Effects of Thermal Shocks and Thermal Spikes on Hygrothermal Behavior of Glass-Polyester Composites

T. BERA[a], S. MULA[b], P. K. RAY[c] AND B. C. RAY[d]*

[a] Department of Metallurgical Engineering

Institute of Technology, Banaras Hindu University, Varanasi 221 005, INDIA

[b] Department of Metallurgical & Materials Engineering

Indian Institute of Technology, Kharagpur 721 302, INDIA

[c] Department of Metallurgical & Materials Engineering

Indian Institute of Technology, Chennai 600 036, INDIA

[d] Department of Metallurgical & Materials Engineering

National Institute of Technology, Rourkela 769 008, INDIA

* Author for correspondence:

B. C. Ray, email: bcray@nitrkl.ac.in, phone: +91 661 2470842, fax: +91 661 2472926

ABSTRACT

The aim of present study is to investigate the degradation behavior of glass fiber reinforced polyester composites during hygrothermal ageing for different lengths of time after suffering thermal shocks and thermal spikes at 100^0C, 150^0C, and 200^0C. The moisture gain kinetics and change of interlaminar shear strength (ILSS), a primary mode of analysis of interfacial strength of the composite, were evaluated. Moisture absorption, found more in spiked samples, showed initial Fickian trend but eventually changed to non-linear pattern as the exposure time increased. It has been found that the composite specimens having a history of thermal spike showed more degradation. The damage was found even more at higher temperature and at lower loading rates.

Keywords: Polymer Matrix composites, Debonding, Environmental degradation, Interfacial strength, Hygrothermal behavior.

INTRODUCTION

Fiber reinforced plastic (FRP) composites are extensively used as one of the advanced engineering materials because of their high specific strength and the ability of being tailored for specific applications [1-3]. Despite these advantages over conventional structural materials, polymer composites are susceptible to heat and moisture when operating in harsh and changing conditions [4]. When exposed to humid environments, composites absorb moisture resulting in dilatational expansion of the fiber and the matrix. 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 [5]. The stresses associated with moisture induced expansion may result in lower damage tolerances, with an adverse effect on long term structural durability. In homogeneous materials, the kinetics of moisture diffusion is governed by the maximum moisture content and the diffusivity. In composites, the diffusion process depends on the diffusivities of the individual constituents, their relative volume fractions, constituent arrangements and morphology. The transient moisture diffusion in composites under normal environmental conditions is approximated as a Fickian process [4].

Another major aspect of the composite materials with respect to the traditional engineering materials relate to the existence of interfaces separating the constituent material phases. In this case the composite may be considered as consisting of three phases, i.e., two actual phases and a third one which may also arise during treatment of the materials, because of component interaction. This extra third phase is obviously inhomogeneous and may be called as interphase [6]. The role of this interface is very important in overall life assessment of composites.

The present work focuses on the effect of prior thermal history on the hygrothermal behavior of glass-polyester composites. The thermal history is introduced by giving thermal spikes and thermal shocks to different batches of FRP composites at three different temperatures, namely 100^0C, 150^0C and 200^0C. It was observed that the interlaminar shear strength (ILSS) decreased with increasing exposure to a hygrothermal environment irrespective of the thermal history. However the rate of deterioration seems to be more pronounced for specimens with a thermal history as compared to the specimens without any thermal history.

EXPERIMENTAL

Woven E-glass (Saint Gobain) fiber cloth having a density of 0.36 kg/m^2 and polyester adhesive (1% accelerator, 1.5% catalyst) were used for this work. The conventional hand lay-up method was used for specimen fabrication. After curing samples were cut to the required dimensions for three-point bend test as per the ASTM standard D2344-84, the samples were properly dried by keeping in a desiccator for 100 h. Then the specimens were divided into seven batches. The first three batches were given thermal shocks at temperatures of 100^{0}C, 150^{0}C and 200^{0}C. Thermal shocks involved sudden exposure of the specimens at an elevated temperature for ten minutes followed by quenching in ice-water. The next three batches were given thermal spikes at temperatures of 100^{0}C, 150^{0}C and 200^{0}C. Thermal spikes were given by sudden exposure of the specimens at elevated temperatures for ten minutes followed by slow cooling (in form of furnace cooling). The last batch was not given any prior thermal history.

The specimens were then hygrothermally conditioned in a humidity cabinet where the conditions were maintained at a temperature of 60^{0}C and 96% relative humidity (RH). The humidity cabinet had an inbuilt thermometer for temperature and hygrometer for relative humidity measurements. The temperature variation was maintained between 0-0.5^{0}C whereas the RH variation was allowed in the 0-1% range. The composite laminates were placed on perforated trays. The hygrothermal conditioning was carried out for different lengths of time ranging from zero to hundred hours.

The three-point bend tests were then carried out for the composite specimens. The tests were performed with an Instron 1195 testing machine. The tests were performed on different specimens at crosshead velocities of 2mm/min, 10mm/min and 50 mm/min. The interlaminar shear strength was calculated as follows,

$$ILSS = \frac{0.75P_b}{bd} \tag{1}$$

Where P_b = breaking load

b and d are width and thickness of the specimen respectively.

RESULTS AND DISCUSSION

The amount of moisture absorption by FRP composites in humid conditions is a function of time and temperature [7]. Fig. 1 is representative of the moisture absorption kinetics in FRP composites. The first region shows a marked linearity indicating Fickian absorption, where the moisture is absorbed according to Fick's second law of diffusion. Following this a saturation level is achieved, which is indicated by the horizontal region of the curve. The amount of moisture absorbed depends on the partial pressure of the moisture in the surrounding and the moisture in the composite. Once a temporary equilibrium is reached, a saturation region is attained. Prolonged exposure to hygrothermal environment results in the third stage of the curve clearly indicating non-Fickian moisture absorption kinetics. Fickian and non-Fickian moisture absorption kinetics have been explained by Li-Rong Bao and coworkers [8]. The diffusion properties of the interface may be different from those of the bulk matrix probably due to the formation of a boundary layer. When the fraction of matrix in the interface region is significant, moisture transport may be considerably affected.

The history of thermal treatment often causes matrix cracking. The initial temperature acts as an activator for moisture diffusion [9]. This may be attributed to the insulating nature of the polymer matrix. The uneven expansion, occurred during the thermal treatments, causes hair line cracking in the polymer matrix as shown in the SEM micrograph (Fig. 14). These cracks get widen up during the prolonged exposure in the environmental conditions, providing faster path for moisture diffusion. The propagation and closure of cracks are associated with the various types of stresses like hygroscopic stresses, curing stresses, residual thermal misfit stresses. The simultaneous action of all these stresses causes the coalescence of the existing microcracks, making the situation more complex to analyze. This leads to the non-Fickian type diffusion behavior.

Surface absorption and diffusion through the matrix is the primary mechanism for moisture pick up in most of the well fabricated composite materials during the initial period of exposure [10]. The composite materials contain cracks and micro voids in the matrix. These are formed during the polymerization of the matrix. The free polymer chains get entangled with each other and create these micro voids in the matrix [11]. These micro voids are the major sites for the moisture pick ups in the composite materials, especially during the initial period. Gradually when the moisture diffuses inside the matrix, it starts to interact chemically with the polymer.

This is marked by a chemical phenomenon called matrix hydrolysis [7]. When this mechanism is spread through out the composite in a wider range, then the over all chemistry of the polymer is significantly affected. Thus the adhesion between the fiber and the matrix is compromised stupendously, causing the de-bonding at the fiber matrix interface [12]. Finally, the composite fails completely, when its constituents separates out from each other. In other words, the composite fails when the interface between the fiber and the matrix collapses completely. Thus the failure of the composite deals with surface chemistry of the fiber-matrix interface due to physical, chemical and physico-chemical changes of the matrix during its service conditions.

The moisture pick up in the composite depends on the thermal history [9]. The Fig. 2 shows the effect of thermal history on the moisture pick up. As the figure shows there is an enhancement in the moisture absorbance of the composite having a thermal history, whether it is shocked or spiked. Further more, the spiked samples have shown slightly greater moisture pick up than the shocked one. This can be attributed to the fact that spiked samples are exposed to higher temperature for longer duration of time while experiencing a slow rate of cooling. This longer exposure of composite at higher temperature not only enhances the matrix cracking due to the mismatch in thermal strain, but also provides enhanced opportunity of polymerization in them. The crosslinking during the polymerization process results in an increased number of micro voids in the composites. Consequently, there exists more sites for moisture pick ups. On the contrary, the shocked samples having experienced a shorter thermal exposure will have less micro voids. But due to the poor thermal conductivity of the polymer matrix the shocked samples are probably more affected only at the surface. In both ways, the exposure to higher temperature seems to alter the chemistry of polymer and leads to the change in moisture pick ups. However, the fashion in which it is changed and its extent depends on the type and the characteristics on the thermal history.

Figure 3 and 4 show the effect of the exposing temperature on the moisture pick up in the shocked and spiked samples respectively. The figures show the moisture pick up in the shocked and spiked samples respectively. The intensity of the exposing temperature is found to be crucial for the moisture absorption as seen in both the figures. In Figure 3, for obvious reasons, the moisture absorption is more for samples shocked at higher temperature. At higher temperature the thermal stresses are more which leads to higher mismatch in the thermal strain. The polymer, being a poor thermal conductor produces larger mismatch due to the differences in the

temperature at the core and the shell of the composite leading to cracking and micro void formation [13]. This in turn makes it absorb more moisture [14]. The higher temperature also enhances polymerization which leads to the development of more sites for moisture absorption. So both for the strain mismatch and greater polymerization the voids and micro cracks are more in the samples, shocked at higher temperature which makes them absorb more moisture than the samples experienced lower temperature.

Similar trends were observed in spiked samples as shown in Figure 4, but the effect of temperature is not so prominent in these cases. As the moisture absorbance curves for different temperatures are not widely separated in this case. Probably the longer exposing time seemed more predominant than the exposing temperature. It seems that the polymerization was effective above 100^0C when exposed long enough during the furnace cooling.

The rate for the moisture pick up showed feeble cyclic characteristic when observed carefully. Figure 5 shows the rate of moisture diffusion in the composite with time for the samples spiked at 150^0C. It is noticed that the crest of the first cycle in figure 5 corresponds to the second stage of the moisture absorption curve in figure 1. The following peak is due to the onset of non-Fickian kinetics, where moisture absorption is enhanced. The non-linear nature of the non-Fickian region results in non-uniform moisture absorption rate. So, while the process would be somewhat cyclic, the peak amplitude at different stages would differ. The switchover from Fickian to saturation is drastic. This explains the high amplitude in first cycle. The switchover from saturation to non-Fickian is also quite drastic, so here in the second part the amplitude is also high. But, after that, the non-linearity in the non-Fickian regime doesn't really change the moisture pickup mechanisms drastically. So, here the amplitudes would be lower, and slowly with enhanced conditioning, this should tend to even out. It seems that, the moisture was first absorbed at the voids or pores present in the matrix when the rate of moisture in take was higher. Thus there is a fall in the rate in the absorbance, as the voids available for moisture pick up reduces down. The rate continues to fall until there are no more defects to absorb moisture. By then, the moisture thus absorbed starts to interact with the matrix both chemically and physico-chemically. This leads to the spreading of moisture through the matrix, making the path ways for newer sites for moisture pick ups. Hence, during this, the rate gets enhances again till the newer sites are completely occupied with the moisture. This cycle of absorption, dissolution and

diffusion continues till most of the matrix is soaked up by the moisture and the moisture interact with the fiber-matrix interface.

The interlaminar shear strength (ILSS) gives a very good idea regarding the fiber-matrix adhesion strength. The ILSS reflects the resultant of a variety of factors towards the fiber-matrix adhesion possibly including secondary bonding, residual compressive stresses arising during thermal treatments, mechanical locking friction, curing stresses and hygroscopic stresses [15]. Amount of moisture absorbed by the polyester matrix is significantly greater than fibers which absorb little or no moisture. This results in significant mismatch in moisture induced volumetric expansion between matrix and fibers leading to evolution of localized stress and strain fields in the composite [4, 16]. The moisture absorption also leads to changes in thermo-physical, mechanical and chemical characteristics of the polymer matrix by plasticization and hydrolysis [17].

The residual stresses developed in the composites during environmental conditioning as well as fabric geometric parameters such as fiber volume fraction and the fill/warp yarn dimensions have significant role on the overall life of the composites [2]. It is believed that any failure of the material results from its overloaded internal stresses [18]. Now this state of stress becomes more complex when composite is subjected to undergo hygrothermal environment with some prior thermal history. Absorbed moisture can damage the interface over time by interrupting the hydrogen bonding within the matrix and fiber, thereby weakening the interface. Furthermore, stresses created by swelling can be very high and may eventually damage the interface [8].

Figure 6 shows the effect of the thermal treatments on the adhesion strength between the fiber and the matrix. The samples, with a thermal history, have much less adhesive strength than only hygro-thermally conditioned samples. Thus, spiked samples were found to be most affected than the shocked once. This may be because of the fact that the spiked samples were exposed to higher temperature for much longer time. This not only has increased the number of defects in the composite but also has made it much venerable for moisture pick up. With the simultaneous action of thermal misfit stresses and hygroscopic stresses acting in a much greater extent, the damaged caused was found to be much more detrimental than the socked and hygrothermally conditioned samples [19]. The shocked samples, having also experienced a shorter thermal journey and also absorbed quite some amount of moisture, were also found to be depreciated in

ILSS values during the exposure. The hygrothermally conditioned samples, on the other hand, have much less flaws hence showed better performance under three point bend test.

Figure 7 shows the effect of temperature intensity of thermal shock on the ILSS values of the composites. As evident from the figure, it is more damaged when shocked at higher temperature. The general trend for each temperature conditions, though remained similar, but there is a significant damage at steady rate that can be observed beyond about 36 hours of conditioning. Prior to this, the ILSS values were synergistically affected as there seemed equilibrium amongst the thermal misfit stresses, hygroscopic stresses, curing stresses. But beyond that the hygroscopic stresses and the other detrimental stresses are completely dominant over the alimentary stresses causing the composite to reach its failure soon. The damage was found to be very significant for samples shocked at 200^0C. In this case the damage can be seen at much lesser exposing time.

Similar trend was observed for the spiked samples. Figure 8 but in this case the degradation was much profound and another difference being the temperature sensitivity. As compared to the shocked samples the spiked samples are not so temperature sensitive. It seems that holding the samples for long enough time at higher temperature is detrimental enough. They all follow a general trend. The strength was found to depreciate significantly after about 36 hours of exposure. The higher spiking temperature had shown more damage than the lower temperature.

Figures 9, 10 and 11 show the effect of crosshead velocities on hygrothermally conditioned specimens without any prior thermal history, with a history of shock and a history of spike respectively. Mechanical loading is already regarded as the major factor which affects the mechanical properties of composites through a wide range of physical phenomena like plasticization and swelling of matrix which acts as a stress generator and finally may lead to interfacial debonding/delamination [7]. The effect of varying crosshead velocity is to induce different degrees of brittleness in the matrix. Higher crosshead velocities imply less time for matrix to absorb the energy input during loading. This results in the matrix losing its damping properties. Hence, the loading energy cannot be dissipated as it would otherwise be at lower loading rates. Higher crosshead velocities also prevent proper load transfer in the composite. The matrix doesn't play as significant a role as it does for lower crosshead velocities. The composite,

in effect, behaves like a rigid beam [16], which breaks upon rapid loading without much macroscopic deformation.

Figure 12 shows the scanning electron micrograph of a glass-polyester composite spiked at temperature of 100^0C and then subjected to hygrothermal treatment for 16 hours. The degradation of the matrix is evident from the presence of cracks. Figure 13 shows the scanning electron micrograph of a hygrothermally conditioned specimen without any prior thermal history. The loss of interfacial adhesion is evident from de-adherence of the polymer from the fibers. Figure 14 shows the scanning electron micrograph of a composite specimen after a thermal shock at temperature of 100^0C. The shock results in misfit stresses being set up in the composite, leading to development of cracks. At the same time the degraded matrix shows a tendency to form localized "grains" or coagulated clusters. This tendency for thermally assisted localized granulation increases the effective surface area. The effect of enhanced surface area is reflected in enhanced moisture pickup kinetics, possibly by surface and/or interface absorption mechanisms

CONCLUSIONS

The effect of moisture diffusion and hygrothermal ageing on mechanical properties of glass-polyester composites were investigated. Initially, moisture absorption occurs according to Fickian kinetics. The apparent saturation level being reached was indicated by the horizontal region of the moisture absorption curve. Non-Fickian kinetics was observed to govern the moisture absorption in the final stages of conditioning. Several moisture induced interfacial cracks were observed after prolonged hygrothermal ageing. The ILSS values decreased with increased exposure to a hygrothermal environment. It was noticed that the degradation in ILSS was pronounced for specimens with a prior history of thermal spikes as compared to shocks for a given prior conditioning temperature. The effect of crosshead velocity was also studied. Assessment of the interfacial strength at higher crosshead velocities resulted in higher values of ILSS. The combination of high temperature, moisture and prior thermal treatments has derogative effects on the interface and consequently the mechanical properties.

REFERENCES

1. Da Silva Junior, JEL., Paciornik, S and d'Almeida, JRM. (2004). Evaluation of the effect of the ballistic damaged area on the residual impact strength and tensile stiffness of glass-fabric composite materials. *Compos Struct.*; **64(1)**: 123-127.

2. Jang, BZ. (1994). *Advanced Polymer Composites – Principles and applications*. ASM International, Materials Park, OH.

3. Thanomsilp, C and Hogg, PJ. (2003). Penetration impact resistance of hybrid composites based on commingled yarn fabrics. *Compos sci Tech.*; **63(3-4)**: 467-482.

4. Vaddadi, P., Nakamura, T and Singh, RP. (2003). Inverse Analysis for transient moisture diffusion through fiber-reinforced composites. *Acta Mater.*; **51(1)**: 177-193.

5. Adams, RD and Singh, MM. (1996). Dynamic Properties of fiber-reinforced polymers exposed to hot, wet conditions. *Compos Sci Tech.*; **56(8)**: 977-997.

6. Papanicolaou, GC., Michalopoulou, MV and Anifantis, NK. (2002). Thermal stresses in fibrous composites incorporating hybrid interphase regions. *Compos Sci Tech.*; **62(14)**: 1881-1894.

7. Gautier, L., Mortaigne, B and Bellenger, V. (1999). Interface damage study of hydrothermally aged glass fiber reinforced polyester matrix composites. *Compos Sci Tech.*; **59**(16): 2329-2337.

8. Bao, LR and Yee, AF. (2002). Moisture diffusion and hygrothermal ageing in bismaleimide matrix carbon fiber matrix – Part I: uni-weave composites. *Compos Sci Tech.*; **62(16)**: 2099-2110.

9. Vina, J., Garcia, EA., Arguelles, A and Vina, I. (2000). The effects of moisture on the tensile and interlaminar shear strengths of glass or carbon fiber reinforced PEI. *J Mater Sci Lett.*; **19(7)**: 579-581.

10. Tompkins, SS., Tenney, DR and Unnam, J. (1979). Prediction of moisture and temperature changes in composites during atmospheric exposure. *In: Proceedings of Composite Materials: Testing & Design (Fifth Conference), ASTM STP*. 368-380.

11. Shirrell, CD and Halpin, J. (1977) Moisture absorption and desorption in epoxy composite laminates. *In: Proceedings of Composite Materials*: *Testing & Design, 4th Conf., ASTM STP*. 514-528.

12. Boinard, E., Pethrick, RA., Dalzel-Job, J and Macfarlane, CJ. (2000). Influence of resin chemistry on water uptake and environmental aging in glass fiber reinforced composites-polyester and vinylester laminates. *J Mater Sci.*; **35(8)**: 1931-1937.

13. Zhang, S., Karbhari, VM., Lin, Y and Mai, YW. (2000). Evaluation of property retention in E-glass/vinylester composites after exposure to salt solution and natural weathering. *J of Reinforced Plast & Comp.*; **19(9)**: 704-731.

14. Springer, GS. (1979). Environmental effects on epoxy matrix composites. *In: Proceedings of Composite Materials: Testing & Design (Fifth Conference). ASTM STP.* 291.

15. Gaur, U and Miller, B. (1990). Effects of environmental exposure on fiber/epoxy interfacial shear strength. *Polymer Composite*; **11(4)**: 217-222.

16. Ray, BC. (2004). Effect of crosshead velocities and sub-zero temperature on mechanical behavior of hygrothermally conditioned glass fiber reinforced epoxy composites. *Mater Sci Engg: A.*; 379**(1-2)**: 39-44.

17. Sala, G. (2000). Composite degradation due to fluid absorption. *Composites: B*; **31(5)**: 357-373.

18. Huang, ZM. (2002). Fatigue life prediction of a woven fabric composite subjected to biaxial cyclic loads. *Compos A.* **33(2)**: 253-266.

19. Ip, K.H., Dutta, PK and Hui, D. (2001). Effects of low temperature on the dynamic moduli of thick composite beams with absorbed moisture. *Composites: B.* **32(7)**: 599-607.

FIGURE CAPTIONS

Figure 1   A generalized moisture absorption curve for glass polyester composites during hygrothermal conditioning

Figure 2   Effect of the nature of prior conditioning treatment at a constant prior conditioning temperature of 150^0C

Figure 3   Effect of the prior conditioning temperature on the moisture absorption kinetics of shocked composites

Figure 4   Effect of the prior conditioning temperature on the moisture absorption kinetics of spiked composites

Figures:

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Fig. 14