DURABILITY STUDIES OF FIBRE REINFORCED POLYMERS (FRPs) UNDER ALKALINE SOLUTION

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Abstract

For their several significant advantages, the composite structures are fast gaining their popularity as an effective structural component over their metallic counterparts. In recent years the glass fiber reinforced polymers (GRP), specially glass/epoxy composites are widely applied in several civil engineering applications ranging from seismic retrofit of columns and strengthening of walls, slabs, to new building frames and even bridges. It is also well known that there is a degradation of material property during its service life, as it is often subjected to environments with high temperature and humidity or having a sharp rise and fall of temperature (thermal spikes). The deterioration that occurs in FRP during the service life is in general, linked to the level of moisture that is absorbed. The absorption of moisture can be attributed largely to the affinity for moisture of specific functional groups of a highly polar nature in the cured resin. The absorption of moisture causes plasticization of the resin to occur with a concurrent swelling and lowering the glass transition temperature of the resin. In this work, the specimens were tested for their UTS, FS and ILSS for every 120 hours intervals and studied degradation pattern of Carbon FRPs (CFRPs) when exposed to alkaline solution. Thus, the composite system that absorbed more moisture (Iso-polyester/carbon) showed poor mechanical properties. The percentage drops in mechanical properties is due to moisture absorption which lead to swelling in composites as well as delamination between fiber and matrix. Alkali environment causes CFRPs embrittlement and micro cracks of resin, longitudinal and transverse mechanical properties show a significant decrease. Carbon/epoxy proved superiority over vinylester/carbon and Iso-polyester / Carbon, in terms of lower values of degradation in UTS, Flexural Strength and ILSS specimens

Keywords: Alkaline solution, FRP, SEM, Degradation Studies

I. INTRODUCTION

A reinforced plastic or composite is a polymer resin matrix combined with a reinforcing agent or agents. The reinforcement improves strength and stiffness properties, compared to the neat resins. Almost every type of thermoplastic or thermosetting resin can be reinforced. For many applications it is possible to increase the strength of plastics by means of reinforcement. A reinforced plastic consist of two main components: a matrix, or resin used as the base binding material, which usually takes the form of fibers. The function of the matrix is to support the fibers and transmit the external loading to them by shear at the fiber- matrix interface. Plastics are very suitable in this context since they are easily formed into shape, provided that a good interfacial bond is achieved. A wide variety of combinations of fibers and matrix are used in practice. The major matrices are epoxies, polyurethanes, phenolic and amino resins, bismaleimides and polyamides. The important reinforcements are metal powders, clay, carbon black and fibers such as carbon, aramid, glass etc.

II. EXPERIMENTAL STUDIES

The materials used in the study are carbon /epoxy, carbon / vinyl ester and carbon/isopolyester.

The technique used to prepare the composite is called 'Wet Hand Lay-Up' process and were fabricated with the resin: fiber composition of 35:65. The ingredients used to fabricate epoxy composite are Carbon fiber sheet, Epoxy Resin, Hardener, Cutter, Weighing machine, Mylar sheet, Teflon mould.

III. ALKALI SOLUTION PREPARATIONS AND IMMERSION

Alkali solution was prepared by adding 1.4% KOH, 1% NaOH, 0.16% $Ca(OH)_2$, and distilled water. The solution checked for pH using pH meter and it found to be 13.5

Table 1. Proportions of Hydroxides used for preparation of alkaline solution.

Sl.No.	Hydroxide	Quantity (g/litre water)
1	KOH	14
2	NaOH	10
3	$Ca(OH)_2$	1.6

Table 2. Alkali absorption of neat casting at RT

No. of hr of exposure	Epoxy	Vinyl ester	Isopolyester
0	0	0	0
120	0.37	0.3	0.308
240	0.46	0.37	0.5
360	0.48	0.43	0.56
480	0.5	0.42	0.583
600	0.48	0.37	0.585

Table 3. Alkali Absorption of neat casting at 70°C

No. of hr of exposure	Epoxy	Vinyl ester	Isopolyester
0	0	0	0
120	0.45	0.4	0.5
240	0.531	0.472	0.609
360	0.56	0.5	0.627
480	0.531	0.513	0.62
600	0.549	0.54	0.64

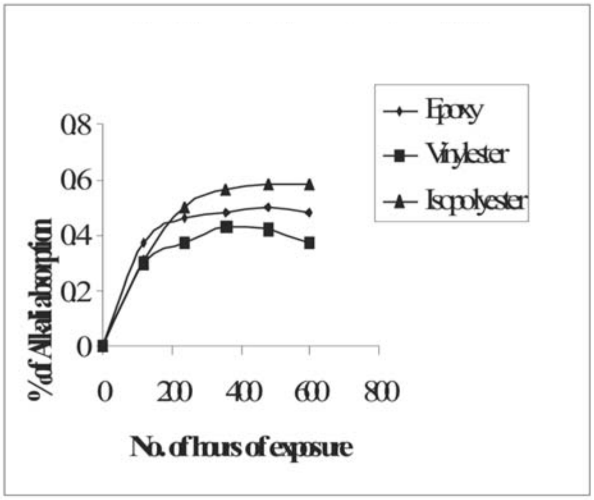


Fig. 1. Alkali absorption of neat casting at RT

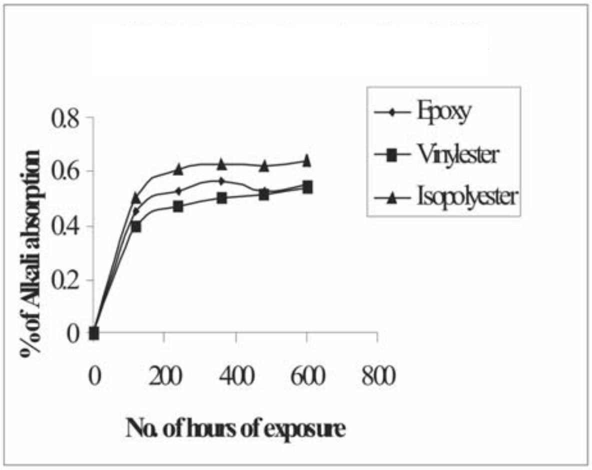


Fig. 2. Alkali absorption of neat casting at 70°C

Table 4. Alkali absorption of CFRP at RT

No.of hr of exposure	Carbon-Epoxy	carbon -Vinylester	carbon -Isopolyester
0	0	0	0
120	1.06	0.95	1.2
240	1.13	1.05	1.3
360	1.11	1.08	1.37
480	1.14	1.1	1.37
600	1.08	1.02	1.38

Table 5. Alkali absorption of CFRP at 70°C

No. of hr of exposure	Carbon-Epoxy	carbon -Vinylester	carbon -Isopolyester
0	0	0	0
120	2	2.24	2.64
240	2.08	2.28	2.84
360	2.04	2.36	3
480	2.16	2.44	3.12
600	2.58	2.44	3.12

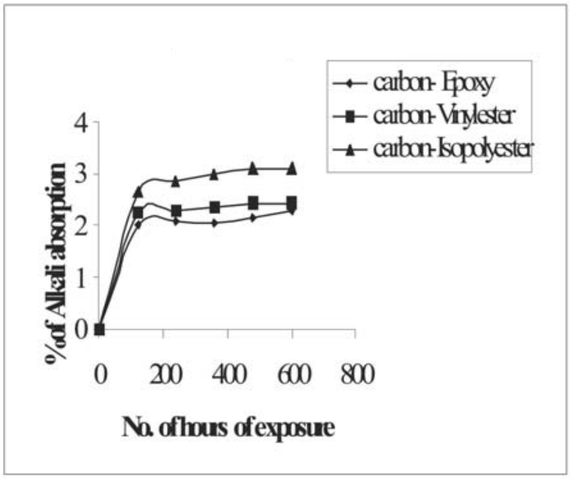


Fig. 3. Alkali absorption of CFRP at 70°C

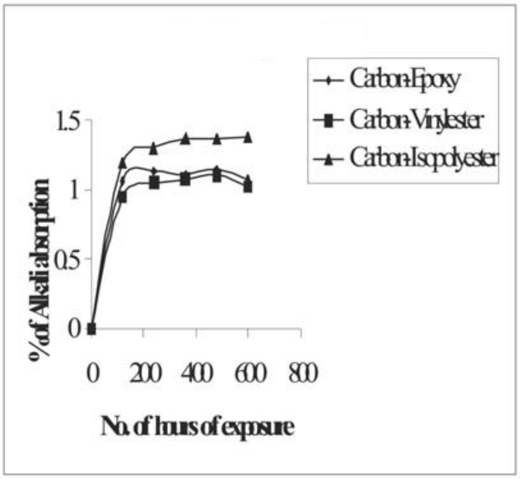


Fig. 4. Alkali absorption of CFRP at RT

IV. DEGRADATION STUDIES

The flexural strengths of the specimens were determined for different alkali exposure durations using the three-point bending test as per ASTM-D790.

Table 6. Degradation of Flexural strength at T = 70°C

No. of hr of exposure	Carbon-Epoxy	carbon -Vinylester	carbon -Isopolyester
0	834.452	432	370
120	765.92	380	304
248	732	348	264
365	684	320	232
480	648	300	216
600	636	294	208

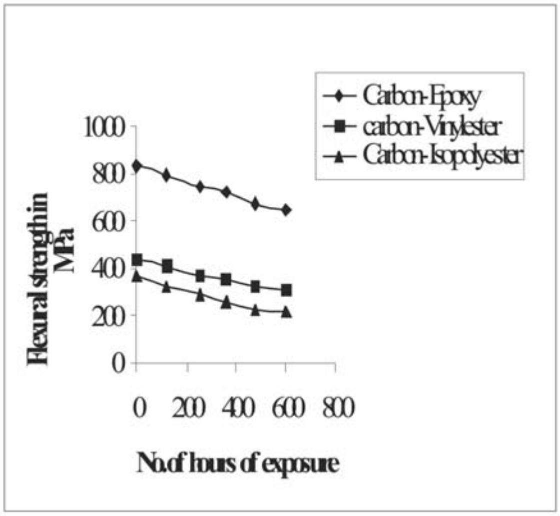


Fig. 5. Degradation of Flexural strength atRT

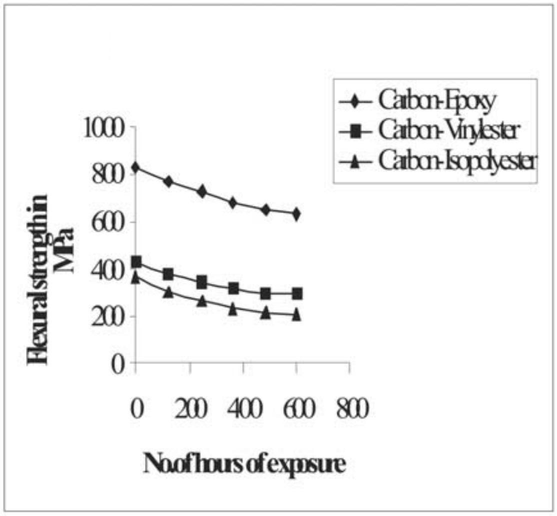


Fig. 6. Degradation of Flexural strength at T = 70°C

Table 7. Degradation of Ultimate tensile strength at T = Room temperature (RT)

No. of hr of exposure	Carbon-Epoxy	carbon -Vinylester	carbon -Isopolyester
0	508.014	358.666	295.183
120	480	340	251
240	463	317	223
360	440	300	200
480	424	291	186
600	407	283	180

Table 8. Degradation of Ultimate tensile strength at T = 70°C

No. of hr of exposure	Carbon-Epoxy	carbon -Vinylester	carbon -Isopolyester
0	508.014	358.666	295.183
120	468	336.667	256
240	446	314	225
360	430	298	203
480	415	273	180
600	393	260	172

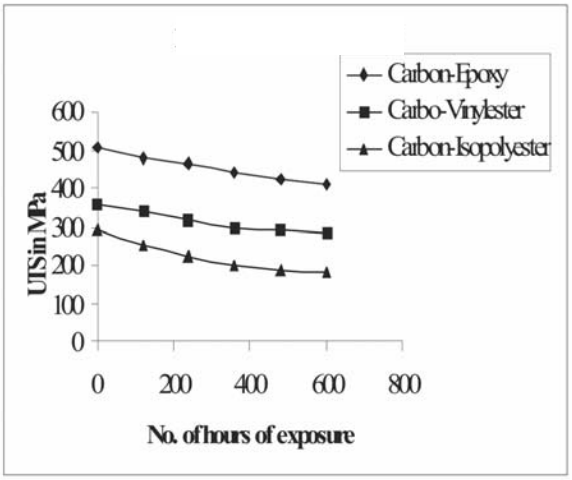


Fig 7. Degradation of UTS at RT

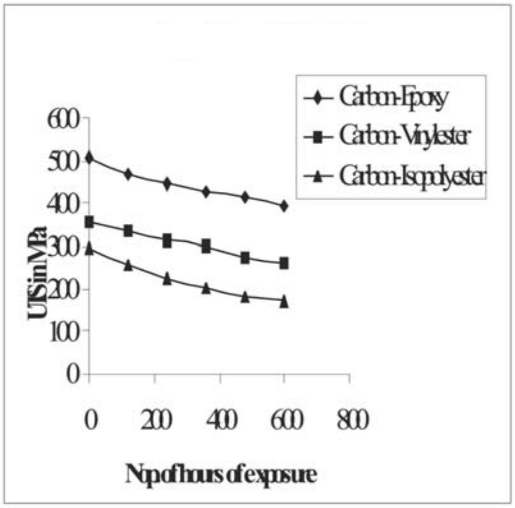


Fig 8. Degradation of Ultimate tensile strength at T = 70°C

V. INTER LAMINAR SHEAR STRENGTH

Three-point bend test was carried out to determine the Inter Laminar Shear Strength (ILSS) values of the specimens in accordance to ASTM D2344.

Table 9. Degradation of Inter laminar shear strength at T = Room temperature (RT)

No. of hr of exposure	Carbon-Epoxy	carbon -Vinylester	carbon -Isopolyester
0	51.2396	22.4003	16.7829
120	49.5	21.3327	15.7743
240	49	20.9263	15.191
360	48	20.6755	14.6753
480	47.1	20.1972	14.2338
600	45.7	19.9684	14.0867

Table 10. Degradation of Inter laminar shear strength at T = 70°C

No. of hr of exposure	Carbon-Epoxy	carbon -Vinylester	carbon -Isopolyester
0	51.2396	22.4003	16.7829
120	50	21.7016	15.1
240	48	20.921	14.7
360	46.6	20.1743	14.3
480	45.3	19.2967	13.4
600	44	19.009	12.9

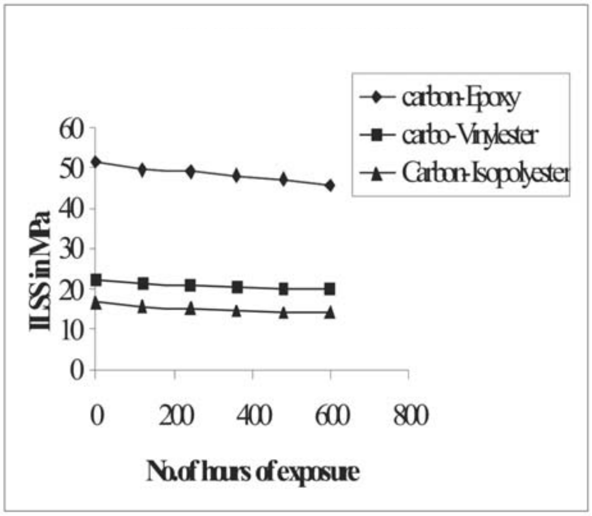


Fig. 9. Degradation of ILSS at RT

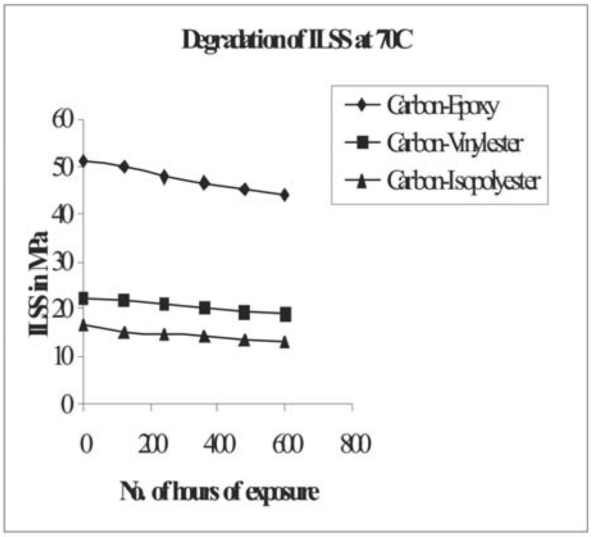
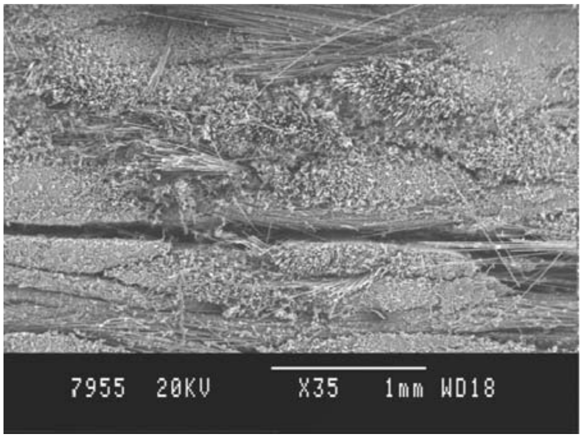


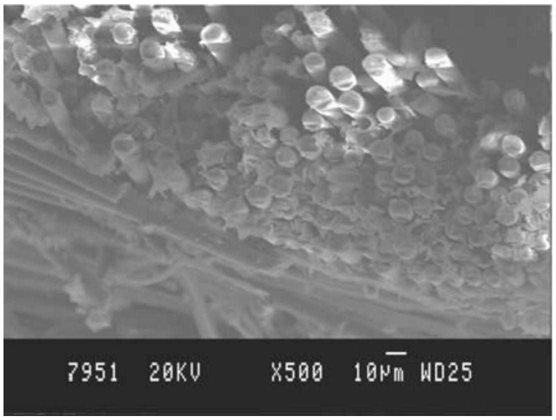
Fig. 10. Degradation of Inter laminar shear strength at T = 70°C

VI. SCANNING ELECTRON MICROSCOPE STUDIES

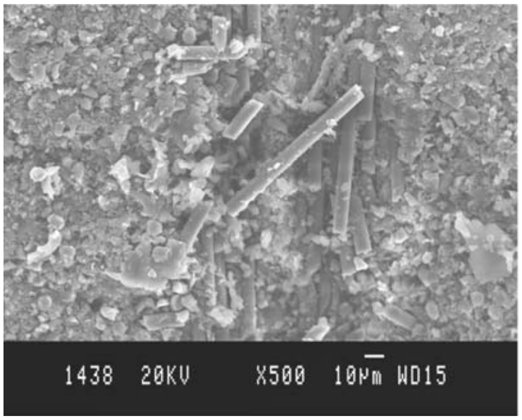
Scanning electron microscopy (JEOL, Japan, JSM 840A) was employed to characterize the tensile fractured specimens before and after alkali exposure. The effect on the interface region after the alkali exposure and its changes in the mechanical property analysis before and after the exposure can be studied using SEM. The scanning electron micrographs provide good evidence of the binding between the resin and the fiber before and after the exposure. The exposure to alkali environment has lead to a reduction in mechanical properties of specimens by the degradation in the fiber matrix interfacial bonding. The voids present in the matrix are the main reason for moisture diffusion.



(a) Epoxy-carbon 0 hrs



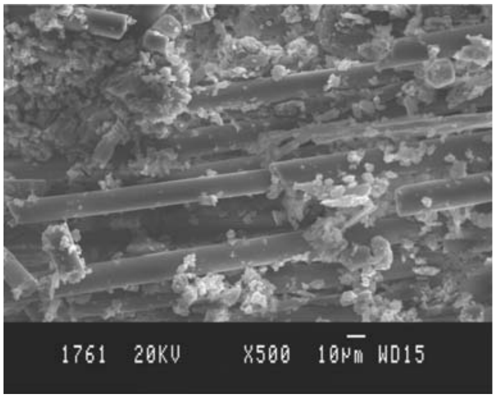
(b) Vinylester-carbon 0 hrs



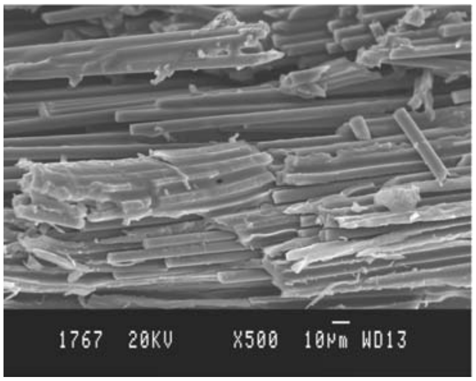
(c) Isopolyester-carbon 0 hrs

Fig. 11. (a-c) Micrographs of specimens without exposing to alkali solution.

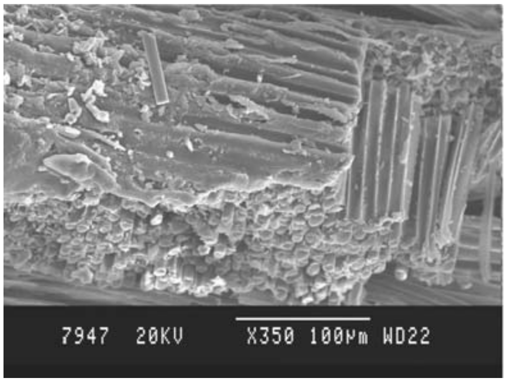
SEM images of tensile fractured unexposed specimen of epoxy /carbon, vinylester /carbon and iso-polyester / carbon specimens showed the failure mode due to fiber breakage. There are many hackles can be observed on the surface of the fiber are the matrix bonded to the fiber even after the fracture. This shows that there is a strong bond at the interface between fiber and matrix before degradation.



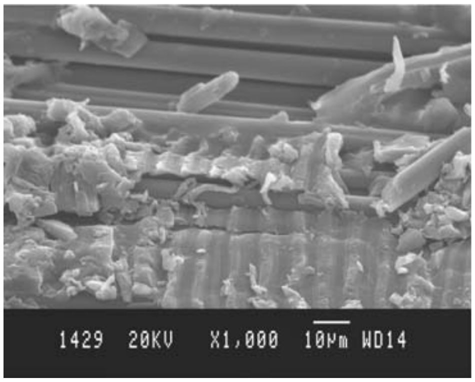
(a) Epoxy-carbon 600 hrs at RT



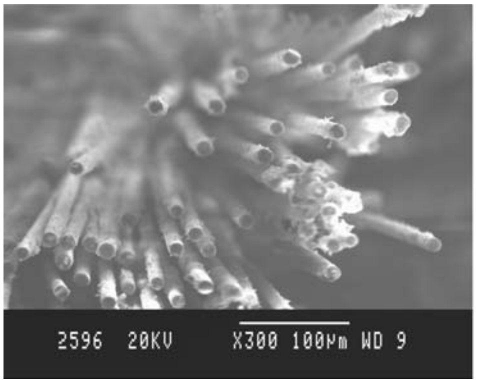
(b) Epoxy –carbon 600 hrs at 70°C



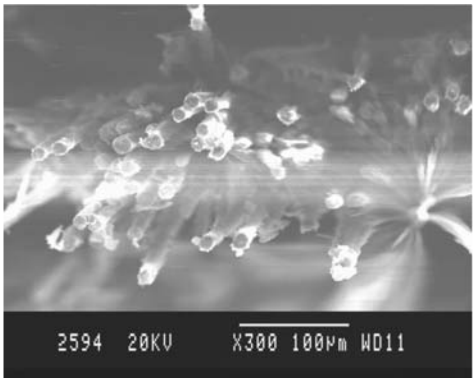
(c) Vinylester-carbon 600 hrs at RT



(d) Vinylester-carbon 600 hrs at 70°C



(e) Isopolyester-carbon 600 hrs at RT



(f) Isopolyester-carbon 600 hrs at 70°C

Fig. 12. (a-f) Micrographs of specimens after 600 hrs of exposure to alkaline solution

The fractured specimens after 600 hours of exposure showed fiber fracture as well as fiber pull out. After 600 hours of exposure the specimens showed greater degree of matrix plasticization in Iso-poly ester/carbon than that of epoxy/carbon and vinyl ester/Carbon evidencing that vinyl ester and epoxy is superior to Iso-polyester. Thus, matrix degradation increased with duration of exposure in all the cases. The matrix degradation is more in case of elevated temperature 70°C because of more moisture absorption takes place in case of elevated temperature. This is due to hygrothermal aging of polymers at elevated temperature may create damage in the form of crazing, micro cracking and other types of morphological changes, thus allowing additional moisture absorption to occur. On the other hand, immersion time increased, fewer hackles can be seen at the fiber surfaces for the specimens immersed in the alkyl solution. The relatively clean fiber surface resulted from the weak fiber-matrix bonding is observed. As temperature increased the matrix bonded to the fiber could hardly be identified. Alkali environment damages the epoxy /carbon, vinylester /carbon and iso-polyester / carbon specimens causing embrittlement and micro-cracks on surface are seen, longitudinal and transverse mechanical properties show significant decrease.

VII. RESULTS AND DISCUSSIONS

The maximum moisture absorption was found be in Iso polyester, i.e. 0.583 % at RT and 0.64 % at 70°C. The least moisture absorption was in the case of vinyl ester specimens being, 0.37% at RT, 0.54 % at 70°C The maximum moisture absorption was found be in Isopolyester/carbon, i.e. 1.38 % at RT and 3.12 % at 70°C. The least moisture absorption was in the case of vinyl ester/carbon specimens being 2.58 % at RT, 2.44 % at 70°C. Diffusion coefficient (D) was found in both cases (RT and 70°C) the highest for Iso polyester/carbon $(3.1973 \times 10 - 10 \,\&\, 1.029 \times 10 - 8)$ and the lowest for vinyl ester/carbon $(4.354 \times 10 - 11 \,\&\, 3.802 \times 10 - 10)$.

The percentage drops in UTS for epoxy/carbon, vinylester/carbon and Iso-polyester/carbon after 600 hours of exposure were 24.81, 26.73, and 63 % respectively at RT and 29.26, 37.94 and 71.61% respectively at 70°C. It is seen that Carbon/Epoxy performs the best amongst the 3 PMCs under study and carbon/Iso polyester shows poor performance. The percentage drops in flexural strength for epoxy/carbon; vinyl ester/carbon and Iso-polyester/carbon after 600 hours of exposure were 28.73, 41.17, and 71.29 % respectively at RT and 31.20, 46.93, and 77.88 % respectively at 70°C. This can be attributed to the minimal alkali absorption of Carbon/epoxy that results in least mechanical degradation. Similarly, carbon/Iso-polyester shows poor performance owing to high degree of alkali absorption that result in mechanical degradation. The percentage drops in ILSS for epoxy/carbon, vinylester/carbon and Iso-polyester/carbon after 600 hours of exposure were 12.12, 12.7 and 19.14 % respectively at RT and 16.45, 17.84, and 30.1 % respectively at 70°C. The reason for these phenomena could be the same ie, Carbon/Epoxy and Carbon/vinylester absorbing least % of alkali compared to carbon/Iso- Polyester resin system.

The percentage drops in Young's modulus for epoxy/carbon, vinylester/carbon and Iso-polyester/carbon after 600 hours of exposure were 33.01, 37.70 and 71.11 % respectively at RT and 39.71, 45.83, and 81.71 % respectively at 70°C. It is seen that young's modulus of epoxy/carbon is better than young's modulus of carbon/vinylester and Iso-polyester carbon.

SEM images of tensile fractured unexposed specimen of epoxy /carbon, vinylester /carbon and iso-polyester / carbon specimens showed the failure mode due to fiber breakage. The relatively clean fiber surface resulted from the weak fiber-matrix bonding is observed. As temperature increased the matrix bonded to the fiber could hardly be identified. Alkali environment damages the epoxy /carbon, vinylester /carbon and iso-polyester / carbon specimens causing embrittlement and micro-cracks on surface are seen, longitudinal and transverse mechanical properties show significant decrease.

VIII. CONCLUSIONS

Alkaline durability of PMC specimens (Iso-polyester/carbon, Epoxy/Carbon and Vinyl ester/carbon) was studied by exposing them to pH.13.5 alkaline treatment (KOH-1.4%, NaOH-1%, Ca(OH)2-0.16%) at room temperature and at 70°C up to 600 hours. The maximum alkali uptake and the mechanical property degradations were studied. The percentage drops in mechanical properties is due to moisture absorption which lead to swelling in composites as well as delamination between fiber and matrix. Alkali environment causes CFRPs embrittlement and micro cracks of resin, longitudinal and transverse mechanical properties show a significant decrease. Carbon/epoxy proved superiority over vinylester/carbon and Iso-polyester / Carbon, in terms of lower values of degradation in UTS, Flexural Strength and ILSS specimens. SEM images of tensile fractured unexposed specimen of epoxy /carbon, vinylester /carbon and iso-polyester / carbon specimens showed the failure mode due to fiber breakage. Among the epoxy /carbon, vinylester /carbon and iso-polyester / carbon specimens the carbon/epoxy retained better mechanical properties. But the rate of degradation for vinyl-ester showed lesser value.

REFERENCES

[1] Wong. T.C and Broutman. L. J. 1985 "Moisture Diffusion in. Epoxy Resins. Part I. Non-Fickian Sorption Processes," Polym Eng Sci, 25, 521

[2] Choi H.S., Ahn K.J., Nam J.D., Chun H.J., 2001 "Hygroscopic Aspects of Epoxy/Carbon Fiber Composites Laminates in Aircraft Environments", Comp: Pt A., 32, 709-720

[3] Gupta V.B., Drzal L.T., Rich M. J., 1985 "The Physical Basis of Moisture Transport in a Cured Epoxy Resin System", J. of Appl Polym Sci, 30, 4467-4493

[4] Thomason J.L., 1995 "The Interface Region in Glass fiber Reinforced Epoxy Resin Composites: 2.Water Absorption, Voids and the Interface", Comp, 26, 477-485

[5] Ishai. O, 1975 "Environmental effects on deformation, strength, and degradation of unidirectional glass-fiber reinforced plastics", Polym Eng Sci, 15, 491

[6] Marshall J.M., Marshall G.P., Pinzelli R.F., 1982 In Proc. 37th SPI Conf. Sect 9-C

[7] Shen CH, Springer G, 1999 “Moisture absorption and desorption of composite materials”, J of Comp Mate, 10, 2-20

[8] Roy S. Xu WX, Park SJ, Liechti KM, 1987 “Anomalous moisture diffusion in viscoelastic polymers; Modeling and testing”, J of Appl Mech, 67(2), 391-6

[9] Pritchard.G, Speake S.D, 1987 “The use of Water Absorption Kinetic Data to Predict Laminate Property Changes”, Comp, 18, 227-232

[10] Carter. HG, Kibler. KG, Langmuir 1978 - Type Model for Anomalous Moisture Diffusion in Composite Resins, J. of Comp Mate, 12, 118-31

[11] Camino. G. Luda. MP, Polishchuk Aya, Revellino. M, Blancon. R, Merle. G, 1997 “Kinetic Aspects of Water Sorption in Polyester Resin/ Glass- Fiber Composites”, J. of Comp Sci and Tech, 57(11), 1469-82

[12] Estelle Kalfon, Hannah Harel , Gad Marom , Esther Drukker, Anthony K. Green, Iddo Kressel, 2005 “Delamination of Laminated Composites under the Combined Effect of Nonuniform Heating and Absorbed Moisture”, Polym Comp, 26 (6), 770 – 777

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