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Environmental stability of GFRP laminated composites: An emphasis on mechanical behaviour

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ABSTRACT

Purpose - The main objective of this experimental investigation is to assess the effect of thermal and cryogenic treatment on hygrothermally conditioned glass fibre reinforced epoxy matrix composites, the impact on its mechanical properties with change in percentage of individual constituents of the laminates.

Design/methodology/approach - The present investigation is an attempt at evaluating the performance of the laminates subjected to different thermal and cryogenic treatments for varying time with prior hygrothermal treatment. The variability of hygrothermal exposure is in the range of 4-64 hours. GFRP laminates with different weight fractions 0.50-0.60 of fibre re enforcements were used. The ILSS, which is a matrix dominated was studied by three point bend test using INSTRON 1195 material testing machine.

Findings - The post hygrothermal treatments (both thermal and cryogenic exposures) resulted in an increase in the rate of desorption of moisture. It is noted that the hygrothermal treatment prior to the exposure to thermal or cryogenic conditioning is the major attribute to the variations in the ILSS values. The extent of demoisturisation of the hygrothermaly conditioned composites due to a thermal or a cryogenic exposure is observed to be inversely related to its ILSS, independent of the fibre weight fractions. Also the ILSS is inversely related to the fibre weight fraction irrespective of the post hydrothermal treatment.

Originality/value – The reported data is based on experimental investigations.

Keywords – FRP composites, Weight Fraction, Hygrothermal, Thermal, Cryogenic, Mechanical properties

Paper type – Research Paper

INTRODUCTION

The employment of glass fibre reinforced composites is ever increasing in engineering structures and components.

Composites because of their wide spectrum of properties find enormous usage in the aircrafts, civil, automotive, marine and other industries. The use of composite materials in commercial transport aircraft is attractive because of reduced airframe weight which enables better fuel economy and therefore lowers operating costs. Initially the use of composite materials in aircraft was limited to less than 2% but with extensive research in the field, the usage has gone to excess of 50%. Fiber reinforced composites are now used in application ranging from space craft frames to ladder rails, from aircraft wings to automobile doors, from rocket motor cases to oxygen tanks. The composite components so engaged experience repeated absorption/desorption of moisture in a wide range of humidity and temperature conditions. The ingress of water molecules into the epoxy matrix composites is a diffusion-controlled process dependent largely on the environmental conditions. The polymer micro-molecules, forced apart by the absorbed moisture cause the GFRP composite to expand or swell. This phenomenon apart from affecting the fibre-matrix adhesion resulting in de bonding of the interface and generating micro cracks in the composite, causes an increase in the chain separation which causes a reduction in the secondary intermolecular bonding forces in the polymer itself. As a consequence the material becomes softer and more ductile. In this condition if the ambient temperature is also decreased the apparently strong matrix housing the fiber becomes rubbery and weak. It must also be clearly understood that the transport of moisture in to the body of the composite, which depends on the free volume available in the body of the epoxy matrix also depends on the segmental mobility of the polymer chains. The segmental mobility, on the other hand, is affected by the degree of unsaturation, cross linking and the degree of crystallinity. The glass transition temperature, Tg, is greatly influenced by the transport of moisture. Polymers with a greater segmental- mobility will have a decreased Tg and therefore, will have higher diffusivity. The diffusivity, on the other hand, being increased with a decrease in the Tg value also depends on temperature, fibre obstruction, moisture concentration in the laminate, i.e., the swelling of the composite.

The thermal mismatch between the constituents of GFRP composites may result in the development of residual stresses in the microstructure when it is exposed to a low temperature. If the temperature is significantly low, as experienced by an aircraft during its service, micro cracks may be developed which contribute to the degradation process by reducing stiffness and increasing permeability and water ingress through the fibre-matrix interface. GFRP composites with a previous exposure to hydrothermal condition, when exposed to low temperatures, may exhibit an increase in the strength due to matrix hardening. However, longer exposures may give rise to stress concentrations at a defect tip (result of volumetric expansion of water converting to ice) nucleating a micro-crack. On the other hand, thermal treatment to a hygrothermally conditioned sample may lead to a relatively non-equilibrium desorption kinetics similar to the moisture absorption kinetics. The non-equilibrium desorption of moisture may result in preferential moisture outlet links either in the form of fine whiskers or in the form of interconnected pores. The generation of these outlets will result in the nucleation of residual stresses in the matrix or at the interface.

There are, however, conflicting observations about the role of absorbed moisture on the characteristic properties of GFRP composites. Though, in general it is believed that moisture accumulation at the fiber-matrix interface causes de bonding and thus substantially lowers the shear strength of the composite, some believe that the moisture induced swelling of the epoxy matrix around the fibre reduces the residual compressive stresses at the interface caused by shrinkages during curing. They believe that this reduction in the residual stresses results in the reduction of the mechanical interlocking stresses between the fibre and the matrix, thereby increasing the load bearing capacity of the composite component.

The primary mechanism of moisture pick up by the FRP composites is surface absorption and diffusion through the matrix is given by Fick’s second law of diffusion. The water sorption behavior is affected by two competitive processes 1) Hydrolysis, which tends to subtract water to the diffusion process and 2) Hydrophilisation, which results in increased uptake of water through swelling and plasticization as per Polishchuk et al. (1996) and Petropolus (1984). Mikols et al. (1982) have also acknowledged that these changes decrease Tg and elastic modulus. The amount of moisture absorbed by the epoxy matrix is significant with respect to the fibres which absorb little or no moisture. This results in mismatch between the matrix and fibres which can be attributed to relative volumetric expansion between the two components. This leads to the evolution of localised stress and strain fields which are responsible for the generation of cracks. Additionally the moisture weakens the interface by reducing interfacial energy along the fibre-matrix interface as investigated by DiBenedetto (2001). The moisture gradient in a composite is responsible for the generation of compressive stresses in the outer ply during absorption and similarly tensile stress is generated during desorption. According to Bunsell (1994) the net effect of moisture is deterioration of matrix dominated properties such as compressive strength, ILSS, fatigue resistance and impact resistance influencing long-term durability and performance of composite.

FRP subjected to elevated temperature conditions generates thermal stresses due to unequal expansion of the matrix and fibre owing to the unequal co-efficient of thermal expansion of the two phases. As a result of which the interfacial bond strength reduces due to the development of misfit stresses along the interface. This accentuates to the deterioration of the mechanical properties of the composites. On the other hand FRPs are subjected to cryogenic conditions, develops complex stresses along the interface as well due to the mismatch of co-efficient of thermal expansion of the fibre and matrix as per Mukherjee et al (2002) and Ray (2005). Loken et al. (1988) and Salin et al. (1996) reported potholing, delamination and micro cracking are the most commonly observed damage phenomenon in composites subjected to cryogenic conditions. A hygrothermally treated FRP composite when exposed to low temperature causes matrix hardening initially and thus strength is increased. However exposure to longer exposure causes development of compressive residual stresses and thus the mechanical properties are reduced.

In the present work we shall try to assess the impact of thermal and cryogenic treatment on glass fibre reinforced composites with varying fibre weight fraction [Vf] after the initial hygrothermal conditioning for different duration of time[4-64 hrs], the impact on its physical and mechanical properties as well.

One would, therefore, appreciate that during its service life the GFRP composite is exposed to stringent conditions of ambience having complex combinations of effects of these severe conditions under which it must perform. These potential dangers need to be understood well and appropriately addressed to.

In view of the above the recent experiment is designed to assess and hence address to the complexities of the combined effect of moisture, high and low temperatures to which a GFRP composite is supposed to be exposed to during its service life. The impact of thermal and cryogenic treatment on GFRP composites with varying fibre weight fraction (Vf) after the initial hydrothermal conditioning for different duration of time [4-64hrs] pertaining to its physical as well as mechanical properties, have been assessed.

EXPERIMENTAL WORK

The glass fibre reinforced composite laminates comprising of 20 layers were fabricated with the use of woven glass fibre and epoxy resin (Ciba-Geigy; India, LY-556 Araldite, HY-951 hardener) in accordance with ASTM standards. Different batches of composite laminates were fabricated with weight fraction of fibre being maintained [Vf] as 50%, 55% and 60%. The laminates after being room cured where cut into appropriate dimensions, according to ASTM D2344-84, by diamond cutter for three point bend test [SBS]. The specimens were subjected to hygrothermal treatment for 4, 9, 16, 25, 36, 49 and 64 hours at 60^0C and 95% relative humidity. Humidity chamber was used for the hygrothermal treatment of the laminates. The net temperature and humidity fluctuation ranged to a maximum of 0.7% and 0.4% respectively. The specimens were divided into 5 batches. One batch was left as treated, two batches were subjected to thermal conditioning at $+80^0$C for 2 hours and 10 hours respectively and the remaining two batches were subjected to cryogenic conditioning at -80^0C for 2 hours and 10 hours respectively. The thermal treatment was carried out in an oven maintained at 80^0C whereas the cryogenic conditioning was done at a temperature of -80^0C in a double compressor fitted deep freezer and were then immediately tested for determination of ILSS. The SBS test of the conditioned samples was carried out in an INSTRON tensile testing machine at a cross head velocity of 2 mm/min. The purpose of the SBS test is to determine the ILSS of the composite laminate. The reported ILSS values are the average of three specimens which is done to enhance the precison. The Interlamellar Shear Stress is determined as follows:

$$ILSS=0.75\ P/b\ t\ [MPa]$$

where, P= Breaking load,[N]

b= Breadth of the specimen. [mm]

t= Thickness of the specimen. [mm]

RESULT AND DISCUSSIONS

The details of the moisture absorption kinetics is given in table 1 and the variation is shown in fig 1

TABLE 1 Test results for moisture absorption for composites with different volume fraction of fibers

SL NO	SQRT OF EXPOSURE TIME IN (HRS)^0.5	SAMPLE TYPE (RATIO OF FIBER TO POLYMER)		
		E-50	E-55	E-60
1	0	0.049	0.047	0.029
2	2	0.139	0.112	0.09

3	3	0.167	0.165	0.143
4	4	0.205	0.2	0.195
5	5	0.225	0.226	0.21
6	6	0.24	0.28	0.23
7	7	0.26	0.3	0.3
8	8	0.295	0.325	0.36

The details of the moisture desorption data when the composites are subjected to thermal and cryogenic conditions are given in table 2 and 3 and the variation of the amount of moisture desorbed with square root of time is shown in figures 2 and 3.

Fig 1: The relationship between moisture absorbed with square root of Hygrothermal exposure time.

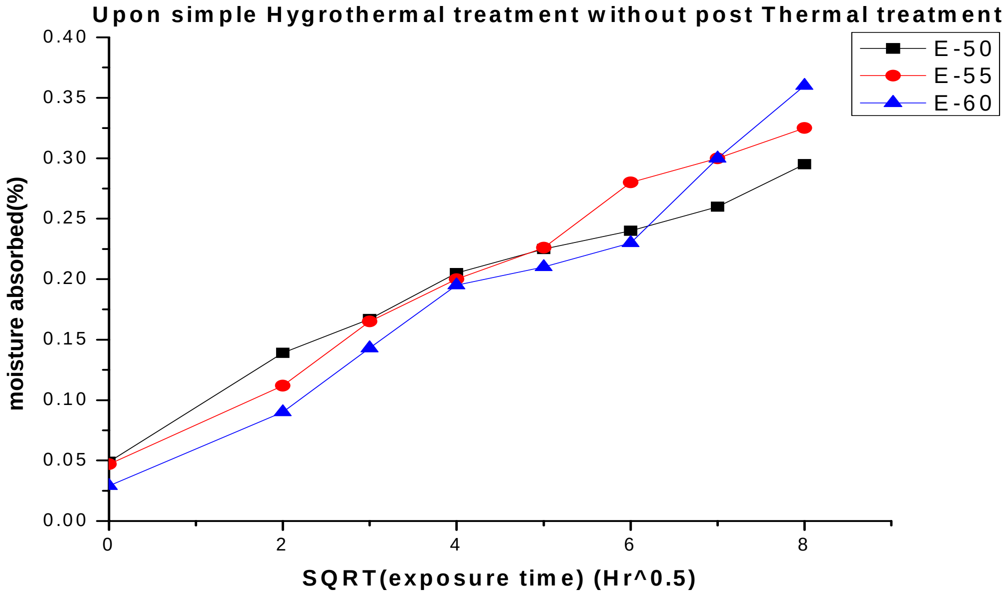


Table 2: Test results for moisture desorption upon cryogenic conditioning post hygrothermal treatment for longer duration [10 hours at -80ºC]

SL NO	SQRT OF EXPOSURE TIME IN (HRS)^0.5	SAMPLE TYPE (RATIO OF FIBER TO POLYMER)		
		E-50	E-55	E-60
1	0	0.031	0.028	0.020
2	2	0.044	0.035	0.015
3	3	0.095	0.062	0.040
4	4	0.100	0.077	0.065
5	5	0.118	0.106	0.080
6	6	0.095	0.095	0.070
7	7	0.101	0.113	0.105
8	8	0.095	0.125	0.120

Fig 2: Effect of cryogenic conditioning on moisture desorption upon Post-hygrothermal treatment of composites.

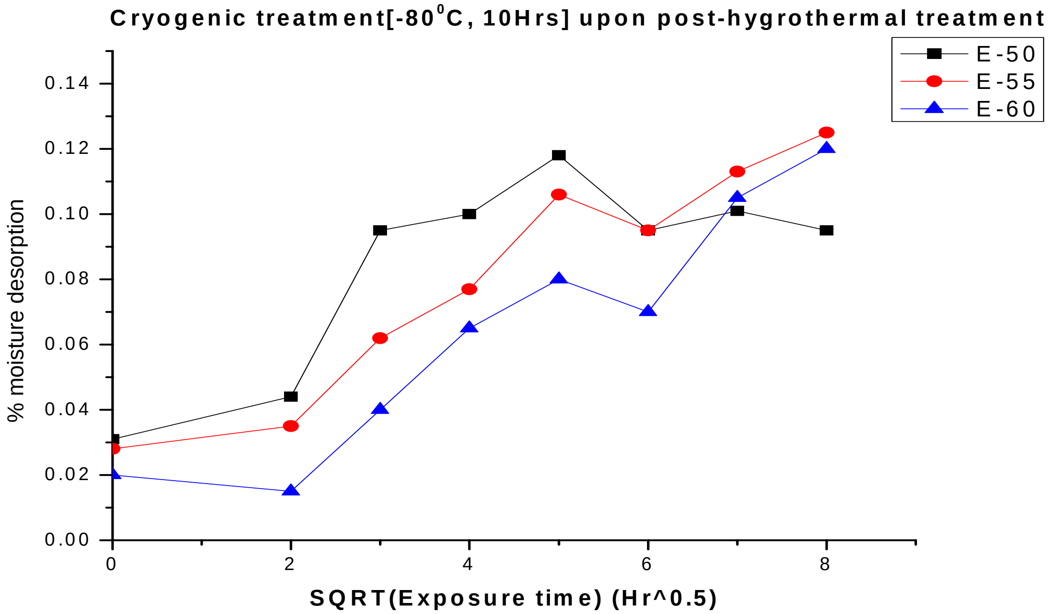
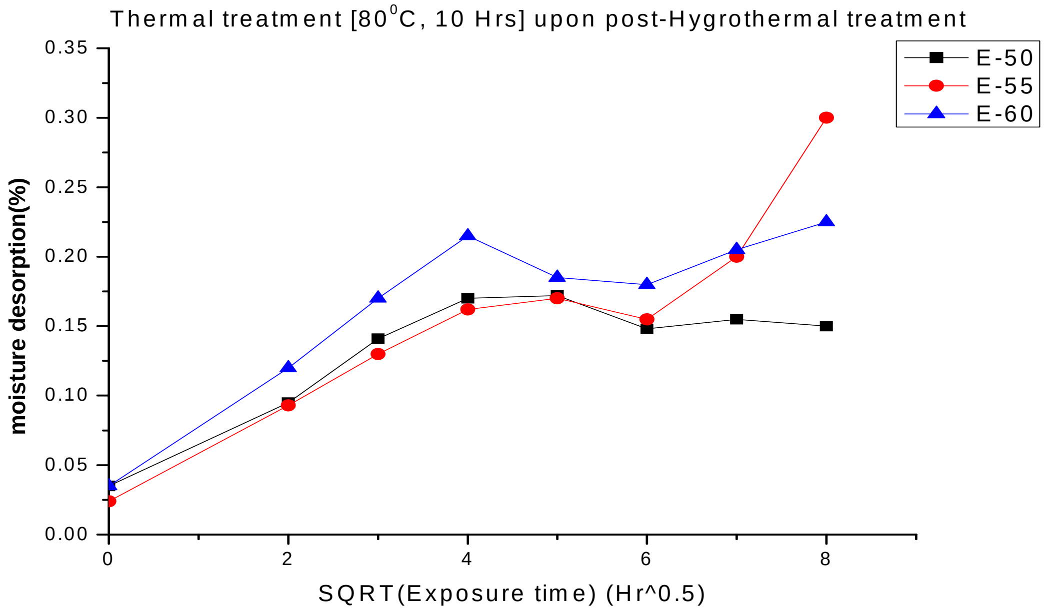


Table 3: Test results for moisture desorption upon thermal conditioning post hygrothermal treatment for longer duration [10 hours at +80°C]

SL NO	SQRT OF EXPOSURE TIME IN (HRS)^0.5	SAMPLE TYPE (RATIO OF FIBER TO POLYMER)		
		E-50	E-55	E-60
1	0	0.035	0.024	0.035
2	2	0.095	0.093	0.120
3	3	0.141	0.130	0.170
4	4	0.170	0.162	0.215
5	5	0.172	0.17	0.185
6	6	0.148	0.155	0.180
7	7	0.155	0.200	0.205
8	8	0.150	0.300	0.225

Fig 3: Effect of thermal conditioning on moisture desorption upon Post-hygrothermal treatment of composites.



The details of the moisture desorption due to exposure of different grades of composites at different temperatures for different time period is listed in Table 4 [Table 4.1-4.3] and the moisture desorption kinetics is shown in the Figure 4 [figure 4.1-4.3]

Table 4: Test results for combined effect of Hygrothermal treatment and post thermal exposure on moisture desorption kinetics for different fibre-volume fraction.

Table 4.1 for E-50 grade composites

Sl no	Sqrt of time of hygrothermal exposure [(hours)^0.5]	Samples treated for 2 hours at +80ºC after hygothermal exposure	Samples treated for 2 hours at -80ºC after hygothermal exposure	Samples treated for 10 hours at +80ºC after hygothermal exposure	Samples treated for 10 hours at -80ºC after hygothermal exposure
1	0	0.023	0.031	0.035	0.031
2	2	0.070	0.054	0.095	0.044
3	3	0.105	0.070	0.141	0.095
4	4	0.125	0.080	0.170	0.100
5	5	0.138	0.102	0.185	0.118
6	6	0.138	0.108	0.148	0.095
7	7	0.120	0.090	0.155	0.101
8	8	0.145	0.130	0.150	0.095

Table 4.2 for E-55 grade composites

Sl no	Sqrt of time of hygrothermal exposure [(hours)^0.5]	Samples treated for 2 hours at +80ºC after hygothermal exposure	Samples treated for 2 hours at -80ºC after hygothermal exposure	Samples treated for 10 hours at +80ºC after hygothermal exposure	Samples treated for 10 hours at -80ºC after hygothermal exposure
1	0	0.016	0.017	0.024	0.028
2	2	0.086	0.020	0.093	0.035
3	3	0.112	0.048	0.130	0.062
4	4	0.130	0.090	0.162	0.077
5	5	0.122	0.070	0.170	0.120
6	6	0.130	0.120	0.155	0.095
7	7	0.140	0.120	0.200	0.113
8	8	0.215	0.150	0.300	0.125

Table 4.3 for E-60 grade composites

Sl no	Sqrt of time of hygrothermal exposure [(hours)^0.5]	Samples treated for 2 hours at +80ºC after hygothermal exposure	Samples treated for 2 hours at -80ºC after hygothermal exposure	Samples treated for 10 hours at +80ºC after hygothermal exposure	Samples treated for 10 hours at -80ºC after hygothermal exposure
1	0	0.017	0.012	0.035	0.020
2	2	0.085	0.010	0.120	0.015
3	3	0.140	0.097	0.170	0.040
4	4	0.185	0.090	0.215	0.065
5	5	0.170	0.065	0.185	0.080
6	6	0.225	0.110	0.180	0.070
7	7	0.270	0.110	0.205	0.105
8	8	0.340	0.125	0.225	0.120

Fig 4: Combined effect of Hygrothermal treatment and post thermal exposure on moisture desorption kinetics for different fibre-volume fraction.

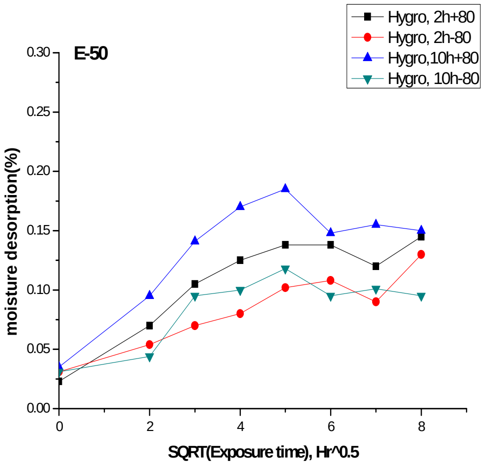


Fig 4.1

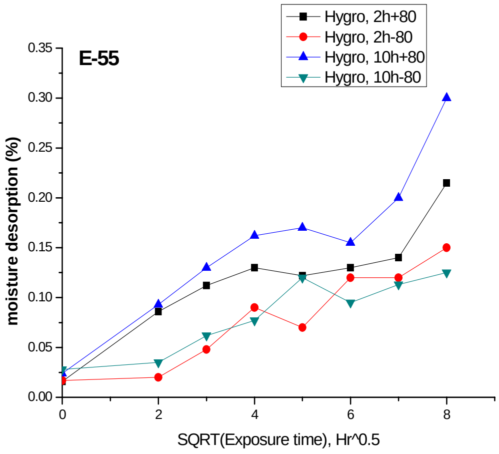


Fig 4.2

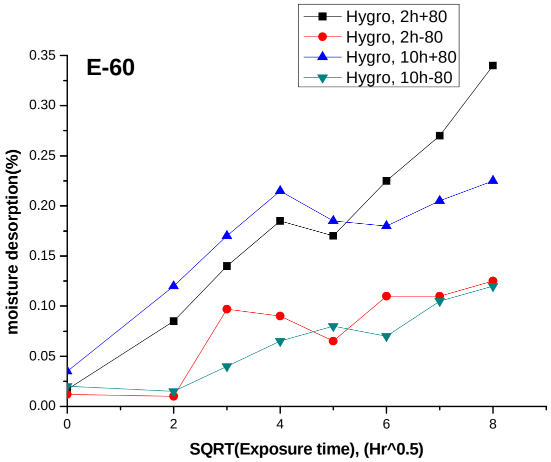


Fig 4.3

The details of the yield load and the ILSS found out in the SBS test for different grades of composite samples, subjected to different temperature and for different time after hygrothermal treatment for various time period [4, 9, 16, 25, 36, 49, 64 hours] is given in the Table 5 [Table 5.1-5.3] and the variation of the ILSS Vs time of exposure is shown in Figure 5 [Figure5.1-5.3]

Table 5 Test results for variation of ILSS with thermal and cryogenic demoisturization on different grade composites

Table 5.1 for E-50 grade composites

		Only	Samples treated	Samples treated	Samples treated	Samples treated

Sl.no	Time(hrs)	hygrothermal treatment		for 2 hours at +80ºC after hygothermal exposure		for 2 hours at -80ºC after hygothermal exposure		for 10 hours at +80ºC after hygothermal exposure		for 10 hours at -80ºC after hygothermal exposure	
		Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]
1	0	219.90	32.33	222.46	33.30	232.60	35.22	213.90	32.14	202.46	31.69
2	4	201.93	31.45	211.90	32.57	237.56	33.70	215.10	31.60	227.76	32.60
3	9	214.00	32.57	197.10	30.40	209.76	31.05	188.36	28.70	215.36	30.72
4	16	204.20	32.00	222.4	31.88	221.06	32.47	220.30	31.10	221.40	33.35
5	25	209.83	32.37	202.15	30.60	211.33	32.18	191.20	29.33	221.63	32.86
6	36	210.06	31.40	227.00	31.39	214.56	30.95	199.46	29.98	210.90	32.32
7	49	228.53	32.32	229.10	32.67	216.76	30.90	201.66	30.21	214.30	31.88
8	64	186.60	27.96	194.96	30.90	204.30	30.70	206.53	32.02	219.66	32.37

Table 5.2 for E-55 grade composites

Sl.no	Time(hrs)	Only hygrothermal treatment		Samples treated for 2 hours at +80ºC after hygothermal exposure		Samples treated for 2 hours at -80ºC after hygothermal exposure		Samples treated for 10 hours at +80ºC after hygothermal exposure		Samples treated for 10 hours at -80ºC after hygothermal exposure	
		Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]
1	0	213.80	30.42	185.40	30.41	219.46	32.38	194.60	32.14	223.26	31.69
2	4	180.20	29.30	214.70	31.33	198.60	32.12	189.76	30.41	202.73	31.26
3	9	206.16	31.49	195.86	30.77	195.03	30.29	201.53	29.92	179.86	30.11
4	16	205.90	31.50	189.60	29.92	187.10	30.41	193.06	31.60	193.53	32.57
5	25	198.20	30.96	178.90	29.30	207.20	32.37	201.46	30.70	197.20	31.82
6	36	223.33	31.72	172.40	28.70	220.90	32.47	196.80	29.58	218.43	32.57
7	49	215.90	30.65	198.95	29.63	209.00	31.88	206.40	30.90	205.10	30.42
8	64	211.36	31.39	202.30	29.92	185.00	30.90	177.50	29.04	198.35	30.41

Table 5.3 for E-60 grade composites

		Only hygrothermal	Samples treated for 2 hours at	Samples treated for 2 hours at	Samples treated for 10 hours at	Samples treated for 10 hours at

Sl.no	Time(hrs)	treatment		+80ºC after hygothermal exposure		-80ºC after hygothermal exposure		+80ºC after hygothermal exposure		-80ºC after hygothermal exposure	
		Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]
1	0	185.40	30.02	185.60	27.95	198.86	32.38	189.50	29.36	203.53	31.72
2	4	202.43	31.03	184.93	27.71	203.56	32.18	186.10	29.56	214.53	32.42
3	9	198.53	30.90	186.56	29.01	193.86	30.95	179.26	27.86	206.93	31.50
4	16	199.00	31.00	173.40	28.35	177.56	29.09	178.53	27.40	217.16	33.06
5	25	198.76	30.60	184.80	29.23	185.03	30.41	176.70	26.98	202.63	30.90
6	36	191.53	29.88	182.25	28.44	197.20	29.63	194.60	27.44	203.63	31.29
7	49	202.90	30.65	179.65	27.27	191.20	29.63	193.00	29.14	192.63	32.61
8	64	185.40	27.96	181.33	28.15	180.75	28.52	172.05	26.70	185.20	28.74

Fig 5: Effect of thermal and cryogenic demoisturization on the ILSS of the composite laminates with different fibre-volume fraction.

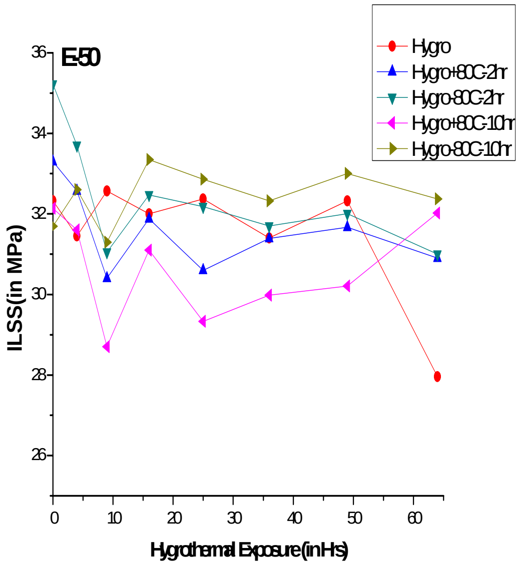


Fig 5.1

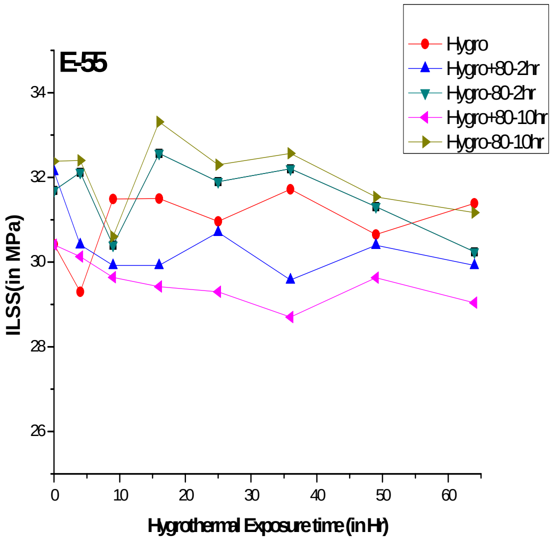


Fig 5.2

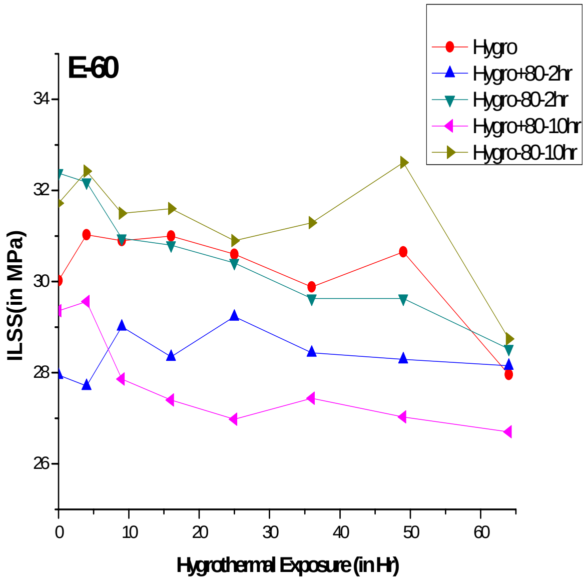


Fig 5.3

Table 6: Test results for variation of ILSS of different grade composites with particular post hygrothermal treatment

Table 6.1 for composites samples [only hygrothermal exposure]

Sl no	Exposure time [hours]	E-50		E-55		E-60	
		Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]
1	00	219.90	32.33	213.80	30.42	185.40	30.02
2	04	201.93	31.45	180.20	29.30	202.43	31.03
3	09	214.00	32.57	206.16	31.49	198.53	30.90
4	16	204.20	32.00	205.90	31.50	199.00	30.50
5	25	209.83	32.37	198.20	30.96	198.76	30.60
6	36	210.06	31.40	223.33	31.72	191.53	29.88
7	49	228.53	32.32	215.90	30.65	202.90	30.65
8	64	186.60	27.96	211.36	31.39	185.40	27.96

Table 6.2 for composite samples [10 Hours, +80ºC]

Sl no	Exposure time [hours]	E-50		E-55		E-60	
		Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]
1	00	213.90	32.14	194.60	30.12	189.50	29.36
2	04	215.10	31.60	189.76	30.41	186.10	29.56
3	09	188.36	29.10	201.53	29.92	179.26	27.86

4	16	220.30	31.10	193.06	31.60	178.53	30.60
5	25	191.20	29.33	201.46	30.70	176.70	26.98
6	36	199.46	29.10	196.80	29.58	194.60	27.44
7	49	201.66	30.21	206.40	30.90	193.00	29.14
8	64	206.53	32.02	177.50	29.04	172.05	26.70

Table 6.3 for composite samples [10 Hours, -80ºC]

Sl no	Exposure time [hours]	E-50		E-55		E-60	
		Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]	Max load at yield	ILSS [Mpa]
1	00	223.26	31.69	223.26	30.50	203.53	31.72
2	04	202.73	32.60	202.73	31.26	214.53	32.42
3	09	179.86	30.72	179.86	30.11	206.93	31.50
4	16	193.53	33.35	193.53	32.57	217.16	33.06
5	25	197.20	32.86	197.20	31.82	202.63	30.90
6	36	218.43	32.32	218.43	32.57	203.63	31.29
7	49	205.10	31.88	205.10	30.42	192.63	32.61
8	64	198.35	32.37	198.35	30.41	185.20	28.74

Details of the yield load and the ILSS values obtained from the SBS test for the different grades of composites samples with different exposure time and temperature is given in Table 6 and a detailed comparison between the composites with different volume fraction of fibers and their ILSS values is given in Figure 6

Fig 6: Comparison of ILSS for composites with different fibre-volume fraction.

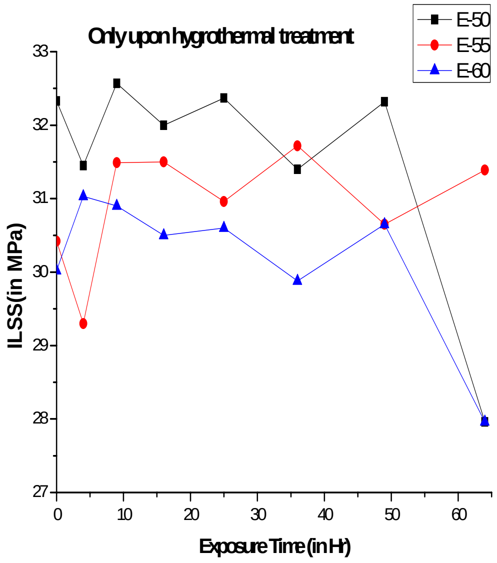


Fig 6.1

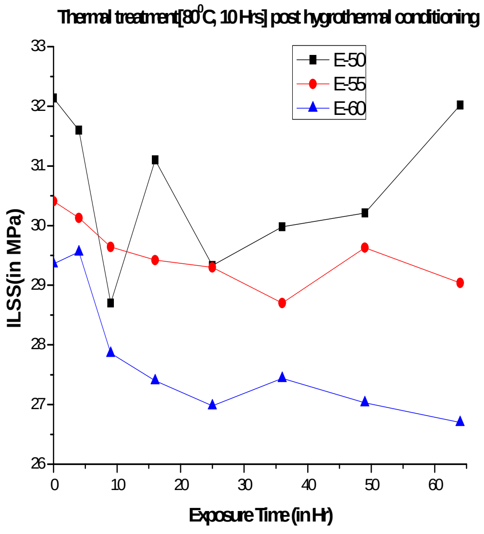


Fig 6.2

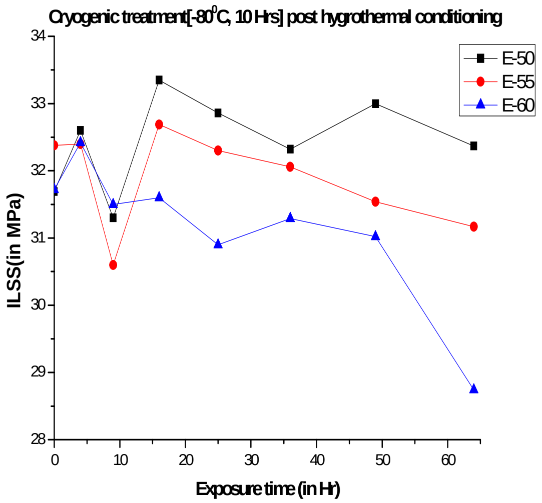


Fig 6.3

The variations of moisture absorped, moisture desorped, with weight fractions of fiber and time of exposure along with the variation of ILSS values with post hygrothermal treatment, and weight fraction of fibers are discussed below.

The composite properties are affected by the water aging, through variations on chemical and physical characteristics as well as the fiber/matrix interface which is in accordance with Ishida et al. (1978). The mechanisms for entry of water into the composite material include diffusion, capillarity along the fibers, the interface and transport by micro-cracks as per Loos et al. (1981). Fig 1 shows that the water absorption kinetics for composite specimens with different weight fraction of fibers where E-50 indicates 50% fiber weight fraction. The transient ambience condition thus results in a fickian diffusion mechanism for all fiber weight fractions as investigated by Adams et al. (1996). Initially, the rate of absorption is higher for E-50 composite, indicates that moisture uptake is primarily into the matrix phase without the generation of sufficient cracks or voids along the interface. Shen et al (1981), Weitsman (1990) and Wang et al. (2007) have also found out that water brings about plasticization of the polymer matrix and the degradation of fiber/matrix interface. This result in creation of voids, cracks and crevices along the interface and the rate of absorption of moisture is increased. With increase in hygrothermal exposure, the rate of absorption is dominated by the interfacial area in a composite. Interfacial area increases with fiber weight fraction. Hence, the rate of absorption is highest for E-60 composite upon longer hygrothermal exposure durations.

Thermal degradation of plastics involves a chemical reaction and physical changes as per Naruse et al. (2001). The initial moisture content in composites is an inverse function of the fibre fraction of the composite. For lower hygrothermal exposure durations, the cryogenic treatment plays a little role as the moisture desorption is more or less constant, as most of the moisture absorbed earlier accounts for formation of ice. However, upon exposure for longer durations, there is a stiff loss of moisture due to the fact that the moisture absorption or desorption depends strongly on the relative humidity inside the chamber of treatment as per James et al. (2005). The moisture loss can be attributed to the formation of a moisture gradient across the section of the composite with concentration of moisture being the minimum within the chamber and maximum within the composite.

The moisture desorption is maximum for the case of E-60 composite laminate is because of the highest proportion of moisture absorbed earlier owing to the largest interfacial area. Composites show a linear increase in desorption rate with increase in hygrothermal exposure time, prior to thermal treatment. However, after a certain amount of exposure time, desorption rate decreases and then again show an increase. This is true for all the three different fibre- weight fraction of composites. With prolonged exposure at 80^0C for 10 hours there is a constant loss of moisture, creating fissures and pores. Further chemical reactions are represented by cross-linking and further reaction of untreated monomers, while physical change is typical of viscoelastic behavior as per Colin and Verdu (2005). It is demonstrated that, during thermal aging in air, organic matrix composites undergo a superficial oxidation leading to a “spontaneous” cracking without application of external load as per Bowles et al. (1994) and Hamada et al. (1994). At the macromolecular scale, chain scission, and cross linking affect the polymer network and thus, alter the mechanical properties of the oxidized layer; at the macroscopic level, the hindered shrinkage of the oxidized layer induces a stress gradient susceptible to initiate and propagate cracks as per Hamada et al. (1994). Polymer composites are susceptible to heat and moisture when operating in harsh and changing conditions as per Adams and Singh (1996). The differential coefficients of thermal expansion of the matrix and fibers result in development of internal misfit stresses. Hence, the net effect of moisture absorption is the deterioration of matrix dominated properties as per Ray (2005).

Fig 4 shows that the moisture desorption is affected my both hygrothermal exposure as well as the post treatment subjected to the composites. It can be clearly observed that irrespective of the fibre volume fraction, moisture desorption is highest for the laminates subjected to thermal treatment post hygrothermal exposure. The duration of thermal exposure is a key factor affecting desorption kinetics. It is observed that for all the cases the moisture desorption increases with the increase in duration of thermal exposure. Composites subjected to cryogenic treatment show lowest moisture desorption rates. The desorption rates is primarily affected by the duration of hygrothermal exposure. For lower durations of hygrothermal exposure, desorption rate remains constant. However with increase in hygrothermal exposure, desorption rate increases. If carefully observed, this increase is followed with a decrease in desorption rate. This is again followed with an increase in desorption rate.

Effects of hygrothermal treatment can be seen in the fibre, in the matrix, and at the interface or interphase between, even though the effect on glass fibre is negligible as compared to the resin (epoxy). Hygrothermal effects can range from damping characteristic improvements, strength degradations, and little change to moduli. If effects are present, lesser differences are usually seen on fibre-dominated properties versus resin- dominated properties. Exceptions occur when the interface between the fibre and resin is attacked, preventing load transfer.

In fig 5, the effect of thermal and cryogenic demoisturization on the ILSS of composites is illustrated. It is interesting to note that the demoisturization due to thermal and cryogenic treatment is related to the ILSS of the composites. A cryogenic treated composite laminate showed highest ILSS values. Composites, cryogenically conditioned for 10 hrs showed comparatively higher values than composites treated for 2 hours. On the contrary, thermally treated composites showed comparatively lower ILSS values with the decrease in ILSS being directly related to the duration of thermal exposure. Comparing Fig 4 and Fig 5, it can be ascertained that ILSS of composites is an inverse function of demoisturization values and the effect is independent of the fibre-weight fraction of the composite.

In Fig 5, the general trend in all the above plots is decreasing ILSS values with some rise in the initial time period. In case of cryogenic conditioning for lower duration, the movement of the polymer chains is restricted and also there is mechanical keying which accounts for the rise in the ILSS values. The cryogenic conditioning causes differential contraction and increases the resistance to debonding by mechanical keying factor. The fall may be attributed to excess absorption of moisture due to which the swelling of the matrix occurs resulting in poor interfacial bonding between the fibre and the matrix. The initial increase in the ILSS values may be due to polymerization of the polymer matrix. But the rate of decrease in all the specimens is different, due to variable amount of moisture uptake due to different fibre-weight fractions. The initial increase in ILSS of cryogenically treated composites may also be attributed to the matrix hardening but for longer exposure durations, the strength decreases due to the interaction of stress concentration at the defect tip (upon volumetric expansion caused due to moisture to ice transformation). The characteristic of the interfacial adhesion is strongly influenced by the presence of residual stresses. However, some of the stresses developed by differential expansion/contraction are relaxed by viscoelastic flow or creep in the polymer matrix as per Hull and Clyne (1996). In cases of thermal conditioning after hygrothermal treatment the ILSS values show an increasing trend in all E-50, E-55, E-60, specimens due to mitigation of the thermal stress generated due misfit strains. But prolonged exposure causes the mechanical property deterioration due to the formation of micro cracks and crazing (more misfit stresses are generated due to differential coefficient of thermal expansion of the fibres and the matrix). It may also be due to the removal of moisture accounting for the formation of fissures and cracks.

In Fig 6, it is impressive to note that irrespective post hygrothermal treatment, ILSS is an inverse function of the fibre-weight fraction [Vf] of the composite which can be compare from the data given in Table 6. Obviously as mentioned earlier, thermal or cryogenic desorption also affects the ILSS.

The investigation needs to be extended in the direction of revealing critical and comprehensive details of the specimen by adopting optical as well as scanning electron microscopic examinations. These approaches could definitely nucleate the convincing explanations in support of variations of statistically significant fluctuation of mechanical behavior of FRP composites under the influences of environmental impact.

CONCLUSION

In retrospection, it can be concluded that the key factors affecting the ILSS is the duration of hygrothermal exposure of the composites. Higher exposure leads to reduced values of ILSS irrespective of the post thermal treatment. It is observed that thermal or cryogenic demoisturization of hygrothermally conditioned composites is inversely related to its ILSS and this effect being independent of the fibre-weight fraction. It is also observed that irrespective of the post hygrothermal treatments, fibre-weight fraction of composites has a significant impact on its ILSS.

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