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Microstructural and Mechanical Aspects of Carbon/Epoxy Composites at Liquid Nitrogen Temperature

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ABSTRACT

Woven carbon fibers of 50, 55, 60 weight percentage were reinforced with epoxy matrix to prepare the laminated composites. These were exposed to liquid nitrogen temperature and mechanical tests were carried out at a range of 2 to 500 mm/min crosshead speeds. The main emphasis of the investigation was to evaluate the role of percentage matrix phase and interfacial areas on tensile and interlaminar shear failure mechanism of carbon/epoxy composites at cryogenic temperature for different loading rates. The mechanical performance of the laminated composites at cryogenic temperature compared with room temperature property. The woven carbon/epoxy laminates were found to be loading rate sensitive. An improvement in tensile strength and reduction in ILSS was reported after cryogenic conditioning of the carbon/epoxy laminates. Microstructral analysis was done to show low temperature damage mechanisms. The phenomenon may

be attributed to cryogenic hardening, matrix crackings, carbon fiber and epoxy (matrix) contraction, anisotropic nature of carbon fibers and stress relaxation after cryogenic conditioning.

Keywords: carbon/epoxy composites, cryogenic temperature, tensile strength, interlaminar shear strength, stress relaxation, fracture, differential thermal coefficient of expansion.

INTRODUCTION

Carbon fiber is the most expensive of the more common reinforcements, but in space applications [1] the combination of excellent performance characteristics coupled with light weight make it indispensable reinforcement with cost being of secondary importance. Cryogenic liquid fuel is preferred to solid fuel of propellants of launch vehicles and rockets in aerospace applications because of their high specific impulse; the low calorific energy to volume ratio of the cryogenic liquid fuels makes the pressurized tanks large and heavy when made up of metallic materials. So now PMCs are contenders for use in reusable launch vehicle components. Mostly such components are cryogenic fuel tanks, cryogenic fuel delivery lines, and parts of the cryogenic side of turbo-pumps which are made up of carbon/polymer composites [2]. Carbon/polymer composites are used in aerospace industry on account of their high specific stiffness and strength which are higher than the metallic materials. The behavior of a composite to change in temperature is for two main reasons. Firstly the matrix response to an applied load is temperature dependent and secondly, change in temperature can cause internal stresses to be set up as a result of differential thermal contraction and expansion of the two constituents [3]. These stresses affect the thermal expansivity i.e. the expansion

coefficient of the composite. Potholing or localized surface degradation, delamination, and micro cracking are some of the more dramatic phenomena that can occur as a result of cryogenic cycling [4]. Increased thermal stresses are the underlying cause of micro cracking in composites at cryogenic temperatures [5]. 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 [6, 7]. The generated residual stresses influence the overall thermo-mechanical properties of the composite. In some cases, the resulting stresses are sufficient to initiate plastic deformation within the matrix immediately around the fiber. Therefore, it is important to determine the current state of the residual stresses and their effects on the behavior of the composite when subsequently subjected to various uniaxial and multiaxial mechanical loading [8, 9]. The stresses can also be large enough to initiate material damage such as matrix micro cracking. These micro cracks can reduce the strength of the material, as well as act as sites for environmental degradation and nucleation of macro cracks [10]. At low temperature the polymer matrices become brittle and do not allow relaxation of residual stresses or stress concentrations to take place. Till now very few investigations were done to evaluate the mechanical performance of carbon/polymer composites at low temperature.

The carbon fibers exhibit anisotropic behavior [11], unlike glass fibers, which shows negative coefficient of thermal expansion in fiber direction and a large positive one perpendicular to it (transverse direction). The basal planes of graphite are aligned parallel to the fiber axis and the atoms in these planes are held together by strong covalent bonds. These aligned graphitized basal planes were bind together by weak Van der Waals forces.

Hence, their transverse mechanical stiffness is weak and depends on temperature. High stiffness or strength exists only in the fiber direction. In a perpendicular direction, the fibers are rather brittle. Most anisotropic fibers are more brittle and have a lower fracture strain than isotropic ones [12].

EXPERIMENTAL

Woven carbon fibers (T-300) of epoxy compatible sizing (PAN based high strength carbon fibre, M/S CARR Reinforcement Ltd., UK) were used with Araldite LY-556, an unmodified epoxy resin based on Bisphenol-A and hardener (Ciba-Geigy, India) HY-951, aliphatic primary amine to fabricate the laminated composites. Three weight percentages of carbon fibers (50, 55 and 60 wt %) were targeted to prepare the composites. They were cured for 48 hours at room temperature and were cut into tensile test and short beam shear (SBS) test specimens by diamond cutter. The cut laminates were dried at a 50 ^{0}C temperature in oven for a sufficient time unless the variation of weight change was almost negligible. The tensile and SBS 3-point bend tests were conducted to determine the tensile strength and interlaminar shear strength (ILSS) of composites. The moisture free carbon/epoxy composite 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 tensile test and 3-point bend test at cryogenic temperature. The untreated as-cured composite specimens were tested in tensile test and the former specimens after exposure to room temperature and untreated specimens were tested in 3-point bend test at room temperature. All the

mechanical flexural tests were performed at a range of 2 to 500 mm/min crosshead speeds. The tensile strength was measured as fallow,

$$UTS = P_{max}/A$$

Where, 'P_{max}' is the maximum load, 'A' is original cross sectional area.

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 tensile and SBS tests in accordance with ASTM D3039 and ASTM D2344-84 standards. Multiple samples were tested at each point of experiment and the average value was reported.

RESULTS AND DISCUSSIONS

It is known that the unidirectional carbon fiber composites are relatively strain rate independent when loaded in fiber direction due to rate insensitivity of the carbon fibers and also the tensile strength predominantly depends on the strength of the fibers [13] and shear properties are influenced by the matrix (polymer) [14]. But for woven carbon fiber composites the fiber/matrix interactions are more that leads to strain rate dependence of the laminate (epoxy matrix is highly strain rate sensitive [15]) and some influence of matrix and the interface on tensile properties. Figure 1 shows the tensile response of

cryogenically treated specimens and untreated specimens for different fiber weight fraction at crosshead speeds of 2 mm/min, 200 mm/min and 500 mm/min. From the charts it is clear that the cryogenically conditioned specimens have higher values of tensile strength for 0.5 and 0.55 fiber weight fractions and lower value for 0.6 fiber weight fraction as compared to untreated samples except for the crosshead speed of 500 mm/min. Improved tensile strength of laminates may be due to contribution of increased stiffness for both carbon fibers and epoxy matrix after cryogenic conditioning. The matrix hardens after contraction at cryogenic temperature and develops high strength [16]. This contraction of the matrix is resisted by stiff fibers through fiber/matrix interfacial bonding that originates residual stresses. Thus, for composites of 0.6 fiber weight fraction lower strength at cryogenic temperature was seen due to the presence of more interfaces leading to the generation of large amount of residual stresses which are difficult to accommodate in the strong interface. It results in interfacial microscopic cracks, which transforms to macroscopic level by coalesce, and debonding phenomena to release the developed stresses. The anisotropic property of carbon fibers may enhance the amount of debondings at interface. Figure 2 shows the effect of crosshead speed on the tensile behavior of carbon/epoxy composites of different weight fractions for both cryogenically conditioned and untreated samples. Overall the tensile strength values decreases with increase in crosshead speeds for both the cases. The sensitivity of the laminate to strain rate is dependent on the resin behavior. Lower strength at higher speed may be due ineffective load transfer through the interface by the matrix leading to greater amount of matrix crackings. It is reported that [17] an optimum time is required for proper load transfer through interface from matrix. In addition, higher crosshead speed

restricts the relaxation process at the crack tip and results in the growth of the cracks without blunting. For cryogenically conditioned samples the ductility of the matrix becomes the limiting factor at high loading rates and more severely effected than the untreated samples. The matrix contracts when temperature decreases due to which internal stresses are generated in the matrix. Destruction of the matrix is induced when the thermal stress exceeds the strength of the resin. The epoxy contraction at cryogenic temperature can be minimized by modifying the three dimensional molecular structure with two dimensional polymer or by adding the two dimensional polymers [18]. Figure 3 shows effect of crosshead speed on ILSS values for 0.6, 0.55 and 0.5 fiber weight fractions. From the graphs it is evident that specimens tested at cryogenic temperature shows lower ILSS values than the untreated laminates. The cryogenic conditioning causes matrix hardening due to contraction leading to stone like structure in which disentanglement is almost absent. Here the anisotropic behavior of carbon fibers plays a critical role. The research [19] shows that the glass/epoxy composites at liquid nitrogen temperature show higher ILSS values than at room temperature. This is due to generation of compressive residual stresses at the interface by differential contraction of glass fiber and epoxy matrix at cryogenic temperature. This enhances the bonding at the interface by mechanical keying principle. The glass fiber is isotropic in nature, unlike carbon fibers. Carbon fibers show negative coefficient of thermal expansion in fiber direction and large positive one in transverse direction [20]. Hence, at cryogenic temperature the carbon fibers contracts in transverse direction i.e. in radial direction and expands in longitudinal direction simultaneously with the contraction of epoxy matrix in all directions. This inhibits bonding by mechanical keying principle and results in weaker interfacial bond

between the carbon fiber and epoxy matrix. Thus, lower ILSS values were reflected at cryogenic temperature. The graphs (figure 3) also shows that the specimens tested at room temperature after one hour cryogenic exposure have higher ILSS values than specimens tested at cryogenic temperature and lower values than ambient temperature. This proves existence of stress relaxation phenomena i.e. the stresses generated due differential contraction of epoxy matrix and fibers at cryogenic temperature are relaxed by spatial rearrangement of molecules when exposed to room temperature after cryogenic conditioning. This relaxation results in reversion of some mechanical properties such as ILSS in the present case but not completely. All the graphs indicate increase in ILSS values upto 50 mm/min and decreases there after. Lower ILSS values at low speed may due to high failure strain at low strain rates which increases with increase in speed. As above, at higher crosshead speeds the matrix is unable to transfer load properly due to less availability of time i.e. it is like an impact and crack propagates without blunting phenomena at the crack tip [21, 22].

Examination of fracture surfaces of cryogenically conditioned samples revealed many low temperature damage mechanisms. Figure 4 compares SEM micrographs of both untreated and cryogenically conditioned samples. It shows contraction of carbon fiber and matrix that leads to debonding at the interface due to cryogenic conditioning. Here the carbon fiber contracts radially due to negative coefficient of thermal expansion at low temperature. Untreated samples showed neither debonded interfaces nor any contraction of fiber and matrix. Figure 5 shows a large amount of matrix crackings which may be attributed to brittleness of the epoxy resin at low temperature leading to nucleation of delamination cracks in the composite interface. Figure 6(a) shows fracture profile of

carbon/epoxy sample after cryogenic treatment that mainly consist rows of cups. These cups are formed due to the development of transverse micro-cracks along the interfacial area [23, 24]. Increase in brittleness of the epoxy matrix after cryogenic conditioning causes opening of these micro-cracks easily that develops profile with rows of cups. When these cracks accumulate and merge to form longitudinal cracks along the fiber then failure of the composite results as shown in figure 6(b).

CONCLUSION

From the present findings it can concluded that cryogenic conditioning of carbon/epoxy composites leads to high amount of residual stresses at the interface that are difficult to accommodate that contributes in massive matrix crakings and interfacial debondings. Woven carbon/epoxy composites were found to be strain rate sensitive and change loading rate can change the failure modes. The overall strain rate sensitivity of a laminate is mostly controlled by the resin. The anisotropic nature of carbon fibers plays a vital role in interlaminar shear strength of the laminate at cryogenic temperature. Stress relaxation due spatial rearrangement of molecules of the resin result in reversion of some mechanical properties to some extent after cryogenic treatment. Cryogenic conditioning stimulates the formation of rows of cups due to coalesce of transverse microcracks that originate longitudinal cracks along the fiber.

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FIGURE CAPTIONS

Figure 1 Bar chart showing Ultimate Tensile Strength for different fiber weight fractions of cryogenically conditioned and untreated specimens at 1(a) 2 mm/min, 1(b) 200 mm/min and 1(c) 500 mm/min crosshead speeds.

Figure 2 Graph showing the effect of crosshead speed on tensile strength of carbon/epoxy composites for both cryogenically conditioned and untreated specimens of 2(a) 0.5 fiber weight fraction, 2(b) 0.55 fiber weight fraction and 2(c) 0.6 fiber weight fraction

Figure 3 Graph showing the effect of crosshead speed on ILSS of carbon/epoxy composites at ambient temperature (▲), cryogenic temperature (77K) (♦) and at room temperature after cryogenic conditioning (■) for 3(a) 0.5 fiber weight fraction, 3(b) 0.55 fiber weight fraction and 3(c) 0.6 fiber weight fraction.

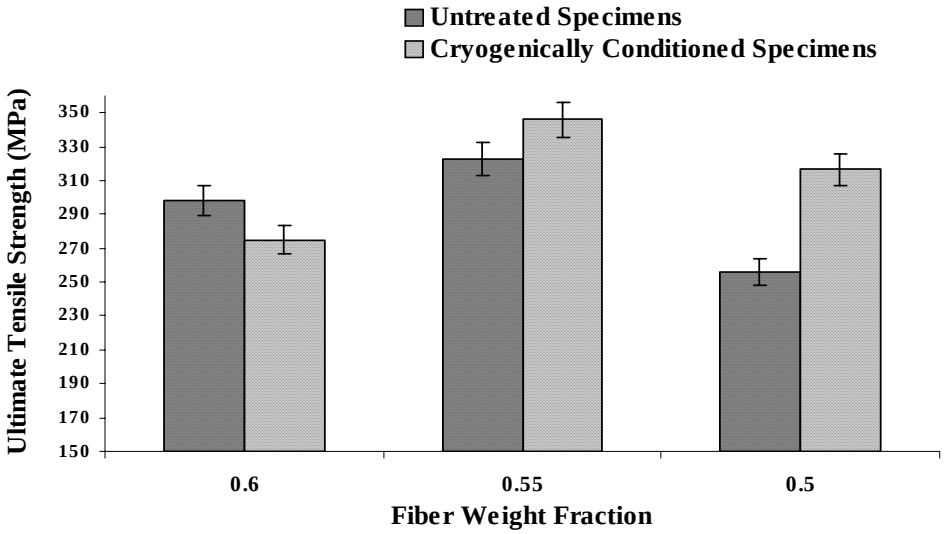
Figure 4 Scanning micrographs of 4(a) cryogenically conditioned (77K) and 4(b) untreated carbon/epoxy composites specimen.

Figure 5 Scanning micrographs showing large amount of matrix crackings and delamination of cryogenically conditioned (77K) carbon/epoxy composite specimen.

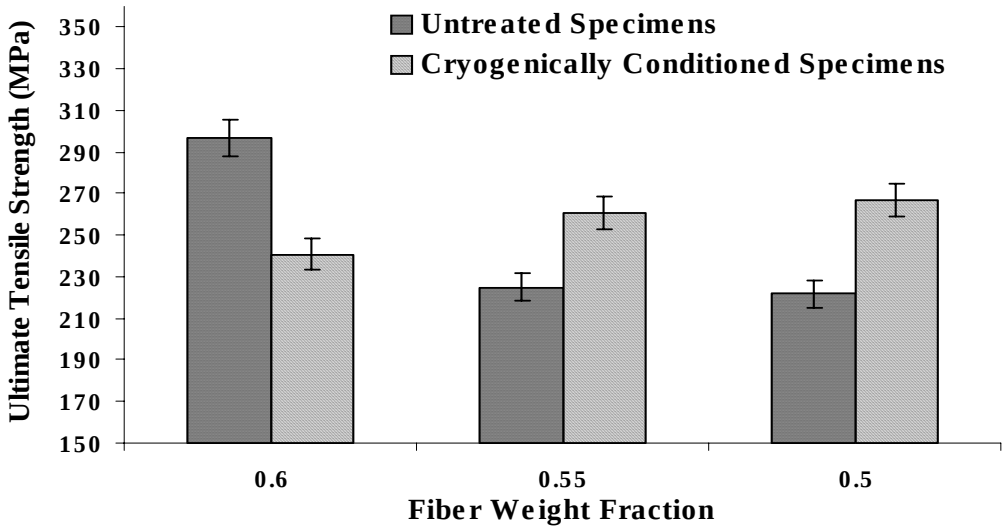
Figure 6 Scanning micrograph showing 6(a) rows of cups and 6(b) longitudinal cracks

along fiber of carbon/epoxy cryogenically (77K) conditioned specimen.

1(a)



1(b)



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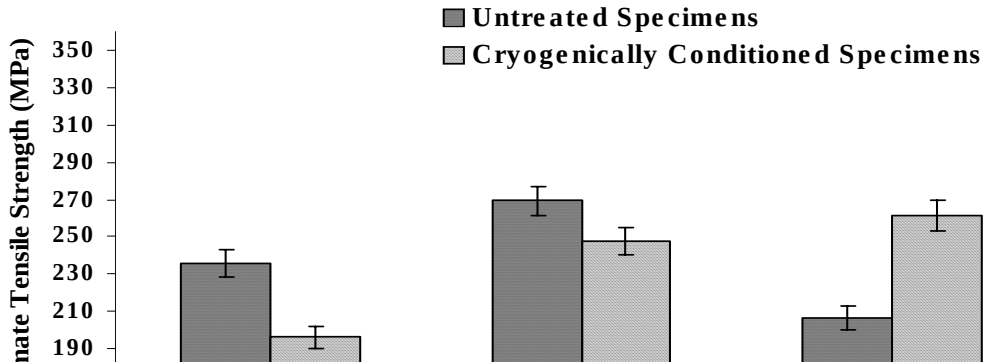
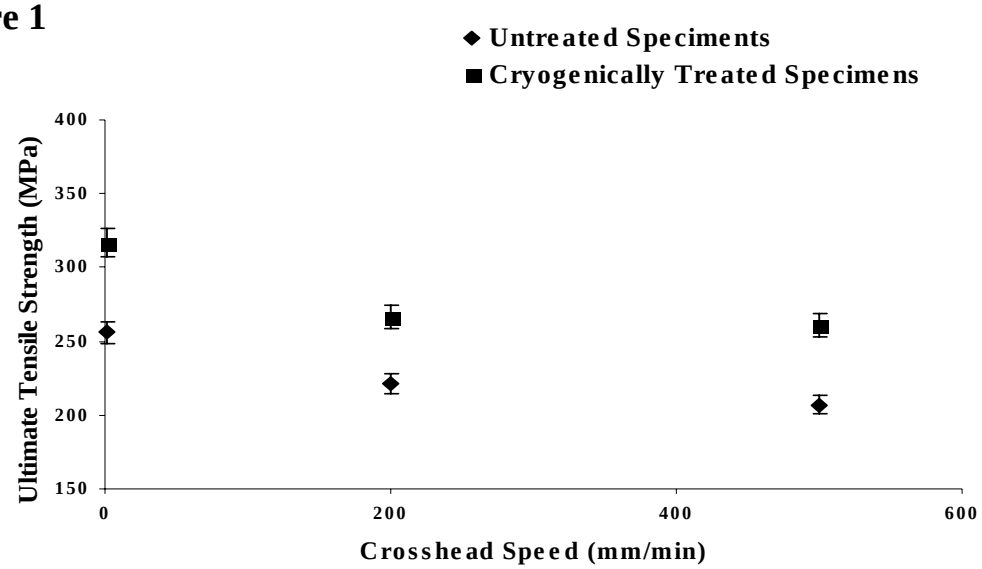
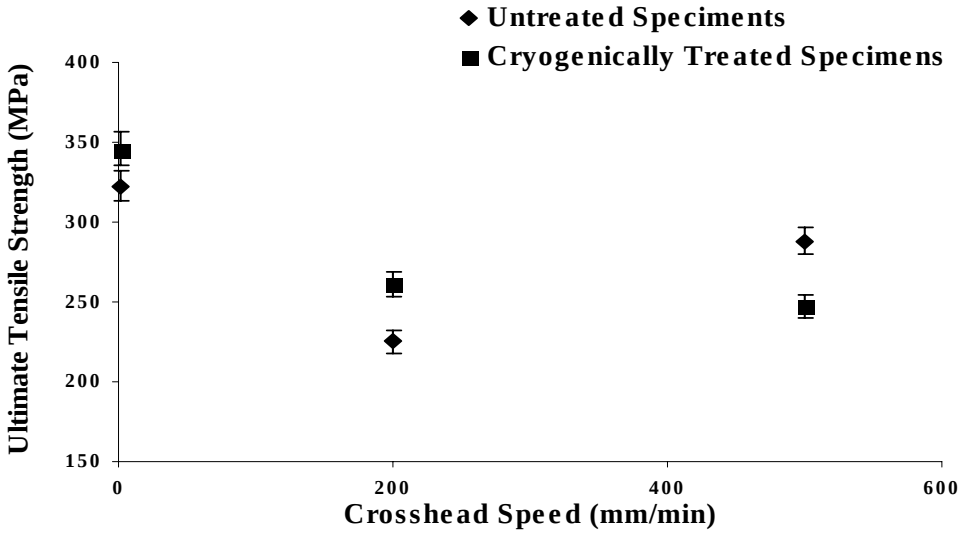


Figure 1

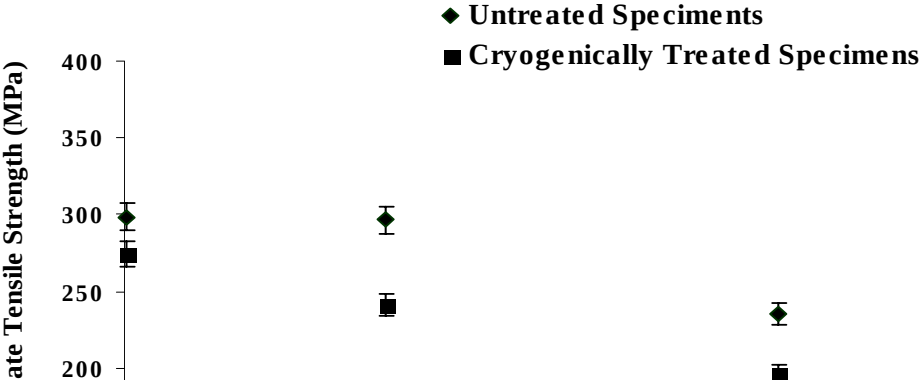
2(a)



2(b)



2(c)



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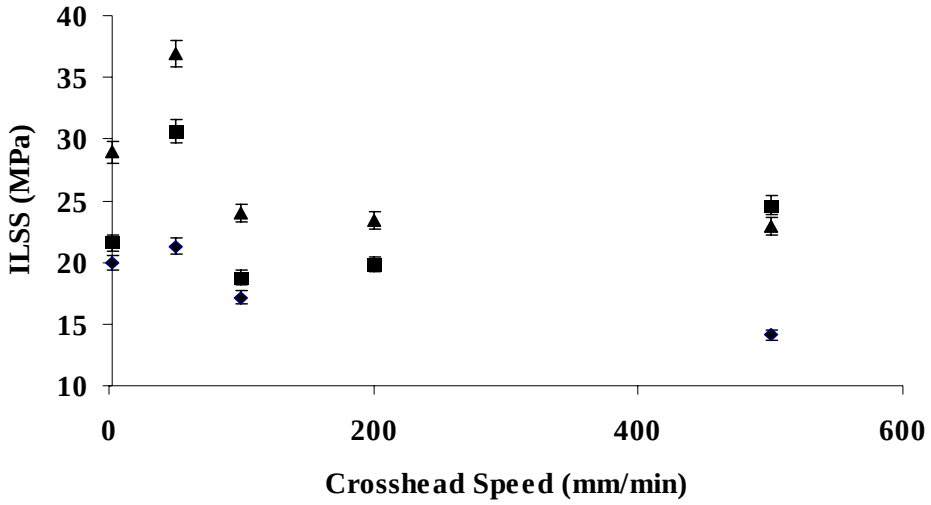
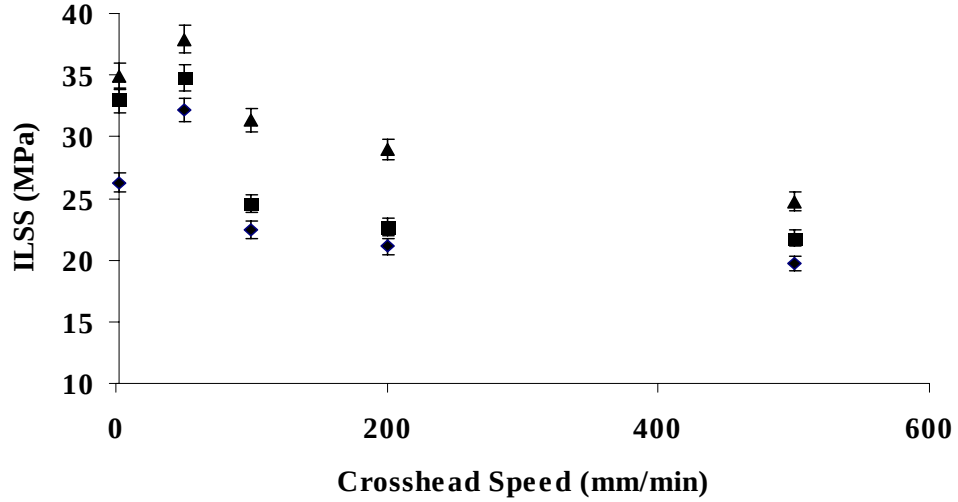

ILSS (MPa)
40
35
30
25
20
15
10
0
200
400
600
Crosshead Speed (mm/min)

3(b)


ILSS (MPa)
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Crosshead Speed (mm/min)

3(c)

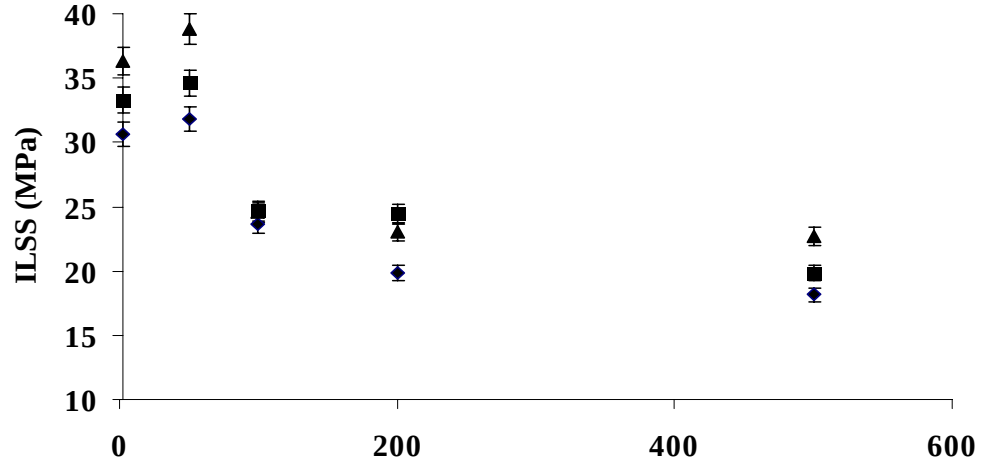
ILSS (MPa)
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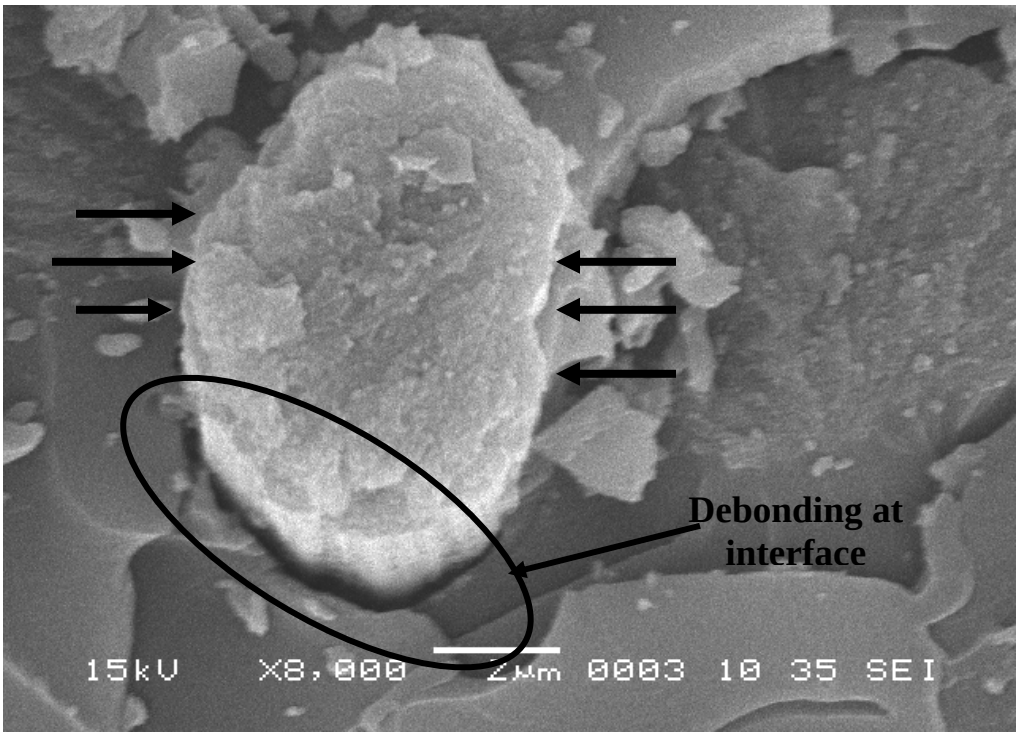
Figure 3

4(a)



4(b)

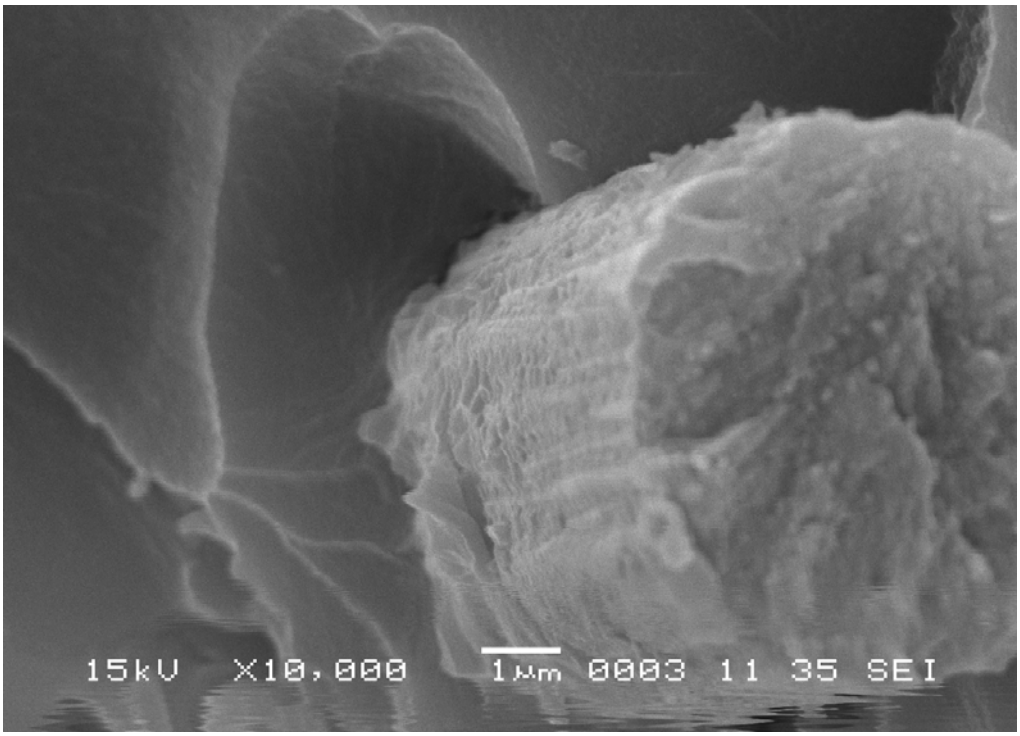


Figure 4

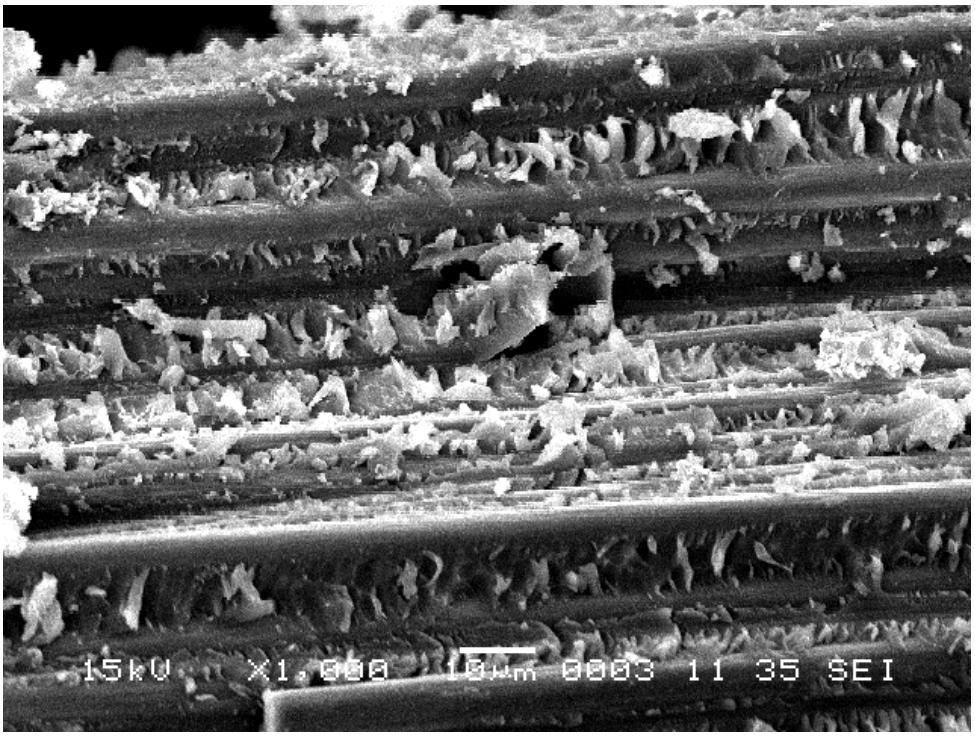
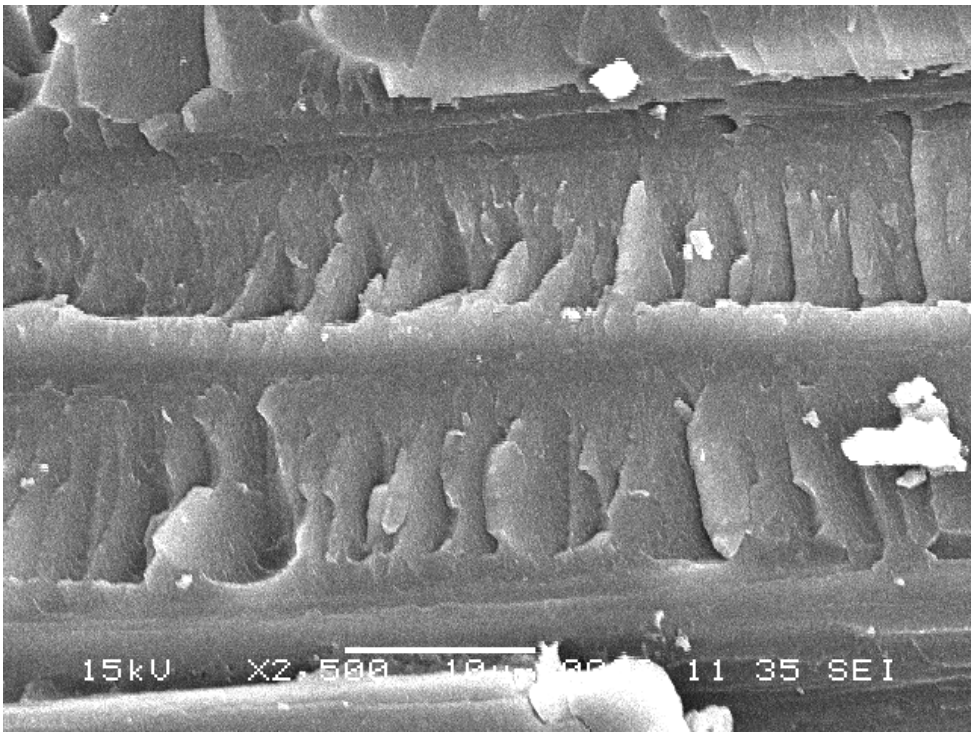


Figure 5

6(a)



6(b)