Title – Evaluation of structural integrity and mechanical behavior of advanced FRP composites

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Abstract

Purpose - In this investigation, microstructural integrity at the interface and consequently an implicating effect on mechanical behavior was analyzed.

Design/methodology/approach - In the light of Fourier Transform Infrared Spectroscope (FTIR-Imaging) and Temperature Modulated Differential Scanning Calorimeter (TMDSC), a sorption mechanism was established. Thermal spike and thermal shock treatment was carried out at 150°C and 80°C respectively. This suggested that fiber/matrix adhesion rests on the structure and properties of both the fiber and matrix in the region near the interface during the hygrothermal treatment.

Findings - The carbon surface of **micro-composite (carbon/epoxy)** was found to selectively absorb the tertiary amine catalyst and to modify the chemical state of the cured resin apparently through the effects of absorbed water. The higher values of **glass transition temperature (Tg)** resulted for longer immersion time and higher exposure temperature. Together, these techniques provide a comprehensive picture of chemical and physical changes at the interphase region. Thermal spike of **hybrid composite (carbon and glass fiber with epoxy)** at 150°C temperature might possibly improve the adhesion level at the interface. Whereas, in case of thermal shock treatment at 80°C the fall in ILSS value at higher number of cycles. This degradation of the interface region has been monitored by Scanning Electron Microscope (SEM) analysis.

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

Keywords - Fiber/matrix adhesion, Structural integrity, degradation, Thermal spike, Thermal shock, Glass transition temperature (Tg).

Paper type - Research paper

1. **Introduction**

The mechanical properties of fibrous composites such as tensile strength, stiffness, elastic modulus, fracture toughness, and mode of failure depend on the properties of the fiber and its architecture, the extent of resin cure and resultant matrix properties, and the nature of the

fiber/polymer interface (the region between the fiber and matrix.)[1-2]. It is well known that these has vast applications including ground based and air borne vehicles, space structures and sporting goods [3]. Producing a high-modulus composite requires adequate adhesion between the fiber and the matrix. The fiber-matrix interface is also important in influencing load transfer in the vicinity of a broken fiber and therefore plays a role in determining the tensile strength [4]. The transition region, known as the interphase, between the bulk fiber and the bulk matrix is extremely complex. The effectiveness of load transfer at the interface depends upon the extent of chemical and mechanical bonding. In addition, composite properties are further compromised by structural defects such as voids, impurities and microcracks which tend to concentrate at the interfacial region [5]. Environmental attack by moisture, for example, can degrade the strength of fiber; plasticize, swell, or microcrack the resin: and degrade the fiber/matrix interface [6]. Besides, among other effects, a small amount of water in epoxy resins may cause poorer mechanical properties (lower value of modulus, brittleness) due to: a) plasticization which decreases the value of glass transition temperature, Tg (it is reported a reduction of about **20°C** for every 1% of water absorbed) b) stress generation due to swelling of the system and c) a possible chemical degradation [7]. Remarkable progress has been achieved owing to a lot of excellent work published. However, the information is still far from being well established. Several models have been put forward to address the issue of the state of water molecules in epoxies. Moisture wicking along the fiber/matrix interface degrades the interfacial bond strength, resulting in loss of microstructural integrity [8]. Fig 1 represents the fiber/matrix interface region. It is known that Fick's law is frequently inadequate for describing moisture diffusion in polymer and polymer composite. Non–Fickian diffusion is likely to be prevalent when a polymer composite consists of internal damage in the form of matrix cracks [9]. Langmuir type diffusion

is reported to explain the penetration of water in to epoxy. The driving force of diffusion result in energy released by the hydrogen bonds, where as the transportation rate was essentially subject to the local-chain mobility as well as the dislocation of water molecules from the epoxy network. In addition absorbed water molecules forming double hydrogen bonds will cause an increase of Tg, which has been found in epoxy resin. It should be noticed that the change of Tg depends not only on the double bound water molecules but also on the plasticizing effect [10]. The result here does not indicate that only after a long period of sorption can water molecules form double hydrogen bonds.

If the fiber/matrix interface strength is high, the degree of debonding will be limited before fiber failures occur and crack propagates across the fibers. This will lead to a flat, relatively smooth fracture surface, offered to as brittle fracture. However, if the fiber/matrix interface strength is weak, the degree of debonding will be extensive before fiber failure occurs. This leads to broomlike failures [11]. Certain aircraft components can be exposed to temperature in excess of 100°C for only a few minutes [12]. Under such conditions of rapid heating followed by atmospheric cooling, studied have shown that there is increase of adhesion level at the interface region. The mechanism for this enhancement when laminates are thermally spiked is not clear. Thermal expansion differences between the fiber and matrix can contribute to stresses at the interface. Differential thermal expansion is a prime cause of thermal shock in composite materials [13]. To cause overall composite failure it is generally accepted that there is need to be a critical cluster of fiber breaks adjacent to one another to trigger the catastrophic fracture [14].Although our quantitative understanding of the fiber-matrix interface and the mechanisms of adhesion is not completely developed at this time, it is possible to optimize the fiber-matrix interphase in the same manner as composite design methodologies are optimized [15]. The key

to success in this endeavor is using the concept of a fiber-matrix interphase as a framework upon which to build this methodology.

2. Methods

A simple, model epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) (Araldide LY-556) and hardener HY- 951 an aliphatic primary amine (Ciba-Geigy) used as matrix and PAN based carbon fiber was used for preparing the micro-composites for hygrothermal treatment. It provides a low viscosity,solvent free room temperature curing laminating system.The micro-composite was cured for 24 hrs. In the humidity chamber it is kept at 60°C at 95% humidity for 10 hr, 60 hr and 100 hrs and one batch remain for the ambient visulation. Silane treated woven roving E-glass fibers and woven carbon fibers (T-300 PAN based high atrength) with 60 percentage were used for fabrication of glass,carbon/epoxy (hybrid) composite.

2.1 Short beam shear test

The flexural methods are applicable to polymeric composite materials. A testing machine with controllable crosshead speed is used in conjunction with a loading fixture. It is a three point flexural test on a specimen with a small span, which promotes failure by inter-laminar shear.

The shear stress induced in a beam subjected to a bending load, is directly proportional to the magnitude of the applied load and independent of the span length. Thus the support span of the short beam shear specimen is kept short so that an inter-laminar shear failure occurs before a bending failure. This test method is defined by ASTM D 2344, which specifies a span length to specimen thickness ratio of 5 for low stiffness composites and 4 for higher stiffness composite. This test has an inherent problem associated with the stress concentration and the non-linear

plastic deformation induced by the loading nose of small diameter. Both specimens have the same span-to-depth ratio (SDR). The stress state is much more complex than the pure shear stress state predicted by the simple beam theory. The short beam shear (SBS) tests are performed on the composite samples at the conditioned temperature and room temperature to evaluate the value of inter-laminar shear strength (ILSS). The SBS test is conducted as per the ASTM standard D2344-84 with an Instron 1195 tensile testing machine. The loading arrangement has a span length of 40 mm .The tests were performed with two increasing crosshead speed ranging 1and 500 mm/min. For each point of testing 4 to 5 specimen were tested and the average value was taken. The ILSS values were evaluated from the short beam shear test according to the following relation:

ILSS= 0.75 P/bd

Where P is maximum load, and b,d are width and thickness of the specimen respectively.

2.2 SEM Analysis

To study the different failure mechanisms of the tested samples micrographs of the failure samples was carried out using a JEOL-JSM 6480 LV SEM. The samples were loaded onto the sample holder, **then, the chamber was closed**, adjusting the working distance then the vacuum was applied.

3. Results and discussion

3.1 Moisture ingression kinetics

Changes of frequency, intensity, and shape of the water-related bands have been interpenetrated in terms of bound and free water (up to four different water species in some systems), water clustering, water orientation, and water networking [16]. The O-H vibration modes of liquid

water lead to a very complicated vibration spectrum, complicated by both intermolecular and intramolecular hydrogen bonding. Internal reflection FTIR Spectroscopy has been used to study the functional groups presents on the oxidized fiber surface. The larger size of the incident beam calls for novel experimental approaches. The carbon surface was found to selectively absorb the tertiary amine catalyst and to modify the chemical state of the cured resin, which was finding in Fig.2 apparently through the effects of absorbed water.

The presence of polar and hydrogen bonding groups, such as hydroxyl and tertiary amine which is more prefer for carbon atom provides the chemical bias for water sensitivity[16].

Therefore, polar groups as well as hydrogen bond taken into **account**. FTIR-Imaging experiments were performed in this study to analysis the hygrothermally treated carbon epoxy micro-composite as IR measurements are very sensitive to hydrogen bonds.

3.2 TMDSC experiments

The increase of glass transition temperature (Tg) of carbon epoxy micro-composite is shown in Fig 3, in which the carbon fiber /epoxy adhesion plays a major role. The absorption and diffusion of water in interface is related to the free volume and polymer-water affinity. The amount of free volume depends on the molecular packing and is affected by both crosslink densities. The increase of Tg value signifies the increase of cross-link density. Higher duration treatments motion of large segments of the polymer chains is frozen-in and restricted motion of small segments can takes place without affecting the remainder of the molecule. This allows further crosslinking and also reducing the free volume.

The increases in the glass transition temperature may reflect increase of mechanical properties of the polymer matrix composite.

3.3 Implication of thermal spike treatment.

The behavior of FRP hybrid composites under possible service conditions is a matter of significant practical interest. The mechanical behavior of FRP composites are dominated by the interfacial adhesion at the fiber-matrix interface. The Interlaminar Shear Strength (ILSS) values have been used for quantification of mechanical degradation. The structural integrity and lifetime performance of FRP composites are strongly dependent on the stability of the fiber/polymer interfacial region. This region is the site of synergy in composite materials and its influence to overall mechanical properties is significant. Thermal expansion coefficients in polymers are considerably high. Thus the interfacial de-bonding may occur under extremes of temperature. The cooling from high temperature to low temperature generally produces tensile stresses at the surface and compressive stresses in the interior. They are also susceptible to crack initiation and propagation along the laminar interfaces in various failure modes. Thermal stresses caused by temperature gradient should be given special attention in many application areas. The presence of these stresses can result in matrix cracking. In an FRP composite, the fiber and the matrix have different coefficients of thermal expansions (CTE). Hence, excursions through the same temperature range results in differential expansion. This induces additional stresses at the fiber-matrix interface, thereby weakening the interfacial region.

Thermal spike at 150°C temperature, initially at lower conditioning times, there exists a marked difference between the ILSS values obtained at different crosshead velocities. At higher conditioning times, the **differences** in the ILSS obtained from testing at different crosshead velocities narrows down gradually. Although in the present study, the conditioning has not been sufficiently prolonged so as to achieve statistical insignificance of cross head velocities, it may be expected that prolonged exposure may result in that effect. This may be attributed to the fact

that at higher levels of conditioning times, the degradation in the epoxy matrix and the interfaces are little colossal which was shown in Fig 4. This effect is supposed to increase with less conditioning time. It is possibly attributed by surface chemistry principle at the fiber/polymer interface. A better fiber/matrix adhesion will impart better properties such as ILSS and delamination resistance to a polymeric composite. A large thermal expansion mismatch between a fiber and polymer matrix can result in a quite possible debonding and matrix/interfacial cracking in polymer composites due to misfit strain at the interface. Thermal spiking carried out at higher temperature than those expected from kinetic heating could therefore be expected to produce a greater degree of permanent damage.

The bond strength depends on the quality of interfacial adhesion. The degree of cross-linking may increase during thermal conditioning. The high cross-linked networks have lower molecular mobility. Consequently, the mechanical behavior of these composites is different from the composites without any form of thermal conditioning. Fracture of epoxy involves breaking of covalent bonds in the chains. So it undergoes ductile fracture at high temperature. At temperature, above glass transition temperature (Tg), at least at slow to moderate rates of deformation, the epoxy is soft and flexible and is either an elastomer or a very viscous liquid. The diffusion rate of segments increases approximately linearly with increase of temperature.

3.4 Implication of thermal shock treatment

Thermal shock is performed to determine the resistance of the part to sudden changes in temperature. The parts undergo a specified number of cycles, which start at ambient temperature. The parts are then exposed to an extremely (low/high-up thermal shock) temperature, and within a short period of time, exposed to an extremely (high/low-down thermal shock) temperature,

before going back to ambient temperature. It is noted that the ILSS assessed at higher crosshead velocity have lower values as compared to those for lower cross head velocity. This anomalous dependence of ILSS on the crosshead velocity may be attributed to the presence of two different types of interfaces. As a compressive force is applied on the material, The carbon-epoxy interfaces have been good adhesion that obstacle the crack propagation as compared to glass-epoxy interface region. This treatment is the result of a thermal gradient, which refers to the fact that temperature change occurs in an uneven fashion. This is due to expansion of the molecular structure of an object, due to weakening of the bonds which hold the molecular in formation. The conditioning at 60°C temperature may impart better adhesion at the fiber/matrix interface by a surface chemistry mechanism presented in Fig.5 (a) and the conditioning temperature at 80°C in Fig.5 (b). The fall in ILSS value at a higher number of cycles which observed in Fig.5 is possibly due to a greater misfit strain effect, which leads to more debonding at the fiber/matrix interface.

3.5 Microscopic interphase analysis

It is at the interfacial region where stress concentration develop because of difference in the thermal expansion coefficient between the reinforcement and the matrix phase due to loads applied to the structure and the time of curing shrinkage. The debonded interfacial regions appear to be nucleated by thermal shock is demonstrated in Fig 6(a).

Fracture of fibers in Fig. 6(b) during processing / in service is generally an undesirable feature. Fracture in fibers, as in bulk materials, initiates at some flaw(s), internal /on the surface. In general, because of the high surface to volume ration of fibers, the incidence of a fiber flaw

leading to fracture is greater in fiber than in bulk material [12]. Very frequently, a near surface flaw such as a microvoids/ or inclusions is responsible for the initiation of fracture of fiber.

In polymeric fibers, the fundamental process leading to failure are chain scission /or chain sliding or a combination thereof. One major problem in glass fiber is that of failure due to static fatigue. According to the chain-bundles model, if a fiber fractures, the matrix translates the load to the neighboring fibers in the composite. The stress concentrations at the broken fiber ends, unless dissipated properly, may induce failure in adjacent fibers and precipitate catastrophic failure of the composite.

4. Conclusion

The present investigation has highlighted the water uptake kinetics, which is found to be nonconventional in nature. The results of TMDSC demonstrate the marked increase in Tg value, due to increase in crosslink density. The presence of increase in absorbance peaks of OH stretching bands at the interphase has been reported by FTIR-Imaging. The degradation at the interface region such as fiber/matrix debonding, fiber fracture was found in SEM analysis. The variation of ILSS value in different thermal treatment reveals that the fiber/ matrix bond strength decisively controls the overall mechanical behavior of FRP composites. There is a wide variation of mechanical behavior which needs to be supported by the understanding of the science at the fiber/polymer interface region.

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Figure captions:

Fig 1: Idealized representation of interphase region between fiber and matrix.

Fig 2: FTIR-Imaging result of water diffusion into carbon epoxy micro-composite.

Fig3:Tg values of carbon epoxy micro-composite with different duration of hygrothermal treatment.

Fig.4.:Variation of ILSS value with respect of conditioning time at 150^0 C.

Fig.5: Variation of ILSS value during thermal shock treatment.

Fig.6: SEM of fiber/matrix debonding and fiber fracture at the interface region.

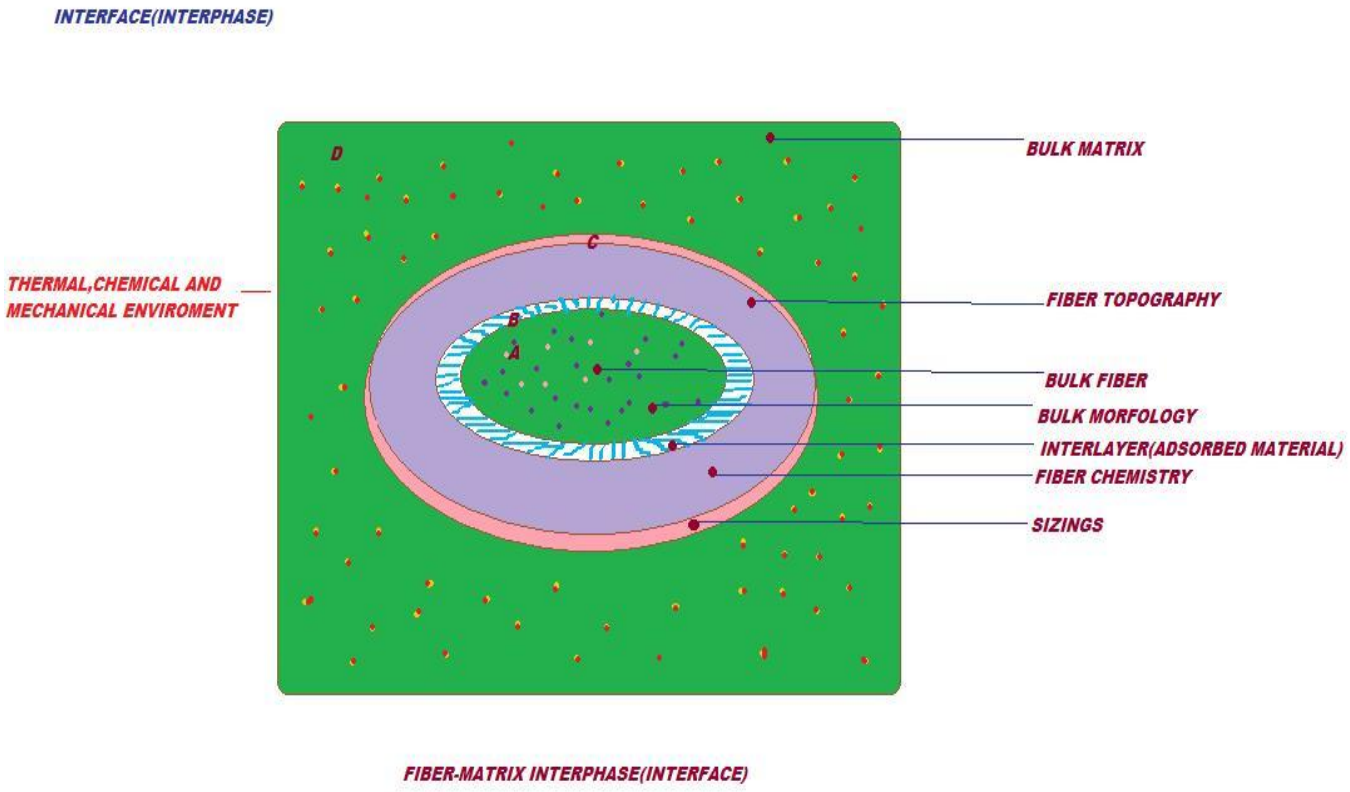


Fig. 1. Idealized representation of interphase region between fiber and matrix.

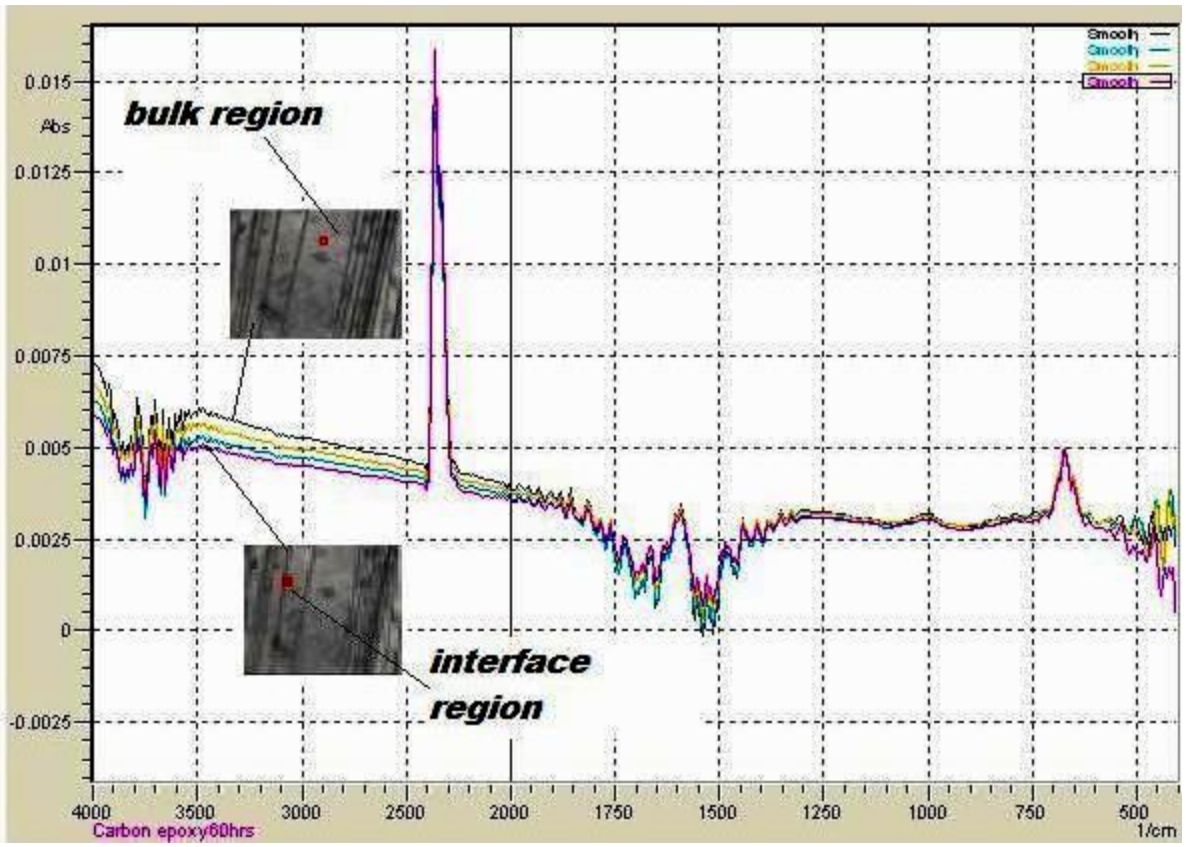


Fig 2- FTIR-Imaging result of water diffusion into carbon epoxy micro-composite.

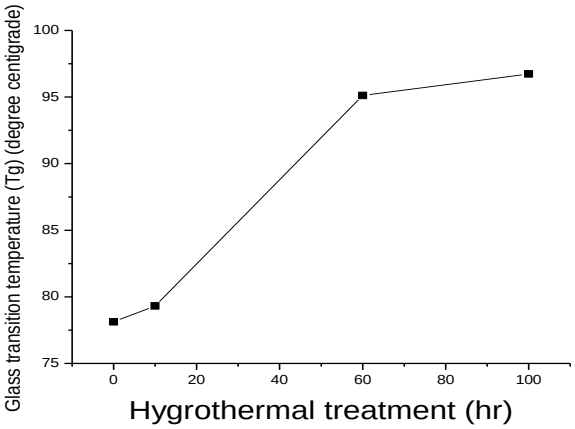


Fig 3- Tg values of carbon epoxy micro-composite with different duration of hygrothermal treatment.

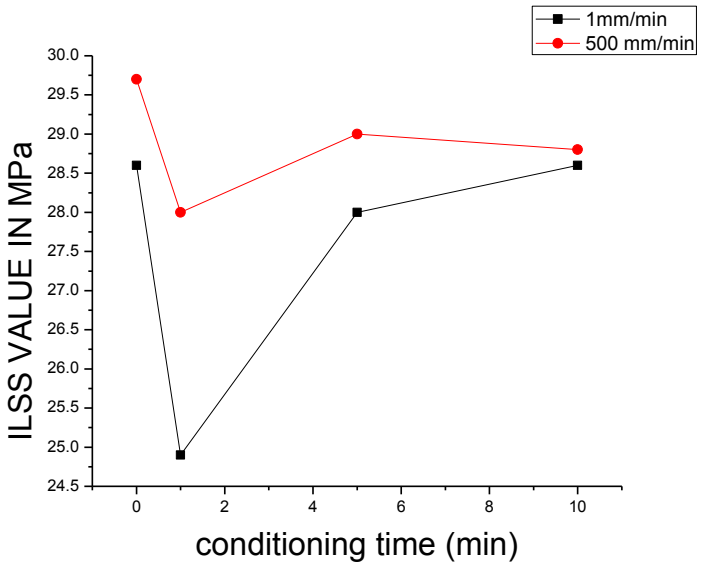
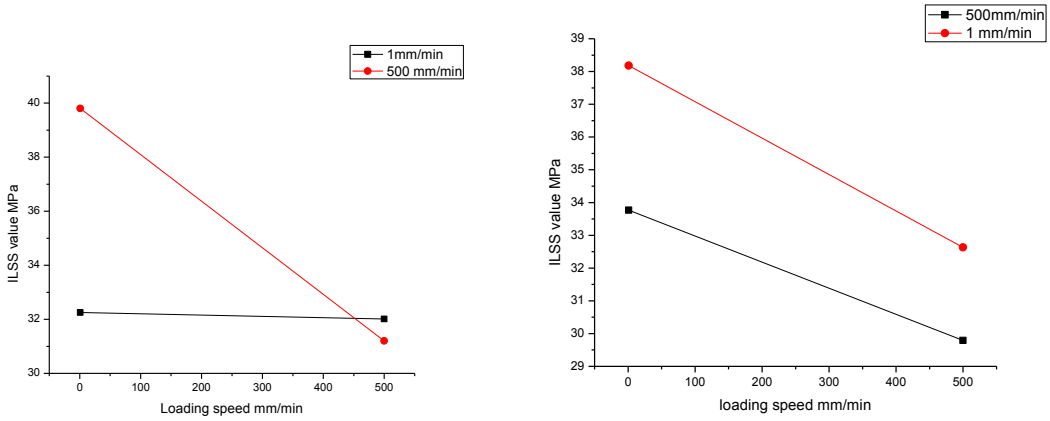
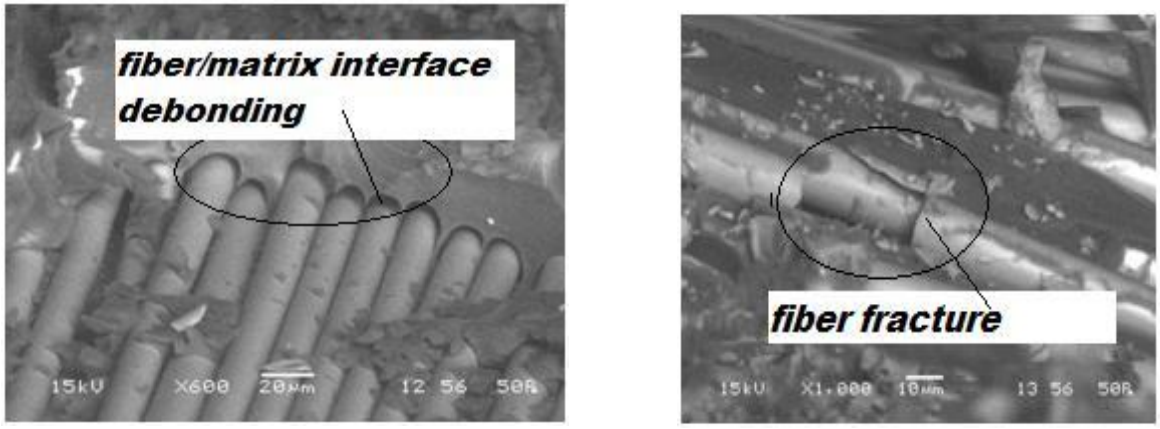


Fig. 4. Variation of ILSS value with respect of conditioning time at 150^0 C.



(b) (a)

Fig.5. Variation of ILSS value during thermal shock treatment.



(a) (b)

Fig. 6. SEM of fiber/matrix debonding and fiber fracture at the interface region.