxide ions causing hydrolysis according to Eq. (1) [22,23]

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}+\mathrm{OH}^- \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH(solid)} + \overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}^-\mathrm{(solution)} \quad (1)$$

As concrete represents a highly alkaline environment base hydrolysis of epoxy can be expected. The SEM was employed to obtain micrographs showing the nature and quantum of damages in the conditioned sheets. In the present investigations the SEM images have been quantified by EDX, an accessory to SEM, which allows simultaneous non-destructive elemental analysis of the sample at a selected spot of about 2 μm size. EDX test was performed to find changes in chemical compositions at selected points

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in the sheets. Though X-ray diffraction (XRD) and X-ray fluorescence are preferred tests by metallurgists these did not yield clarity for the non-metallic substances like glass and polymer. Inductively coupled plasma mass spectrometry (ICP-MS) is a very powerful tool for trace (ppb-ppm) and ultra-trace (ppq-ppb) elemental analysis. This test was done to identify the chemical changes in the conditioned sheets.

2. Experimental investigations

2.1. Alkalinity

The alkalinity of concrete is quantified in the beginning. Three beams were cast and cured in water for 28 days. The beams were allowed to dry for one month. Then parts of beams were crushed very fine. The sample passing 300 micron sieve and retained on 150 micron sieve was taken for alkalinity test. The powder was diluted in water in 1:1, 1:5 and 1:10 ratio. The pH values were 12.25, 12.182 and 12.05, respectively. The actual pH value at the hydrates level is expected to be higher than these values [1]. It may be noted that in the concrete mix ordinary Portland cement was used without any other cementitious materials namely fly ash, silica fumes, granulated ground blast furnace slag etc. As a result, the pH of concrete is rather high and the glass fiber may be susceptible to alkali attack. The mix design used here is commonly used in this part of the world [24]. To study the conditions of the exposed sheets the SEM and the EDX have been employed.

2.2. SEM and EDX tests

2.2.1. Specimens

Specimens of approximately 10 mm wide and of equal length were cut out from sheets along and across the direction of fiber. Four of these were bonded back to increase investigation areas in the sheets as shown in Fig. 1. The surface was polished using sand paper having number 300, 600, 800 and 1200 in sequence. Afterwards fine polishing was done using emery cloth and a wet polishing agent. As GFRP is a non-conducting material, the polished specimens were gold coated. A minimum of six samples for each conditioned sheet were prepared for the tests. JSM-840A scanning electron microscope was used to obtain the micrographs.

2.2.2. Fresh sheet

The micrograph of original sheet composite is given in Fig. 2. The magnification scale, 100 μm here, is presented by a marked line length on the micrograph. The fibers within the matrix are fairly distributed. There is no clustering of fibers. To find microcracks, air bubbles and defects in the fresh sheet composite it was magnified 878 times (Fig. 3). Here it can be seen that there are no air bubbles and micro cracks in the matrix. It can also be seen in Fig. 3 that the fibers have different diameters and average diameter is approximately 20 μm. The fiber volume fraction was estimated at 17.6%. The volume fraction is low as the epoxy thickness is more i.e. 1.647 mm over 0.353 thick sheet. Composites were prepared by hand lay up. It can be concluded that the epoxy has wetted the fiber uniformly and spread evenly on the sheet. Thus the sheet composites used for external bonding on concrete were free from any defects and the fibers were fairly dispersed in the matrix.

Fig. 1. Specimen preparation: 4 layers of sheets bonded for gold coating.

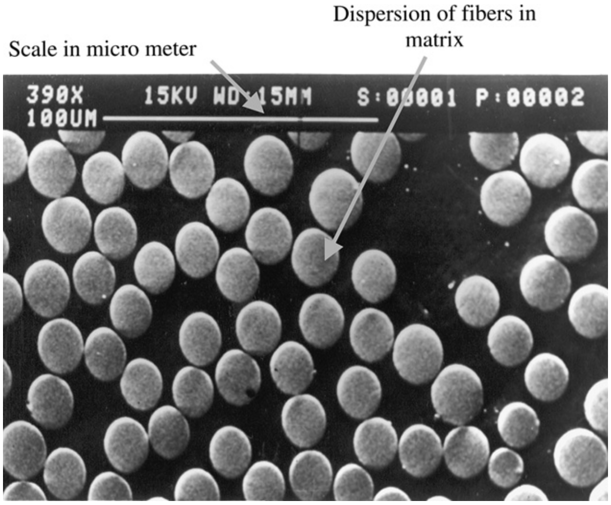


Fig. 2. Distribution of E-glass fibers in original GFRP sheet (X390: magnified 390 times and showing a line scale of 100 μm).

2.2.3. Conditioned sheets

The sheets stripped out of the beams after failure have been investigated. It may be noted that the conditioned portion of the sheets ruptured at failure. The ruptured sheets have been investigated in all the following experi-

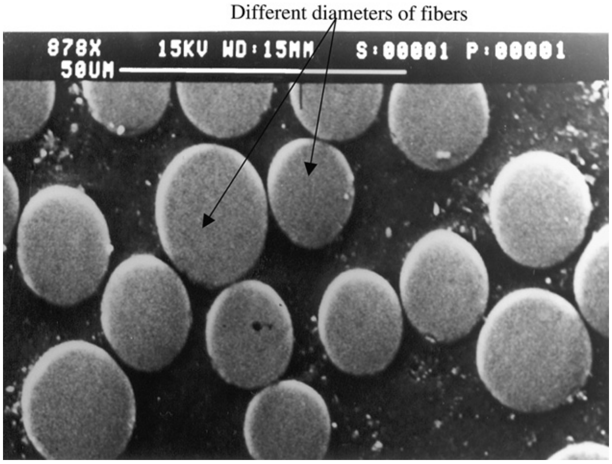


Fig. 3. Size of fibers and absence of defects in original sheet.

ments. As a result, the images depict the conditions of the portions that are affected the most due to the exposure.

2.2.3.1. Sheet conditioned for three months. Samples have been made out of the sheets removed from the three months conditioned beams. The portions of the sheets near the central crack formation of the beams have been selected for the tests. Fig. 4 shows the magnified (895 X) view of the sheet fibers near the surface of the sheet. It can be seen that only a few fibers have degraded. The fibers seem to have segregated from the matrix. The magnification (552 X) is reduced to show the distribution of damage to the matrix in Fig. 5. The matrix appears to have disintegrated all through the scanned micrograph. Most of the fibers are intact in the scanned specimens. In three month of conditioning the matrix is clearly damaged. The reduction in the strength of the sheet was around 20.32%. All the specimens were scanned for damages. The major portions of the areas in the all the four sheet specimens remained unaffected. Only a few spots appeared to be damaged and they were local in nature. At the locations of degradation the matrix got damaged first and subsequently the fibers disintegrated.

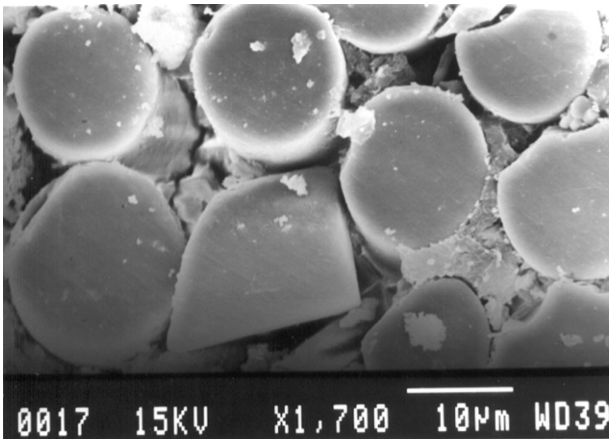


Fig. 4. Damages in the fibers of sheet (SB3-470).

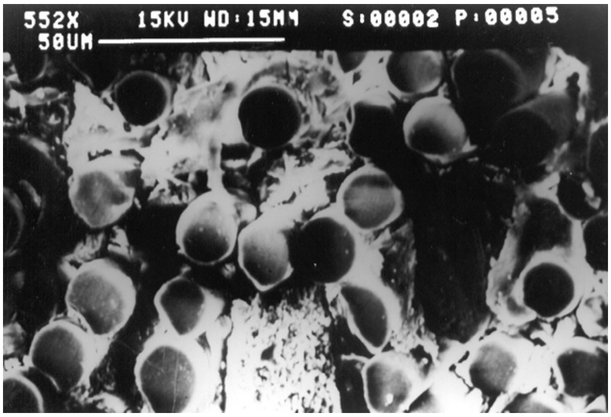


Fig. 5. Enlarged view of damages in the matrix of sheet (SB3-470).

2.2.3.2. Sheets conditioned for six months. The cross section of the sheet after six months of conditioning is magnified (1070 X) to view the damages (Fig. 6). The maximum size of the voids in the damaged matrix is around 40 μm. The fibers are getting disintegrated in larger numbers. A few fibers appear to have completely dissolved making voids in the matrix. An enlarged view in Fig. 7 (1530 X) near fibers shows that matrix is progressively getting damaged. One fiber is completely disintegrated in the matrix. The matrix around other fibers is slowly getting damaged. The fibers are still intact here. It can be concluded that in the sheets first the matrix gets damaged and then the fibers in it slowly disintegrate. The surfaces around the fibers are getting segregated and this is likely to affect shear transfer between the matrix and the fibers. A few spots where matrix did not segregate the fibers also remained unaffected. Gradual disintegration of the fibers in the matrix can be seen in Fig. 8. The fibers are getting disintegrated in flakes. The total strength reduction in the sheet composite was around 33% due to localized damage to large numbers of fibers.

2.2.3.3. Sheet conditioned for nine months. The cross section of the ruptured sheet is magnified (280 X) to assess the

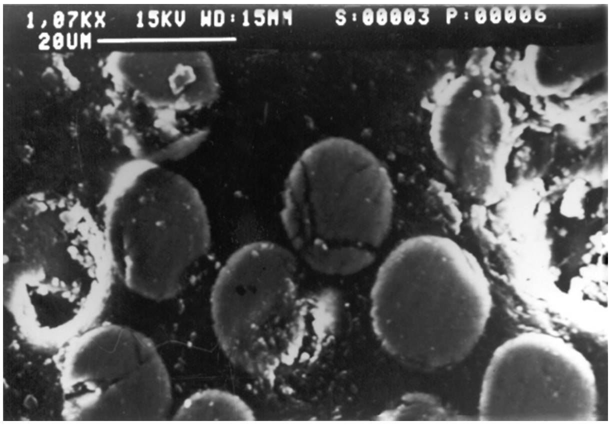


Fig. 6. Nature of damages in the sheet (SB6-470).

Fig. 7. Enlarged view of damages in the matrix of sheet (SB6-470).

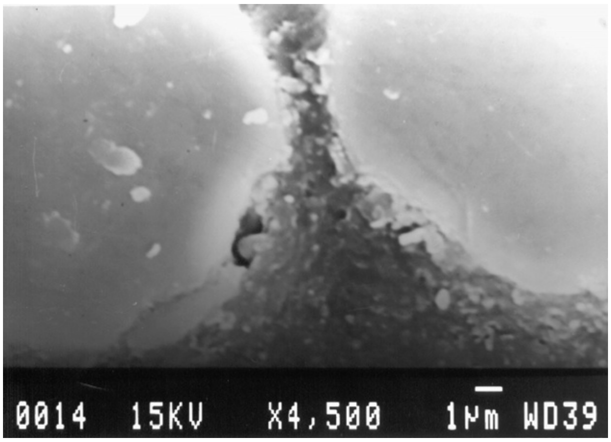


Fig. 8. Enlarged view of progressive damages in the fiber and the matrix of sheet (SB6-470).

comparative damages in the matrix and fibers near to the rupture (Fig. 9). The reduction in the strength of the sheet was 36%. In the specimen all the fibers have snapped and no pull out of the fibers could be seen due to damages at surfaces between fibers and matrix. A magnified view showing the damages in the matrix along the length of fibers is shown in Fig. 10. The matrix gets damaged along the fibers which are around 250–300 μm in length in the micrograph. This damage does not prevent the fibers to take load till rupture of individual fibers. The fibers reduced in cross section in the damaged zones. The micrograph showing the localized nature of damages to fibers and matrix is given in Fig. 11. In the damaged zone both matrix and fibers have completely disintegrated. It may be noted that the fibers and matrix next to the damaged zone is totally unaffected due to conditioning. If the matrix is not damaged the fibers remain totally unaffected due to conditioning. Hence, the matrix plays a vital role in protecting the fibers and enhancing the life of the sheet composite on concrete. The sheets after nine months of conditioning absorbed moisture in a short span of time. This is mainly because the matrix has disintegrated completely resulting in powdery structure which absorbs moisture instantly.

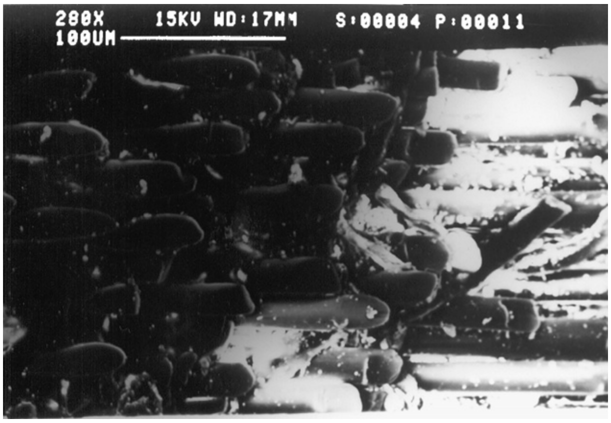


Fig. 9. Micrograph showing rupture of conditioned sheet (SB9-470).

2.2.3.4. Sheet conditioned for 12 months outdoors. The specimens were prepared from the sheets which were removed from the beams weathered in natural environment for 12

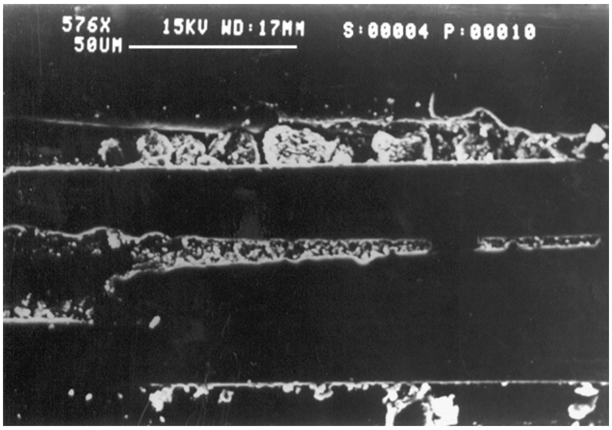


Fig. 10. Micrograph showing damages in matrix along the fibers of conditioned sheet (SB9-470).

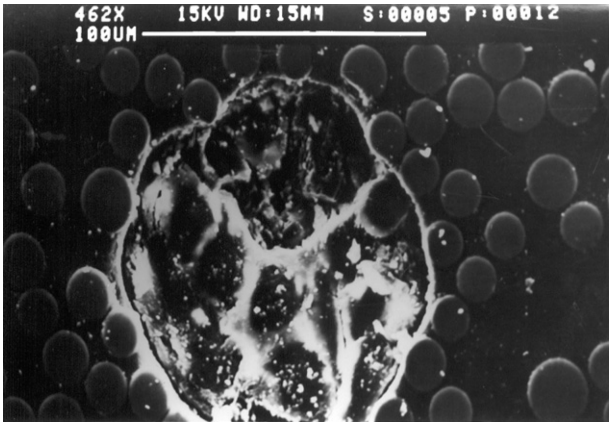


Fig. 11. Micrograph showing localized damages of fibers and matrix of conditioned sheet (SB9-470).

months. The sheets did not loose their strength but surprisingly showed an increase of about 6%. Most of the areas in the scan showed no sign of degradation of both matrix and fibers as seen in the Fig. 12. Very few spots could be located where damages could be observed as shown in Fig. 13. Here the matrix has started disintegrating with partial or negligible damages to the fibers. The increase in the strength of the sheet composite was 29.5% in six months of outdoor conditioning in comparison to 6% in nine months of conditioning outdoor. This can happen only when the strength of the epoxy as a whole increases due to cross linking [21] in outdoor conditioning. The over all strength of composite sheet reduced due to local disintegration of the matrix and fibers with time. More outdoor conditioning time is likely to deteriorate the strength of the sheet. Eight specimens were scanned and it was seen that the nature of the damage is same but quantum of damage is negligible at 12 months.

The highlights of SEM tests are:

In three months of accelerated conditioning the matrix gets damaged with marginal damages to fibers.

In six and nine months of accelerated conditioning both the matrix and the fibers are damaged. The damages to fibers resulted in reduction of the tensile strength of the sheet composite.

Due to six and 12 months outdoor conditioning both the matrix and fibers remain in fairly good condition in comparison to accelerated conditioning.

The matrix gets damaged first and then the exposed fibers get disintegrated.

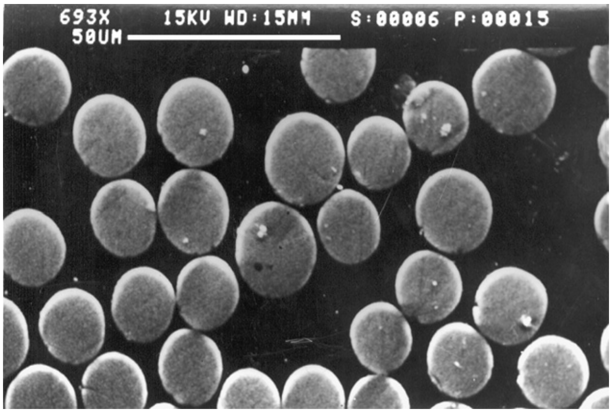


Fig. 12. Micrograph of undamaged area (ASB12-470).

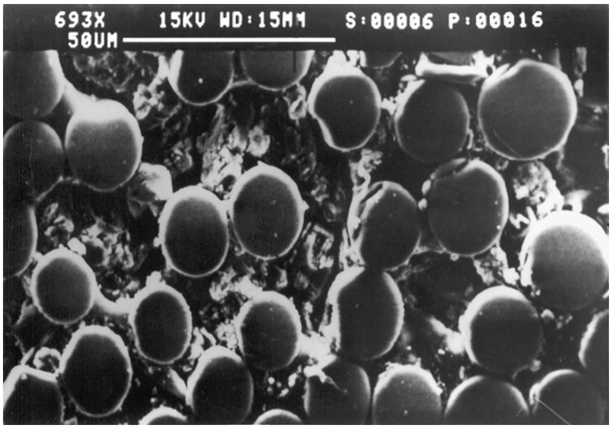


Fig. 13. Micrograph of damaged area of specimen taken from sheet bonded to conditioned beam ASB12-470.

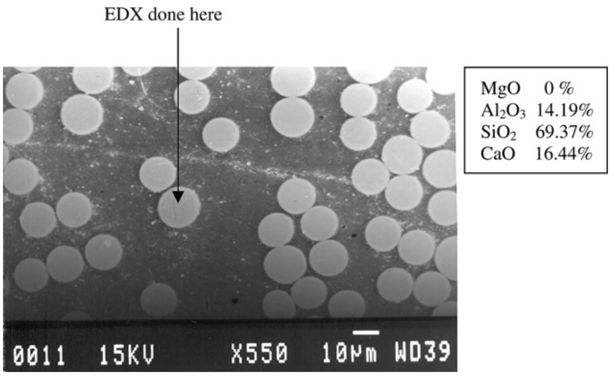
SEM revealed the nature and quantum of degradation of sheet. It is also seen that the glass fiber is corroding locally at a few locations and its cross section is reduced there. EDX test was done on sheets to assess chemical change that causes these damages.

2.3. Energy dispersive X-ray analysis (EDX)

2.3.1. EDX on undamaged E-glass fiber

The SEM tests have shown that the epoxy matrix and E-glass fibers get damaged due to accelerated conditioning. When an incident electron beam hits the atoms of the sample, secondary and back scattered electrons are emitted from the sample surface. The X-rays emitted from the sample atoms are characteristic in energy and wavelength to the element of the parent atom which is used to identify and quantify the elements. The focus is to find if any changes in chemical composition takes place in the E-glass fibers. To evaluate the chemical changes in the specimens EDX was done on a few critical samples. Both the locations where SEM revealed damage and where there was no damage were selected for the test.

To compare the chemical composition of E-glass fibers EDX was done at the centre of the E-glass fiber. The samples were taken from the fresh sheet and sheet conditioned in tank for three months and nine months, respectively in the tank at 60 °C. Chemical compositions obtained by EDX for SB0, SB3 and SB9 have been given along with the micrographs as shown in Figs. 14a–14c. The silica content in E-glass fiber is 69.37%, 70.26% and 67.70%. The average silica content is 69.11% with a standard deviation



MgO 0 %
Al_2O_3 14.19%
SiO_2 69.37%
CaO 16.44%

Fig. 14a. EDX done on fiber of specimen taken from sheet bonded to fresh beam (SB0-470).

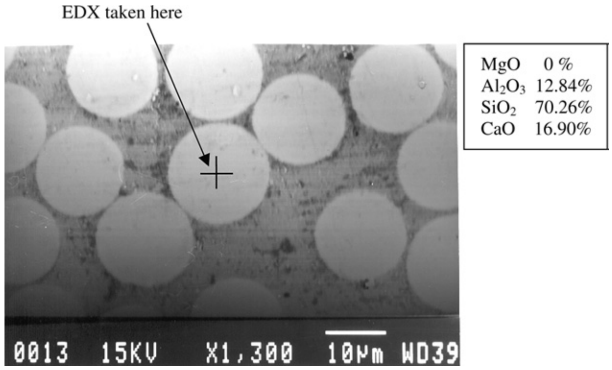


Fig. 14b. EDX done on undamaged fiber of specimen taken from sheet bonded to conditioned beam SB3-470.

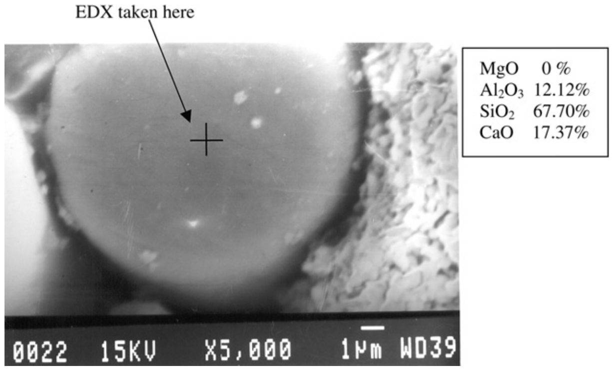


Fig. 14c. EDX done on undamaged fiber of specimen taken from sheet bonded to conditioned beam SB9-470.

of 1.29. The average calcium content is 16.9% with a standard deviation of 0.465. Thus there are no substantial chemical changes in the fibers that are not attacked.

2.3.2. EDX on damaged areas

The EDX test was also done in the damaged zones. The epoxy, matrix, is an organic substance. Hence, it becomes easy to assess the elements present in the damaged zones. The EDX test in Figs. 14d and 14e gives the average composition of silica as 12.15% and calcium as 0.58% in comparison with average values of 69.11% and 16.9% in the undamaged fiber (Figs. 14a(a)–(c)). Thus, silica and calcium content in the damaged area is very much less than that in the undamaged fiber. This is only possible if the molecular structure of the fiber gets broken wherever it is coming in contact with some degenerating agent. This agent displaces silica and calcium from the healthy fibers. EDX taken outside the damaged fiber showed calcium as 100 %. The free calcium can only originate from alkali. The alkali, $Ca(OH)_2$, is formed due to hydration of cement and is in free form in the voids of the concrete. This suggests that the sheet matrix is penetrated by the alkali.

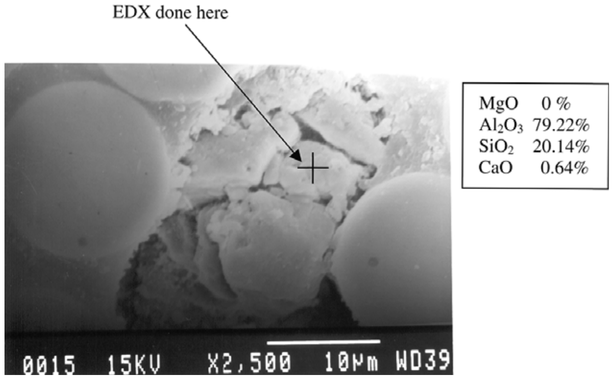


Fig. 14d. EDX done on damaged area of specimen taken from sheet bonded to conditioned beam SB3-470.

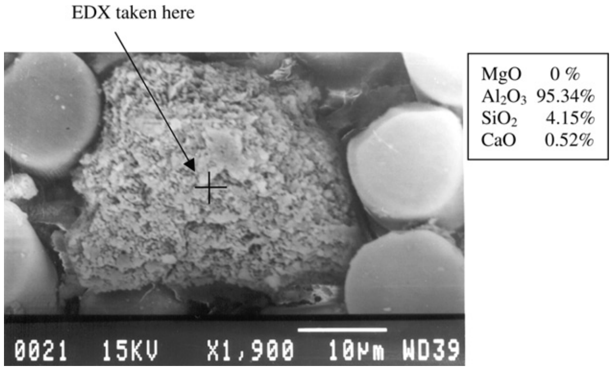


Fig. 14e. EDX done on damaged area of specimen taken from sheet bonded to conditioned beam SB9-470.

The EDX test results can be summarized as follows:

No chemical changes take in the undamaged E-glass fibers with conditioning.
Silica and calcium get displaced from the damaged fibers.
Free alkali is absorbed within the sheet matrix with conditioning.

However, this test did not give the reason for the molecular break down of the E-glass fiber. Hence, ICP–MS test was conducted to identify the chemical inducing molecular break down of the E-glass fiber.

2.4. ICP-MS test

The objective of this test is to find free silica and alkali in the specimens and the reason for it. In this test the elements are extracted into a solvent for analysis. The original sheet and sheet cut out from the nine months conditioned beams were pounded and powdered separately. The powdered specimens were taken up for further investigations to find elements present in the GFRP sheet.

To identify the liberated compounds in the sheet (Eq. (1)) water extract was taken up for further investigation. 25 g of powdered sample was boiled in distilled water in a Teflon beaker for nearly 3 h. Forty milliliter of distilled water was reduced to 20 ml. This water extract was used for the ICP-MS test. The results are tabulated in Table 1.

Table 1
ppm of various elements in water extract

Sample No.	Si	Al	Mg	Ca	B	Na	K
E-glass sheet (water extract)	54.77	2.98	29.46	113.01	3.07	<0.1	<0.1
E-glass sheet nine months conditioning	105.21	ND	22.13	172.15	4.11	<0.1	<0.1

It is seen that the free silica in original sheet specimen was 54.77 ppm where as in conditioned specimen it was 105.21 ppm. The increase is around 92%. This extra silica gets liberated from E-glass fiber.

Again in Table 1 it is seen that free calcium in the original sheet was 113.01 ppm where as in the conditioned sheet it was 172.15 ppm. The increase in calcium is 52%. This high quantity of calcium can only come from alkali $Ca(OH)_2$. This alkali is liberated from the concrete due to hydration of cement and clearly it is getting absorbed in the conditioned sheet with time. Thus the chemical responsible for break down of molecular structure of E-glass is $Ca(OH)_2$ or alkali.

The ICP-MS results showed that alkali is getting absorbed in the sheet or in the matrix itself. As the fibers are protected by the matrix, matrix degradation must precede the damage of fiber. This is only possible if the epoxy matrix is breaking down due to hydrolysis by alkali. It can be concluded that due to the presence of the alkali, high temperature and stressing of sheets the epoxy disintegrated with conditioning time and failed to protect the E-glass fibers. E-glass fibers eventually degenerated due to alkali attack. Therefore, the conditioned sheets lost their tensile strength progressively by 13.9%, 20%, 33% and 36% in 1month, 3 months, 6 months and 9 months of conditioning. The test reveals that the present sheet is susceptible to environmental attack especially in hot and humid tropical conditions. The degradation is triggered by the deterioration in the matrix that allows the attack on the fibers. The matrix may have to be redesigned to develop a more durable composite.

3. Summary and Conclusions

The objective of the experiments was to visualize and identify the mechanism of degradation of sheet composites due to conditioning in tropical environment. With this view in mind microstructural tests were conducted.

The SEM on original sheet shows that there were no defects in the form of air bubbles and micro cracks which could form in the process of application of the epoxy coat. SEM tests also showed that sheets get damaged progressively due to conditioning. Damages in the form of voids can be seen in the micrographs. The voids are formed due to the degradation of the matrix. The fibers in the void get disintegrated with time resulting in loss of tensile strength of the sheet. Thus the matrix gets damaged first and then fibers get damaged due to the alkali. As per micrograph the matrix disintegrates substantially in nine months and at this stage the absorption of water in the matrix increased dramatically. The sheet composite degraded very little due to outdoor conditioning in 12 months.

Both EDX and ICP-MS test prove that no chemical composition change takes place in the unaffected portions of the fibers. SEM micrographs show the damages are scattered and localized in the sheets due to conditioning. This could be the reason why the sheets have not lost its stiffness despite losing its strength. However, change in modulus of elasticity of composite sheet depends also on thickness and properties of the conditioned or damaged epoxy as volume content of fiber is very low (17.6%).

The ICP-MS test on water extract of 12 month conditioned sheet shows large increase in the values of calcium (about 92%) and silica (about 52%) in comparison to the unconditioned specimens. This excess calcium can only come from the free alkali present in concrete. EDX also showed that at some points only calcium existed. The excessive silica can come only from the molecular break down of the E-glass fiber. This molecular disintegration is observed in the SEM micrographs. This displacement of Si from the molecular structure of E-glass fiber leads to collapse of the structure of the fiber. This takes places in the regions where the fiber comes in contact with alkali. The micrographs show the notching and etching of fibers with voids formation within the glass fiber. This test reveals that the matrix of the sheet must be redesigned to resist temperature, moisture, stress and alkalinity conditions of the tropical region.

The synergistic effect of alkali, moisture, temperature and stress has caused high degradation of the sheets. Stressing of sheets cracks the matrix. The moisture and alkali is able to penetrate the sheet through the micro cracks and also through diffusion in disintegrated matrix. Higher temperature increases the diffusion rate. The alkali has damaged matrix first and then the fibers.

If these sheets are to be used on concrete then suitable environmental reduction factor have to be used in the design depending upon the severity of alkali attack. More tests with different temperatures, alkalinity and pre-stressing stresses are required to build a model to predict the rate and quantum of damage to the fibers. Use of mineral admixtures such as ground granulated blast furnace slag (GGBS) and fly ash in concrete to control free alkali is an area of further research to improve the performance of the GFRP sheet bonded externally on concrete.

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