Title – Experimental studies on mechanical behavior and microstructural assessment of glass/epoxy composites at low temperatures

Name - S. Sethi*, P.K.Panda, R.Nayak and B.C.Ray

Sanghamitra Sethi (corresponding Author)
E-mail-sanghamitra65@gmail.com
Department of Metallurgical and Materials Engineering,
National Institute of Technology
Rourkela- 769008, India
Tel: +91-661-2462559 Fax: +91-661-2472926

P.K Panda, R.Nayak, B.C.Ray
Department of Metallurgical and Materials Engineering,
National Institute of Technology
Rourkela- 769008, India

Abstract

A series of flexure tests with varying cross head speed were conducted to study the mechanical behavior of glass/epoxy composites at low temperature. The micromechanics of damage growth and failures underpin the understanding of the revealed fractography. The 3-point flexure test of heat treated and untreated samples which were further exposed to low and ultra-low working temperatures of $-20^{\circ}C, -40^{\circ}C, -60^{\circ}C, -80^{\circ}C$ was carried out. The interlaminar shear strength (ILSS) was found to be affected by these conditionings. The unbalanced and inhomogeneous stress concentration within entangled chain of matrix reduces conformational isomerism which in turn reduces the ILSS value considerably at low cross head speed. As increased cross head speed (strain rate), the matrix becomes brittle, and fracture strain decreases, but at very high strain rate, the fracture strain increases. The reason is anticipated to be adiabatic heating. Temperature modulated differential scanning calorimetry (TMDSC) shows increase in glass transition temperature (Tg). A change in cross head speed may results in variation of failure modes which is observed in scanning electron microscope (SEM).

Keywords: Glass/epoxy composite, 3-point flexure test, ILSS, fractography, glass transition temperature, TMDSC

1. Introduction

Because of their unique architectural features, ease of handling, low fabrication cost, and excellent mechanical properties, woven fabric composites have been finding increasing applications in aerospace and automobile structures, and equipment for superconducting magnets. In particular, superconducting magnets for use in fusion reactors, such as the International Thermonuclear Experimental Reactor (ITER), may use large quantities of woven glass fiber reinforced polymer (GFRP) composite laminates as thermal insulation, electrical insulation and structural support [1]. Advanced composites are being explored for structural applications at extremely low temperatures, for example, in large cryogenic fuel tanks. When the temperature is decreased down to cryogenic temperatures, the internal stress due to the thermal contraction is generated in a matrix resin. Expose to these cryogenic temperatures can cause microcracks as well as delamination in the composites due to thermal residual stresses mainly brought on by the anisotropy in the composite ply coefficient of thermal expansion (CTE). Microcracks and delamination often result in a reduction in laminate stiffness and strength and changes in laminate CTE, and provides both a pathway for the ingress of moisture or corrosive chemicals and a possible pathway for loss of cryogenic fluids in the tanks [2]. A recent example is the Bridge-in-a-Backpack for 2014 Winter Olympics in Russia, an innovative inflatable composite-concrete arch bridge, which was developed to reduce construction time and costs, increase lifespan, reduce maintenance costs and reduce the carbon footprint of bridge construction [3]. It is reported that interface is the heart of the composite. The local response of fiber matrix interface within the composite plays an important role in determining the gross mechanical performance. The concept of two-dimensional interface between fiber and matrix has given way to the evolution of the 3-D region mere properly termed as interphase [4]. At cryogenic temperatures, the microcracks initiate and propagate in laminated composites due to difference in thermal contraction between the fiber and matrix phases [5]. . When the temperature is decreased down to cryogenic temperatures, the internal stress due to the thermal contraction is generated in a matrix resin. Fracture of the matrix is induced when the thermal stress induced stress intensity factor exceeds the fracture toughness of the resin. It is, therefore, important that the fracture toughness of the epoxy resin is improved even at cryogenic temperature [6]. The fracture toughness of epoxies at cryogenic temperatures is thought to be controlled by stress relaxation at the crack tip, the strength of molecular chains, or both. To increase the strength of molecular chains, the crosslinking density should be increased. The mechanical properties of composite at low temperature are influenced by the matrix. The thermal prestress on the matrix is crucial, especially at low temperature where polymers become brittle. This reduces the effective strain to failure and is a source of microcracks in the matrix. Increased thermal stresses are the underlying cause of microcracking in composites at low temperature. As the laminate temperature falls below its stress-free temperature, residual stresses develop in the material. These stresses are the result of a difference in the linear coefficient of thermal expansion (CTE) between the fibers and the matrix [7]. As the temperature of the material deviates more from the stress-free temperature, the amount of thermal stress in the matrix increases. When the residual stresses in the material become large enough they are relieved through physical processes such as potholing, delamination, and/or microcracking. It is observed; microcracks propagate and result in transverse cracks. When the transverse crack develops further, the crack deflects through the interface between layers and delamination initiates [8].

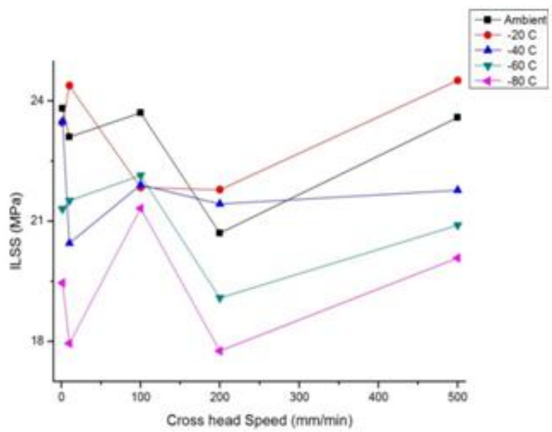
2. **Methods and Experimental**

An unmodified epoxy resin based on Bisphenol-A with woven roving E-glass fibers, treated with a silane-based sizing system was used to fabricate laminated composites. The fiber weight percentage was kept to be 60 in the laminate fabrication process and curing was carried out at ambient temperature. The laminated plates were cut into short beam shear (SBS) specimens by diamond cutter. The ASTM standard for (D2344-06) specimens were then divided into two equal groups. One group of samples was treated at 60°C for an hour and the other group was tested without any pretreatment. Then both the groups of specimens were exposed to low and ultra-low working temperatures of −20°C, −40°C, −60°C and−80°C and the rest of the specimen were left unexposed. Then the mechanical tests of all the ten groups of specimens were carried out with shortest possible off-time after the conditioning. Multiple samples were tested at each point of the experiment and the average value of acceptable level was reported here. The breaking load of SBS test was used to calculate the ILSS value. The tests were performed at1mm/min, 10mm/min, 100mm/min, 200mm/min, and 500mm/min different cross head speed for treated specimens as well as for untreated specimens. The ILSS values and strain at peak were plotted with respect to cross head speed. Fractographic analysis was carried out using a JEOL-JSM 6480 LV Scanning electron microscope. The samples were loaded onto the sample holder, then, the chamber was closed, adjusting the working distance then the vacuum was applied. Glass Transition Temperature is measured by using TMDSC and results were analyzed.

3. Results and Discussion

3.1 Three-point bend test

The effects of different cross head speeds on ILSS value at low temperature and at ambient temperature of untreated samples of glass/epoxy laminates are shown in Fig 1 a) and b).



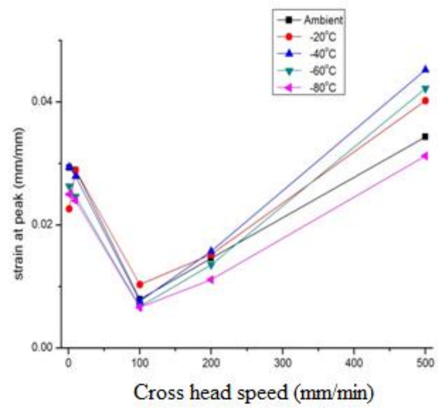
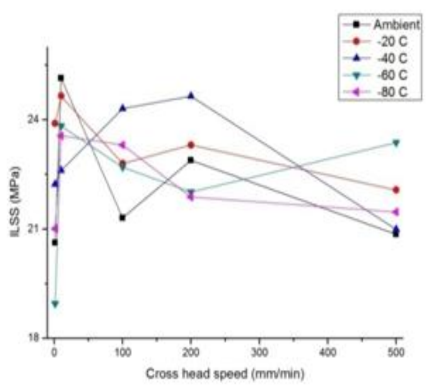


Figure 1: a) Cross head speed with ILSS values b) Strain at peak with cross head speed values



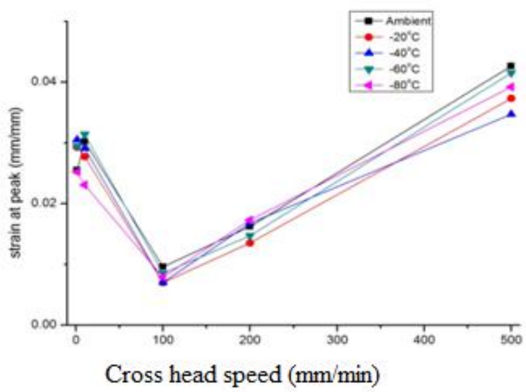


Figure 2: a) Cross head speed with ILSS values b) Cross head speed with strain at peak of treated sample

The lower value of ILSS at lower cross head speed may be due to higher failure strain at low strain rate as shown in the adjacent graph. At lower cross head speed, more time is available for crack initiation and crack propagation to occur, which lead to ease of deterioration, causing the reduction in value of ILSS. The unbalanced and inhomogeneous stress concentration within entangled chain of polymers reduces conformational isomerism, which in turn reduces the strength of the composite considerably at low temperature. The microcracks, voids, crazes, or notches which exist in each polymer, when loaded, may lead to formation of stress concentration at their crack tip. They may become the nuclei of further, microscopic cracks. These stress induced cracks may grow without blunting, leading to low ILSS values.

The crack propagation is mainly controlled by the energy balance of the released energy rate G, and the consumed energy rate, R, which are related to a newly cracked area of a fracture surface. If the released energy rate G is more than the consumed energy rate R, than the unstable crack propagation occur, which is mainly attributed at low temperature. At very low temperature, the yielding minimizes and the fracture may become brittle. At higher cross head speed, above 100mm/min, the time available is very less, for the failure to occur, thus the matrix may not properly be able to transfer the load which, leads to matrix cracking. This results in reduction of ILSS values at 200 mm/min. At still higher cross head speeds of 500mm/min, the shear strength value again is observed to increase. The possible reason may be generation of adiabatic heat, formed locally at the crack tip. An adiabatic condition exists at unstable crack propagation where the rate for heat generation is lower than the rate for heat removal by thermal conductivity. The temperature rise at the crack tip is especially high since the specific heat of matrix is low. In other words, heat is generated as the composite is exposed to very high loading rate, but there is very less scope for removal of heat in a very short time interval. This slow rate of heat dissipation leads to higher amount of heat accumulated at the crack tip. As a consequence the size of plastification zone at the crack tip is enlarged, which increases the energy of the plastification and thus R. This makes the crack tip blunt. In the strongly loaded crack tip zone, some alignment of polymer chain occurs, which additionally increases R. As R increases, the possibility of crack propagation decreases thus increasing the ILSS values.

The fracture value depends strongly on strain rate. At increased cross head speed (strain rate), the matrix becomes brittle, and fracture strain decreases, but at very high strain rate, the fracture strain increases. The reason is anticipated to adiabatic heating [9].

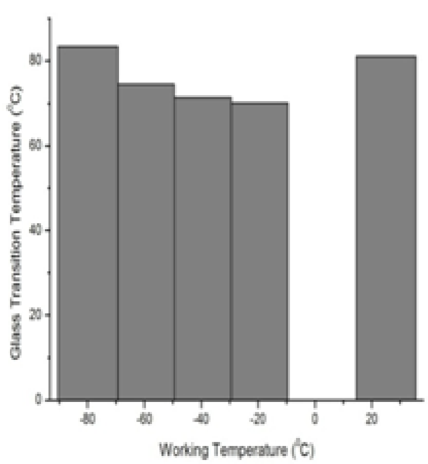
Different processes at a crack tip occur at different strain rates. The fracture processes are controlled mainly by two scales of time: mechanical relaxation time and thermal relaxation time. , which controls the heat removal. Their relative influences are determined by strain rates. If the loading time is much more than the mechanical relaxation time i.e., at low strain rate, small isothermal, plastic deformations at the crack tip increase the crack resistance and make the fracture strain higher. If the loading time is less than mechanical relaxation time, i.e. at medium strain rate, the time is not sufficient for plastic deformations at the crack tip, due to which the polymer becomes more brittle and fracture strain is decreased. In other case, if the loading time is higher than the thermal relaxation time, i.e., at higher strain rate, there is increased heat power generation at the crack tip by deformation and fracture, but most of the heat is removed by thermal conductivity. But at very high strain rate, where loading time is less than the thermal relaxation time, the heat generation is faster than its removal at the crack tip occurs which enhances plastic deformation. Thus fracture stress and strain are increased [10].

Fig 2: During thermal conditioning at 60ºC for 1 hr increases the crosslinking density along with the development of penetrating and/or semi-penetrating network at the fiber/matrix interface.

When it is treated at low temperature, compressive stresses are developed which improves the lock and key adhesion mechanism at the fiber matrix interface, due to which epoxy resin opens more despite of the low temperature hardening. Crack density is less likely to occur; as a result there is improvement of ILSS values at 10mm/min and 200mm/min.

3.2 Differential Scanning Calorimeter (temperature modulated mode) analysis

A glass transition is characterized by unfreezing of molecular mobilities upon warming. This occurs in a narrow temperature range. As the temperature increases, there is an increase in chain branching until the system reaches gelation; further polymerization causes an increase of the crosslinking until the mobility of the reactive centers is progressively restricted and the reaction becomes diffusion controlled. At the molecular level, the glass transition temperature feeds sufficient energy into the matrix to enable the onset of coordinated motion of large molecules. The position of the Tg is very dependent upon the strain rate of the matrix [11].As the crosslinking progresses, Tg of the epoxy increases. For primary glass transitions, molecular chains become fully flexible and many relaxation processes overlap.



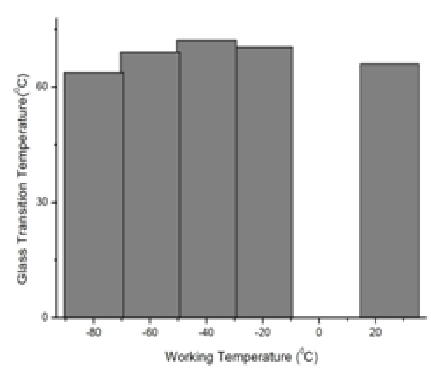


Figure 3: a) Tg value with working temperature b) Tg with low and ultra-low temperature

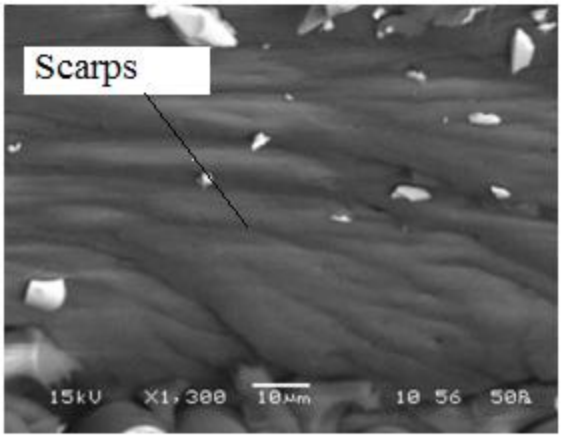
Fig. 3 shows there is increase of glass transition temperature (Tg). At low temperature only low energy barriers allow molecular groups to change places. Increase in Tg values decreases the possibility of formation of plastic zone at the crack tip which in turn reduces the ILSS values promoting brittle fracture.

3.3 Fractographic study (SEM)

Microscopic features of flexural failure

a) Matrix-dominated failures of PMC

Considering the influence of low temperatures on the fracture micromechanisms in composites; the matrix is brittle and residual tensile stresses in the matrix are promoted. Regarding the fracture morphology of interlaminar (intralaminar) fracture, at very low temperature, resin embrittlement dominates and thus lowers the composite toughness. The final pair of fracture modes to consider is the interaction between intralaminar and interlaminar cracks. One of the most important phenomena of matrix fracture is the process by which multiple fractures initiate along the crack front, begin to propagate on several slightly different planes, and then subsequently converge onto one plane. Local failure may initiate along a line defect, such as a fiber, and spread into the surrounding matrix. This phenomena leads to important fractographic features such as scarps and riverlines. Firstly, consider convergence between two adjacent crack planes. At the boundary between these planes, a sharp step can form, called scarps (Fig 4). Secondly the most valuable features for diagnosing crack growth directions is ‘riverlines’ (Fig 5).



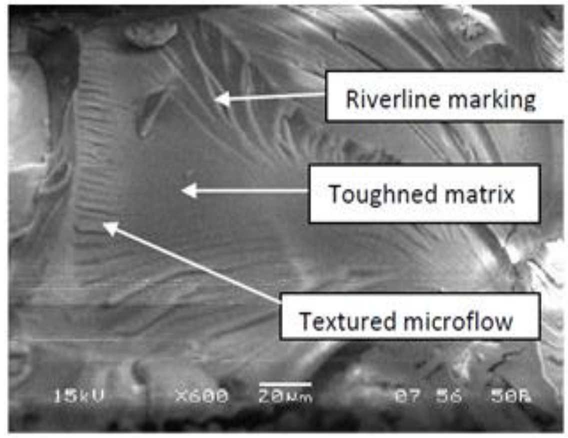
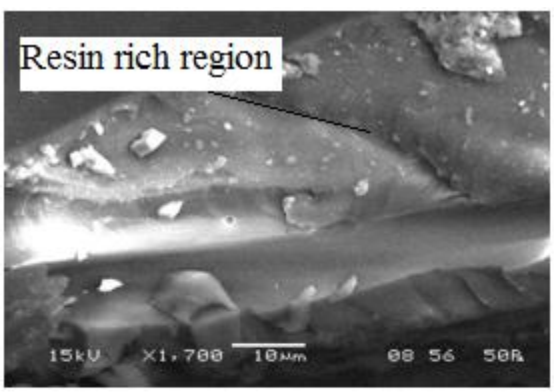


Figure 4 and 5: Matrix failures at low temperature

These are a natural development of scarps and the convergence of crack places. The convergences of pairs of planes form the tributaries of the rivers, ultimately converging into one crack. Therefore, the direction of crack growth is the direction in which the riverlines converge. Another fracture (textured microflow) has initiated from the fibers and grown into the surrounding matrix. However, in the instance of crack propagation the point of these failure modes indicates the initiation site of the fracture (Fig 5).



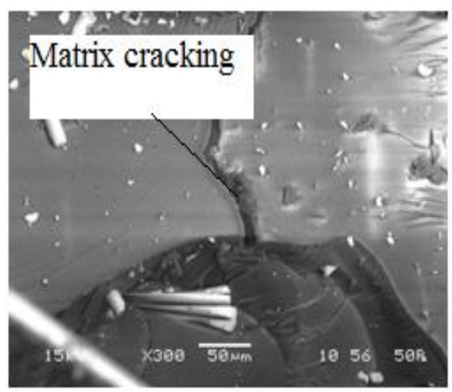
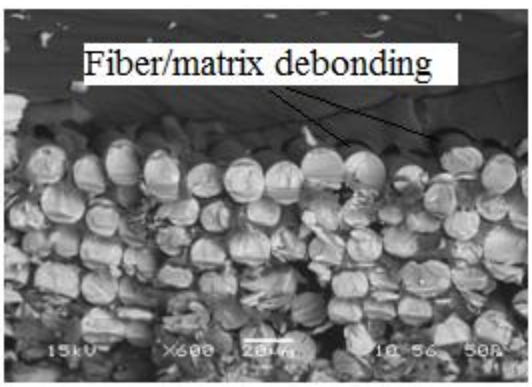


Figure 6 and 7: Resin rich region and matrix cracking in the epoxy region

If the stress level is high enough resin-rich regions (Fig 6) becomes the critical failure mode. Failure of the matrix in these regions is generally brittle. These are often associated with local stress raisers and therefore, caution should be followed when using them to interpret global fracture paths, since the local crack growth direction deduced at their sites may not be consistent with global crack growth. Matrix cracking (Fig 7) failure of the matrix occurs when the stresses greater than the shear stress of the matrix is readily generated.

b) Fiber and fiber/matrix interface-dominated failures

At low temperature the matrix becomes brittle, which tends to have good fiber/matrix strength, the mode I fracture is cohesive. This means that some matrix is left on the fibers and it is unusual for the bare fibers to be exposed. This bond strength can be enhanced by crenulations on the fiber surface. Bare fibers can be observed when there is poor fiber matrix interface strength, such as that induced by temperature, moisture. Under such conditions, the preferential fracture at the fiber/matrix interface will also reduce the degree of matrix deformation. As the matrix toughness increases, the fracture starts to preferentially occur at the fiber/matrix interface.



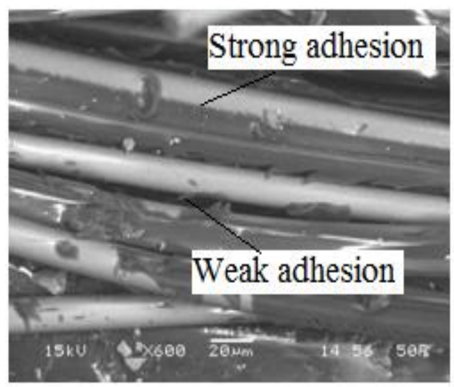
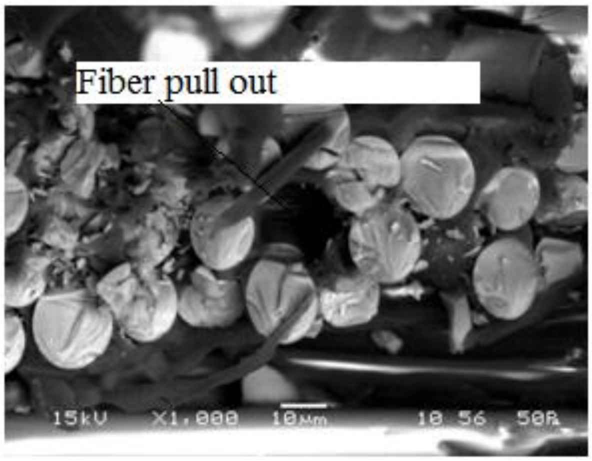


Figure 8 and 9: Fiber/matrix debonding and adhesion in interface of GFRP.

A strong interface (Fig 9) displays an exemplary strength and stiffness, but it's very brittle in nature with easy crack propagation through the interface. A weak interface reduces the stress transmissibility and consequently decreases the strength and stiffness. Here a crack is more likely to deviate and grow at the weak interface resulting de-bonding and/or fiber pull-out and contributes to improved fracture toughness (Fig 8,10).



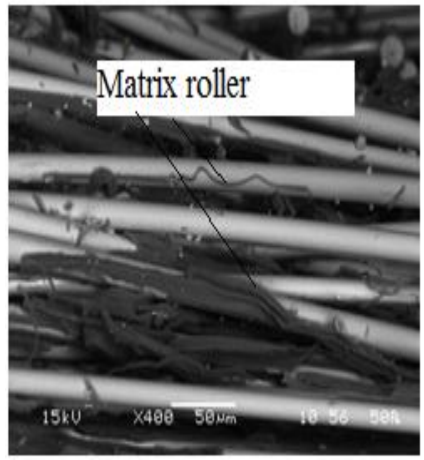


Figure 10 and 11: Fiber pull-out and matrix roller in GFRP composites

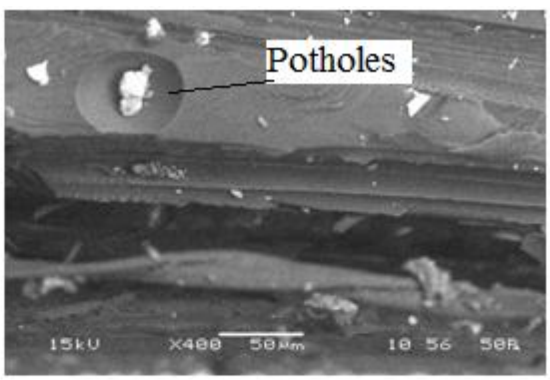


Figure 12: Potholes in epoxy matrix

Intralaminar fracture surfaces produced under shear loading as matrix rollers. Matrix rollers (Fig 11) are apparent and they exhibit a surprising degree of ductility, particularly given that it is a brittle system. At intralaminar fracture surfaces, occasionally the surface impression of the underlying fibers can be seen within the matrix roller [12]. In low temperature, due to shrinkage of matrix, a loss of patch bonding tends to occur over time, particularly if freeze-thaw cycling occurs which is assisted by potholes in the matrix region (Fig12).Low temperature conditioning can be considered as a treatment which makes the microstructure of the composite more orderly.

It was reported that damping behavior of glass/epoxy composites at low temperature is irreversible that is the phase transition because of the temperature change is not always reversible.

Conclusion:

The thermally conditioned glass fibre/epoxy composite is sensitive to cross head speed. The untreated samples show reduction in ILSS values above and below 100mm/min, whereas in thermally conditioned samples, the ILSS values are comparable above, below and at 100mm/min cross head speed. This shows the increase in structural integrity and durability of the composite on thermal preconditioning. The higher Tg values at low temperature exposure decipher the extension of glassy state of epoxy matrix in glass/epoxy composites. Key to both understanding of micromechanics and development of physically based failure criteria is a fractographic analysis, which is defined as the interpretation of fracture morphology to glean information about the material failure.

References

1.Shindo,Y.,Takeda,T.,Narita,F.,Saito,N.,Watanabe,S.,Sanada,K:Delamination growth mechanisms in woven glass fiber reinforced polymer composites under mode II fatigue loading at cryogenic temperature. J.Compos.Sci.Technol.(2009);69;1904-1911

2. Choi,S.,Sankar,V.B.:Fracture toughness of transverse cracks in graphite/epoxy laminates at cryogenic conditions. J. Composites Part B. (2007); 38; 193-200

3.Surendra,K.,Chawla,N.,Priyadarsini,A.,Mishra,I.,Ray,B.C.:Assessmentof microstructural integrity of glass/epoxy composites at liquid nitrogen temperature. J.Reinf.Plast.Compos. (2007);26;1083-1089

4. Ueki,T.,Nishijima,S.,Izumi,Y.Designing of epoxy resin systems for cryogenic use.J.Cryogenics. (2005);45;141-148

5. Sawa,F.,Nishijima,S.,Okada,T.:Molecular design of an epoxy for cryogenic temperature. J.Cryogenics. (1995);35;767-769

6. Timmerman,J.F.,Tillman,M.S.,Hayes,B.S.,Seferis,J.C.:Matrix and fiber influences on the cryogenic microcracking of carbon fiber/epoxy composites. J. Composites Part A. (2002);33; 323-329

7.Greenhalgh,E.S., Failure analysis and fractography of polymer composites, Cambridge,UK ,CRC Publication, Woodhead Publishing, 2009

8. Hartwig,G., Polymer properties at room and cryogenic temperatures. New York, Plenum Press, 1994

9. Jang,B.Z., Advanced Polymer Composites: Principle and Applications. ASM International, Materials Park, OH, 1994

10. Kim,Y.R.,Donaldson,L.S.:Experimental and analytical studies on the damage initiation in composite laminates at cryogenic temperature. J.Compos.Struct. (2006);76;62-66

11.Mahieux,C.A., Environmental degradation in industrial composites, Elsevier Ltd.,Oxford UK,2006

12. Russian company considering UMaine Bridge technology for 2014 winter Olympics, 2010, www.netcomposites.com. Date of publication-19/11/2010