STRUCTURAL INTEGRITY OF GLASS/POLYESTER COMPOSITES AT LIQUID NITROGEN TEMPERATURE

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ABSTRACT

The aim of present study is to investigate the interlaminar fracture behaviour of glass reinforced polyester composites at liquid nitrogen temperature. Short beam Shear (SBS) test, which generally promotes failure by interlaminar shear, was performed to assess interfacial bond strength between fibre and matrix. The mechanical assessment is extended to evaluate and compare the loading rate sensitivity of cryogenically conditioned and untreated glass/polyester composites at 2mm/min, 50mm/min, 100mm/min, 200mm/min and 500mm/min crosshead speeds. Microstructural changes after cryogenic treatment of glass/polyester composites were explained by Scanning Electron Microscope (SEM). The behaviour of these composites at cryogenic temperature may be attributed to stress relaxation, polyester curing shrinkage, large amount of residual stresses, cryogenic contraction of the matrix, greater misfit strains and matrix crackings.

Keywords: composites (A); nitrogen (B); mechanical properties (C); thermal expansion (C); space cryogenics (F)
INTRODUCTION

In the present scenario advanced polymer composite materials are in massive demand for applications in the field of aerospace vehicles, automobile parts, satellites, sports goods, robots, and thermal insulation structures like cryostats for low temperature technology, hydrogen technology tanks, in superconductivity and also in biomedicine for body compatible implants [1, 2, 3]. Many of our modern technology require materials with unusual combinations of properties that cannot be met by the conventional metal alloys, ceramics and polymeric materials. This is especially true for materials that are needed for aerospace, under water and transportation applications. For example aircraft engineers are increasingly searching for structural materials that have low densities, are strong, stiff and abrasion and impact resistance, and are not easily corroded. All the mentioned properties are met by advanced polymer composites. The above properties are strongly dependent on the factors such as the matrix and fibre material and their volume fractions, the fibre orientation, the applied stress levels and strain rates, as well as the loading conditions and the nature of fibre polymer interface [4, 5]. Interface is said to be the heart of the composite. The local response of fibre matrix interface within the composite plays an important role in determining the gross mechanical performance [6]. It provides a means of stress transfer from fibre to fibre through the matrix. In cold conditions, high residual stresses can build up within the fibrous composite materials due to different coefficients of thermal expansion of the fibre and the matrix and at low temperatures the polymer matrix experiences embrittlement which can also affect the properties of the composite [7, 8]. But with change in temperature, or when the component comes from the cold condition to the normal ambient condition, it may affect the residual stresses leading to
either deterioration or enhancement of mechanical properties. The bond strength depends on quality of interfacial adhesion. A better fibre/matrix interfacial adhesion/bond will impart better properties such as interlaminar shear strength, delamination resistance and fatigue resistance to a polymeric composite. The non-zero state of residual thermal stresses at low temperatures is the underlying cause of microcracking in composites and these microcracks propagate results in transverse cracks. When the transverse crack develops further, the crack deflects through the interface between layers and delamination initiates. The delaminations connect the microcracks in adjacent layers and provide leakage paths. The combined cryogenic and elevated temperature thermal cycle produces substantially greater amounts of damage in polymer composites [9, 10]. It is reasonable to assume that the interfacial shear strength is the net result of number of contributions that includes chemical bonding, secondary forces of attraction, residual compression forces due to differential shrinkage and also mechanical interlocking at the interface of fibre and matrix [11]. Unsaturated polyesters are widely used in the composite industry. They can provide excellent mechanical and chemical properties, good chemical and weather resistance, and a low cost. Further advantages of unsaturated polyester resins over other thermosetting resins are that they are easy to handle, can be pigmented, and can be easily filled and fibre reinforced in a liquid form. Glass fibre reinforced polyester composites are used extensively in building and construction, transportation, electric and electronic industries and in domestic applications. One of the major problems is that the cure of unsaturated polyester (UP) resins is accompanied by a high degree of polymerization shrinkage (normally 7–10%). This shrinkage usually causes severe manufacturing problems, which include surface quality flaws such as surface waviness
and sink-mark formation, and dimensional control problems. An efficient way to eliminate/reduce the shrinkage is to introduce thermoplastics as “low profile” additives (LPAs) in the resin system [12]. The present study has been carried out to evaluate and make a comparative study of the mechanical performance of cryogenically conditioned and untreated chopped glass/polyester composites.

**EXPERIMENTAL**

Unsaturated polyester resin with 1% accelerator and 1.5% catalyst was used with chopped E-glass fibres treated with silane based sizing system (Saint-Gobain Vetrotex) to fabricate the laminated composites. The fibre weight percentage 50% was targeted in the laminate fabrication. The fabrication was done by hand lay-up method. First, the glass fibres were cut to required dimensions and placed on the plane mould. Catalyzed unsaturated polyester was then applied on it uniformly and another layer of fibre was put on it. Rolling was carried out with uniform pressure in order to remove the air pockets. They were cured for 48 hours at room temperature. The laminates were cut into short beam shear (SBS) test specimens by diamond cutter. The SBS 3-point bend tests were conducted to determine the interlaminar shear strength (ILSS) of composites. The cured specimens were exposed to liquid nitrogen environment (77K) for one hour. After the exposure one batch of samples were taken out and kept at room temperature for one hour. Another batch of samples was tested in 3-point bend test immediately after exposure to cryogenic temperature. The former samples after exposure to room temperature and the untreated as-cured composite specimens were tested in 3-point bend test at room temperature. All the mechanical flexural tests were performed at 2, 50, 100, 200 and 500
mm/min crosshead speeds. The interlaminar shear strength (ILSS) was measured as follows,

$$ILSS = 0.75p/bt$$

Where,

‘p’ is the breaking load, ‘b’ the width, and ‘t’ the thickness of the specimen.

An Instron1195 tensile testing machine was used to perform SBS tests in accordance with ASTM D 2344-84 standard. Multiple samples were tested at each point of experiment and the average value was reported.

**RESULTS AND DISCUSSIONS**

Cryogenic conditioning of polymer composites leads to the development of residual stresses at the interface, which are of compressive in nature. Surendra Kumar M et.at [13] reported an increase in the resistance to debonding by mechanical keying principle at the interface of woven glass/epoxy composites due to the development of shrinkage compressive stresses after cryogenic conditioning. These residual stresses are generated due to differential contraction of matrix and fibre at low temperature. As the fibre has smaller thermal expansivity than the polymer matrix, the resultant stresses are compressive in the fibre and tensile in the matrix. These compressive stresses at the interface ensure that fibre and matrix are kept in contact and helps in strengthening the adhesion. Figure 1 shows the effect of crosshead speeds on Interlaminar Shear Strength (ILSS) of chopped glass/polyester composites at ambient temperature (▲), cryogenic temperature (♦) and at ambient temperature after one hour cryogenic conditioning (■).

The graph shows that the cryogenically conditioned specimens have lower ILSS values than the untreated laminates. This discrepancy from the results obtained by Surendra
Kumar M et.al [13] may be due to the generation of very large amount of residual stresses at the interface. These residual stresses include compressive stresses due to contraction of polyester matrix at cryogenic temperature and very high shrinkage stresses during curing of polyester (shrinkage >7%) resin [14]. As the chopped glass fibres provide more interfacial area [10], the matrix (polyester) becomes broken up into isolated regions due differential contraction at cryogenic temperature and surrounds on all sides of fibres as shown in the figure 2. Thus, the matrix tends contract away from the fibres, which decreases fibre/matrix bonding. Differential coefficients of thermal expansion would modify the local stress threshold required for interfacial debonding which may eventually lead to nucleation of delamination. That possibly results in higher order of debonding at the interfaces and the fall in ILSS values is reflected in the graph. The debonding phenomena are more pronounced for glass/polyester system due to the weaker interface. It may also be attributed to the very high curing shrinkage of polyester resin during curing. This shrinkage is due to the specific chemical structure of the unsaturated polyester resins, which is further complicated by the exothermic character of the curing reaction results in volumetric expansion due to local temperature rise. Due to this complex interaction between the chemical reaction shrinkage and the expansion due to cure reaction heat generation may lead to a variable temperature distribution in the curing resin. This may accelerate the reaction in a locally higher temperature region and will cause more curing shrinkage there compared to the shrinkage experienced within a lower temperature area. When the unsaturated polyester resin finally turns into the solid state the volumetric shrinkage will most likely vary from region to region, due to the different thermal history experienced [15]. This finally leads to a large amount of residual stress
distribution due to the curing reaction and further influenced in the presence of fibres due
different thermal coefficient of expansion.
The laminates with low bond strength exhibits large areas of interfacial debonding that
intensifies other damage mechanisms to promote laminate failure. The large residual
stresses induced at lower temperatures become potentially damaging for polymer matrix
composites with curing temperature environment. The damage may begin with the
formation of microscopic cracks (crazing) in the matrix or at the fibre/matrix interface.
When these cracks develop to a certain density and size, they will tend to coalesce to
form macroscopic matrix cracks (figure 3). The figure 1 also shows that the specimens
tested at room temperature after one hour cryogenic conditioning has lowest ILSS values.
This is may be attributed to adverse affect of thermal shock [16] at the interface by
weakening the physical and mechanical bonding because of differential thermal
coefficient of expansion and/or contraction for the polymer matrix and the glass
reinforcement. Also it was reported by Ray BC [17] that cryogenically conditioned
polyester matrix composites are more prone to debonding due to thermal shock. Thermal
shock may often result in intense thermal stresses in the structure during service periods
around cracks and other kinds of common manufacturing defects of FRP composite. This
may modify the local stress threshold required for interfacial debonding. It quite possibly
leads to the premature nucleation of delamination failure. The failure in a fibre composite
initiate from small defects such as matrix pores and debonded interfaces (figure 4).
Matrix micro-cracking may also occur near the tip region [18]. The multiple matrix
rackings by the treatment may become a macroscopic form of damage accumulation that
eventually may dictate the initiation of delamination failure (figure 3). The residual stress
distribution, differences in Poison’s ratios and differential coefficient of thermal expansion can influence the crack multiplication stage of failure process. Here the presence of more interfaces [10] in the present composite strongly affected by cryogenic thermal shock. It may lead to generate more interfacial cracking. The damage may possible be accelerated because of poor fibre-polymer adhesion or improper/insufficient wetting.

It is also evident that the nature of the curve is different at above and below 50 mm/min crosshead speed for all the three cases. The ILSS value increases with the crosshead speed upto 50 mm/min but reduces above. The lower value of ILSS at lower speed may be attributed to high failure strain at low strain rates so strength increases with increases in speed. At low crosshead speed the laminate gets more time for failure to takes place, which results in more deterioration causing reduction in the ILSS value. But at crosshead speeds above 50 mm/min the curve is opposite. Here the time available for the failure to takes place is very less; it is more like an impact force. So the matrix may be unable to transfer load properly to the fibres, which leads to matrix cracking. Mechanism for crack tip opening and growth involves the formation and growth of voids ahead of crack tip. Resharpening and advancement of the crack occurs by coalescing with microvoids. The local microstructure near the crack tip plays an important role in the blunting phenomena. Here the severity of blunting decreases with decreasing temperature as void formation is suppressed. It is important to note that a change in loading rate can change failure modes. The higher crosshead speed restricts the relaxation process at the crack tip, so that the stress induced cracks may grow without blunting results in lowering of ILSS at higher crosshead speed [19]. The ductility of a resin matrix could become a limiting factor at
high loading rate for the composite strength. A weaker of interfacial bond may result in a low flexural strength of the laminate. The deteriorated integrity can cause low strength at high loading. All phenomena are possibly contributing the observed non-linear mechanical behavior of glass/polyester composites under cryogenic conditioning.

CONCLUSIONS

The effect of cryogenic conditioning for the glass/polyester composites at different loading rates was experimentally investigated. The glass/polyester composites were found to be loading rate sensitive. Generation of large amount of residual stresses at the interface may be attributed to thermal contraction due cryogenic conditioning and high shrinkage stresses during curing of polyester matrix, which results in fibre/matrix debonding. Also the weakening effects of thermal shock (sudden exposure to room temperature after cryogenic conditioning (77K)) were more pronounced in glass/polyester composites and hence lower ILSS values were reflected.

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REFERENCES


FIGURE CAPTIONS

Figure 1 Variation of ILSS of chopped glass-polyester composites with crosshead speed at ambient temperature (▲), cryogenic temperature (♦) and at ambient temperature after cryogenic conditioning (■).

Figure 2 Scanning micrograph showing matrix (polyester) broken up into isolated regions due to differential contraction at cryogenic temperature and surrounds on all sides of fibres.

Figure 3 Scanning micrographs showing large amount of matrix crackings and delamination of cryogenically conditioned specimen (b) compared to untreated specimen (a).

Figure 4 Scanning micrograph showing debonding at fibre/matrix interface due differential contraction and thermal shock of cryogenically conditioned specimen.
Figure 1
Figure 3
Figure 4