Durability and integrity studies of environmentally conditioned interfaces in fibrous polymeric composites: Critical concepts and comments

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Abstract

Fibre reinforced polymer (FRP) composites are the most promising and elegant material of present century. Their durability and integrity in various service environments can be altered by the response of its constituent i.e. fibre, polymer matrix, and the existing interface/interphase between the fibre and polymer matrix, in that particular environment. The interphase is generally manifested by chemical bonding, molecular segregation and also by van der Waal bonding. The sizing of fibres generally influences the chemistry and character of the interface/interphase and might generate structural gradient in the polymer matrix. Their susceptibilities to degradation are dependent of nature of environments and each of the constituents' responses differently and uniquely. Among the three constituents, the interface/interphase has very critical role to play on the performance and reliability of FRP composites. The reduced glass transition temperature of the interphase may induct low modulus area, which subsequently affect fracture toughness and local stresses of the composite. These result in high fracture toughness at ambient temperatures, but significantly reduced performance at high temperatures.

Keywords: Polymeric composites, Fibre/polymer interface, Environmental degradation, Interfacial properties, Interfacial durability and Micro-characterization.

Contents

Acknowledgement

References

1. Introduction

In the realm of science and technology of fibre reinforced polymer (FRP) composite materials, the role of fibre/polymer interface/interphase on the overall properties of composite is widely acknowledged. A three-dimensional region between the bulk fibre and bulk matrix is referred as "interphase" [1]. It includes not only the two-dimensional (2D) area of contact (interface) between the fibre and the matrix, but also a region of some finite thickness extending on both sides of the interface in both the fibre and matrix [2].

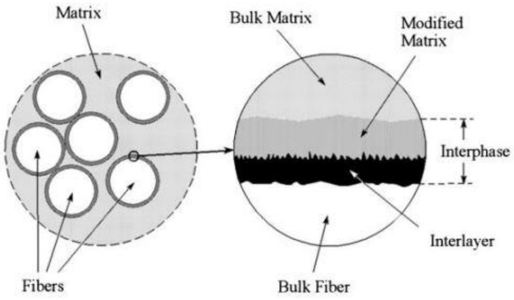

Fig.1.Schematic representation of a composite interphase [1].

The bonding between fibre and matrix dependents on the atomic arrangement, molecular conformation and chemical constitution of the fibre and matrix, further the morphological properties of the fibre and the diffusivity of elements in each constituent also have pronounced effects [2], therefore the interface may be specific to each fibre/matrix system. Fibre/matrix adhesion in general can be attributed to various mechanisms, which include adsorption and wetting, electrostatic attraction, chemical bonding, reaction bonding, and exchange reaction bonding [2]. The behaviour and performance of advanced structural FRP composites cannot be explained only in terms of specific properties of its constituent fibre and matrix but also the existing interface/interphase between fibre and matrix has great significance [3, 4].

The outstanding mechanical properties as high strength to weight ratio, corrosion resistance, good impact resistance, better damping characteristics and improved fatigue properties enables their use in diversified fields. Widespread application spectrum of FRP's covers almost every type of advanced engineering structures. Their usage includes various components in aircraft, helicopters, spacecraft, boats, ships, offshore platforms and also in automobiles, chemical processing equipment, sports goods, and civil infrastructure such as buildings and bridges [5].

All these structures and components are exposed to some environment during their service life. The environmental conditions can be high and low temperatures, high humidity, UV light exposure, alkaline environment and may be more severe if there is cyclic variation of temperature, hygrothermal environment and low earth orbit space environment.

Polymer matrix composites are susceptible to damage in these environments. The mechanical behavior of FRP composites are dominated by the interfacial adhesion at the fiber-matrix interface. Differential thermal expansion of fiber and matrix at elevated temperature can degrade the interface which leads to the lower interlaminar shear strength of the composite. At low temperature most polymer matrix behaves in brittle manner and do not allow the relaxation of residual stresses or stress concentration. These residual stresses at cryogenic temperature may results in larger debonded interfaces. The presence of moisture at the interface can modify the interfacial adhesion thereby affecting the mechanical performance of the FRP composites. The energy associated with the UV radiation is capable to dissociate the molecule bonds in polymer matrix and may lead to the degradation of the materials. Polymer matrix composites are promising materials for mechanical supporters and electrical insulators in the construction of superconducting magnets for fusion reactors [6]. Under such kind of applications the neutron and γ-ray irradiation may modify the structure and microstructure of polymer matrix. FRP's have great potential to meet various structural design requirements of spacecrafts, space stations, space shuttles and launch vehicles. Despite of having a lot of positive aspects of utilizing FRP's in space structures, they are susceptible to maintain their outstanding performance against the harsh space environment.

Delamination is one of the most frequent life limiting damages in laminated composites. Significant efforts have been made to contribute in improving delamination resistance in FRP's. Incorporation of nano-sized second phase has been widely believed to significantly improve polymer mechanical properties by effective load transfer at filler–matrix interface. The nano-filler/polymer matrix interfacial shear strength will depend on the structure and properties of any interphase region formed between the reinforcement surface and the bulk polymer resin [7]. Formation of reversible covalent bonds between the polymer network and the reinforcement material can enhance the healing capabilities of interphase, resulting in improved lifetime of the composite [8].

The advanced characterization techniques are compared with each other with reference to the information that can be gained, and also with reference to applicability to polymer surface and interface analysis.

The present review highlights the different degree of damages and degradations under different enviromental conditionings. The important roles of interface necessitates a critical and comprehensive understanding of environmentally conditioned interfaces in FRP composite systems.

2. Exposure to temperature and its effects on interfacial stability

2.1 High temperature

FRP composites are sensitive to temperature variations as a result of induced thermal stresses between the fibres and polymer matrix [9] due to their distinct thermal expansion coefficients. At elevated temperature differential thermal expansion of fibre and matrix may leads to the formation of microcracks at the fibre/polymer interface [10]. The fibre matrix interface also becomes susceptible to aggressive reactions under the exposure of high temperature environment, which can leads to degradation of both the fibres and the matrix [11]. This in turn affects the integrity of the composites, since it is the interface through which the thermal and mechanical loads are transferred from the matrix to the fibres. Effect of a thermal environment on the residual mechanical performance was evaluated for constant 170°C temperature for 120, 240 and 626 h prior to flexural testing [12]. Both the flexural and shear strength decreased and more pronounced at prolonged exposure time due to weakening of interface as shown in fig 2.

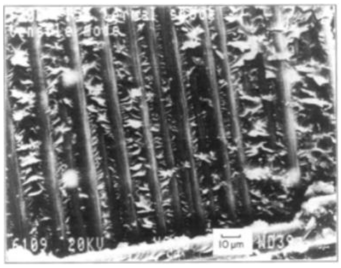

Fig. 2. SEM micrograph of fracture surface specimen thermally aged for longer time [12].

Interlaminar shear strength of unidirectional graphite composites were decreased by 30 % under the exposure of elevated temperature [13]. Investigations on CFRP and GFRP sheets, which are exposed to 600 °C reported, that the residual tensile strength and stiffness severely degraded when the composite is exposed to a temperature, higher than the decomposition temperature of polymer resin and further increase in environmental temperature would not lead any further reduction in the aforesaid properties [14]. Response of liquid-cooled GFRP slabs in fire is investigated by [15]. Tensile behavior of CFRP sheets with two different epoxy resins at different temperatures is studied by [16]. Investigation on epoxy resin at elevated temperature elucidated that the compressive strength of epoxy significantly decreased at temperature close to glass transition temperature and reached to zero with further increase in temperature [17].

2.2 Low temperature

Several investigations have been performed for the assessment of mechanical properties of FRP composites under cryogenic temperatures [18-22]. Under low temperature environment or cycling from room temperature to low temperature with applying loads microcracks may generate and propagate in the polymer matrix and/or at the fibre/matrix interface [23]. Various structural damages such as fiber/matrix interfacial debonding, potholing or delamination [20-21] result in degradation of mechanical properties of FRP composites. Unidirectional CFRP laminate specimens that had been aged at -184 ˚C for 555 h with half of the failure load showed about 20% degradation in tensile strength compared to that at RT [21]. Effect of low temperature and low temperature cycling (room temperature (RT) to -50 ˚C, RT to -100°C and RT to -150 ˚C) on the strength and stiffness of T700/epoxy unidirectional laminate were reported [24] as shown in fig. 3(a) and 3(b).

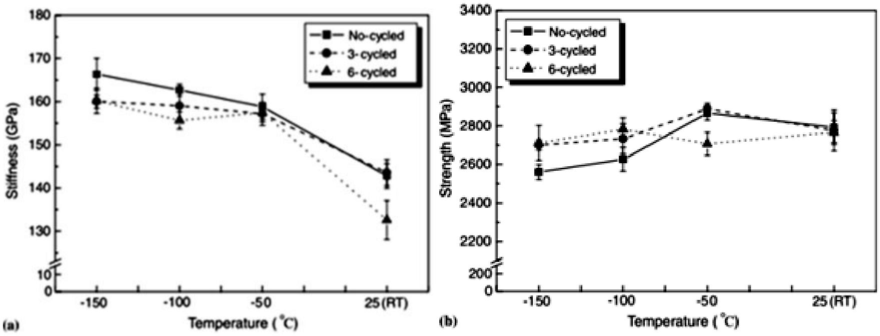

Fig. 3.Results of stiffness and strength of T700/epoxy unidirectional specimen cycled with load at RT/-50 °C/-100 °C/-150 °C. (a) Change of stiffness and (b) change of strength [24].

Fig. 3(a) shows that there is increase in stiffness as temperature decreased and at -150 °C the stiffness increased about 16% more than at RT. It can also be noted from the figure that the rate of increase in stiffness is higher between RT to -50 °C and then gradually lessened below -50°C and the strength of non-cycled composite specimens decreased about 9% more at -150 °C than RT. SEM micrographs revealed the failure of interface as it is clearly removed in the room temperature failed specimens while cryogenic temperature specimens and cryogenic temperature cycled specimen showed the presence of interface (fig. 4). Low thermo-mechanical cycles can result in improvement in interfacial shear strength of laminated composites [20].

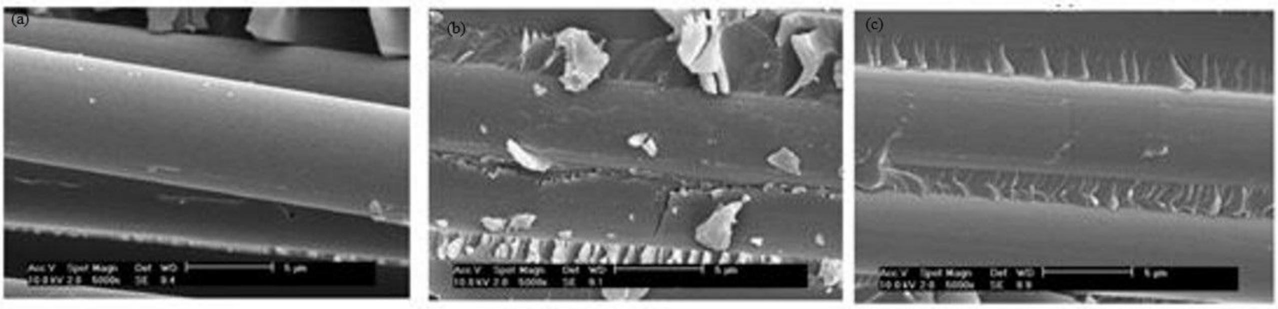

Fig.4.Interfaces of fractured T700/epoxy unidirectional specimens through SEM images. (a) at RT, (b) at -150 ˚C and (c) at -150 ˚C after six cycles from RT to -150 ˚C [24].

Decrease in tensile strength of CF/epoxy composites at -269 ˚C has been reported and measurement through acoustic emission events, it was speculated that crack initiation can occur at lower load level than that at RT [19]. Mechanical behaviour of carbon/epoxy [25] and glass/epoxy [26-27] at liquid nitrogen temperature has been investigated. The roles of percentage matrix phase and interfacial areas on the interlaminar shear failure mechanism of glass/epoxy composites at ultra-low temperatures for different loading speeds were reported [27]. The stress at delamination failure was found to increase slightly with increased crosshead speed at some points of conditionings for three temperatures. The ILSS value increased with more conditioning time for a same loading rate. Here no statistically significant variations of shear strength values were found with change of conditioning temperature. Greater value of shear strength at longer conditioning time may possibly be attributed by enhanced key and lock principle at the fibre/polymer interfaces. Here more percentage of fibres in the composites has resulted more interfacial areas and thus more matrix damages were inducted by misfit strain.

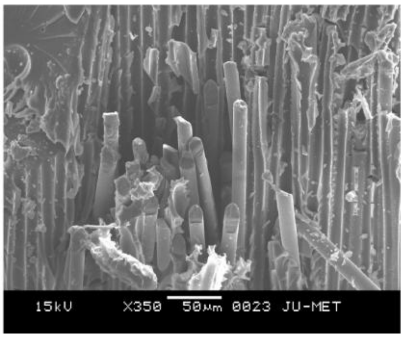

Fig.5. SEM micrograph reveals total loss of adhesion at the fibre/polymer interface and massive matrix cracking at low temperature. [27]

Three weight percentages of carbon fibres (50, 55 and 60 wt %) were targeted to prepare the composites. The moisture free carbon/epoxy composite specimens were exposed to liquid nitrogen environment (77K) for one hour [25].

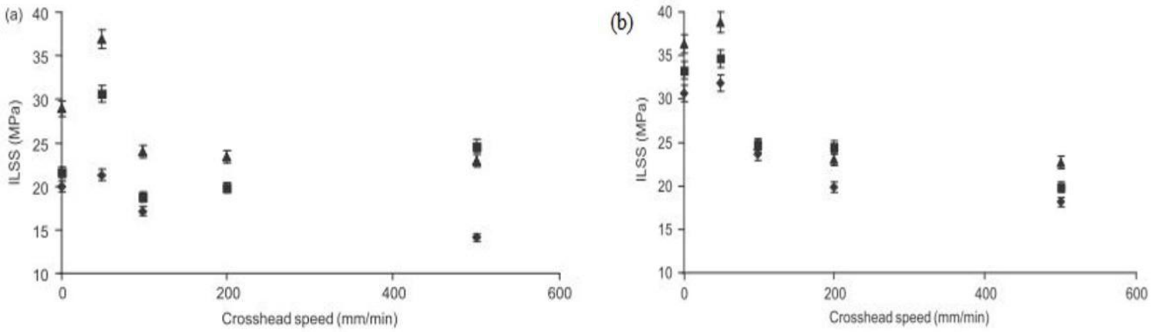

Fig.6. Graph showing the effect of crosshead speed on ILSS of carbon/epoxy composites at ambient temperature (▲), cryogenic temperature (77K) (♦) and at room temperature after cryogenic conditioning (■) for (a) 0.5 fibre weight fraction, (b) 0.6 fibre weight fraction.[25]

From the plots 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 fibres plays a critical role. SEM micrographs revealed fibre/matrix debonding and formation of shear cusps in cryogenically conditioned carbon/epoxy composites as shown in fig.7.

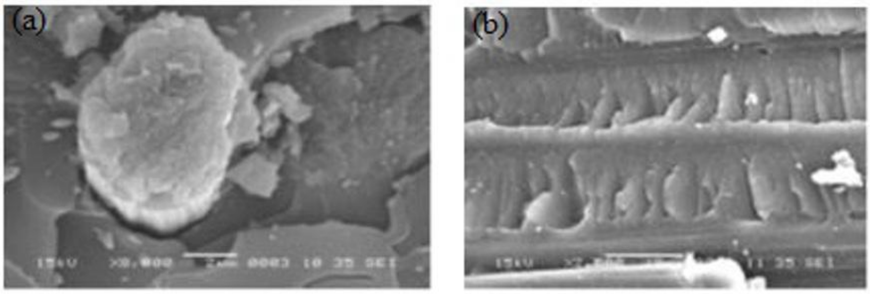

Fig.7. Scanning electron micrographs showing (a) debonding at interface, and (b) rows of cups [25].

2.3 Thermal shock

When any engineering and structural component undergoes a sudden change in the temperature of its operative environment then the material is said to be undergone "thermal shock". Fibre/matrix interfacial adhesion is significantly affected by the thermal shock conditionings [28-32]. An investigation which was focused on the effect of thermal shock on the interlaminar shear strength (ILSS) of glass/epoxy composite has reported that there is increase in ILSS value with the increase in conditioning time as shown in fig.8. [29]

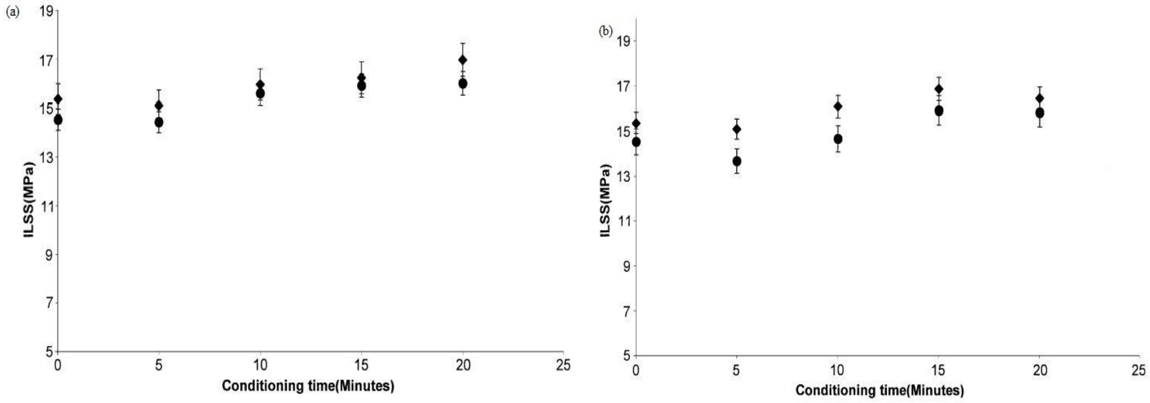

Fig.8. Effect of thermal shock on ILSS value of glass fibre/epoxy composites at 2 mm/min (•) and 10 mm/min (♦) crosshead speeds (a) down-thermal cycle, and (b) up-thermal cycle. [29]

Here the effect of thermal shock is evident at less conditioning time (at 5 min.). But post curing and strengthening phenomena and shrinkage compressive forces dominates at higher conditioning time. Shrinkage compressive forces can improve the mechanical interlocking at the fibre matrix interface. Investigation on glass fibre/polyester composite reveals that the degradation of the composite under hydrothermal shock cycle is less pronounced with the increase of fibre volume fraction [28]. The damaging effects are also loading rate sensitive. ILSS values were found higher for higher loading rates. The decrease in ILSS value with the increase in hydrothermal shock cycles was also noticed. Influence of thermal shock on the mechanical behaviour of Kevlar fibre reinforced with epoxy and polyester resin matrix were also studied [30]. For Kevlar fibre/polyester system, which is thermally conditioned, the ILSS value decreases with increasing conditioning time, whereas the ILSS increases with conditioning time for Kevlar/epoxy composites as shown in fig.9. The weak interface between Kevlar fibre and polyester resin deteriorate by thermal shock.

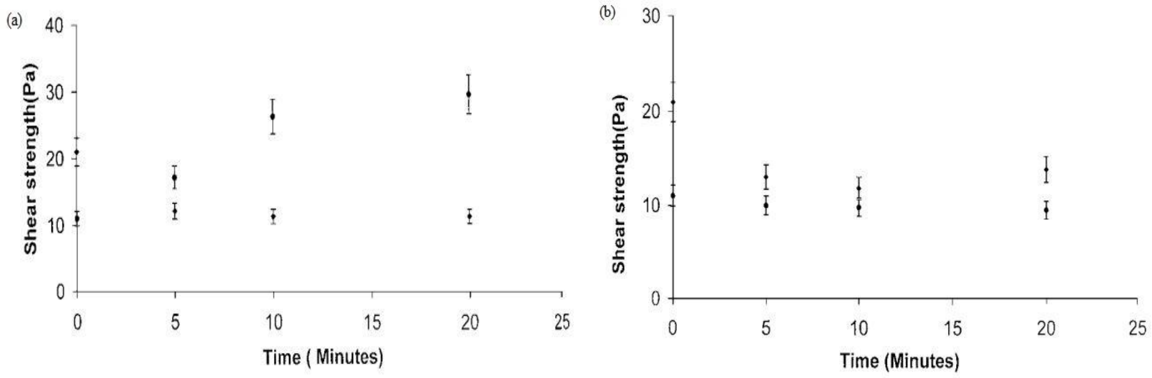

Fig.9. Effect of thermal shock on shear strength of (a) thermally conditioned, and (b) cryogenically conditioned, kevlar/epoxy (●) and kevlar/polyester (♦) composites. [30]

The interface may be unable to accommodate the unfavourable tensile stresses developed due to the radial expansion of Kevlar fibre.

2.4 Thermal fatigue

When continuous fibre reinforced composites subjected to temperature variations, local stresses generate in the composites due to the different coefficient of thermal expansion and/or due to the ply orientation in the lay-up [33]. When these thermal variations are cyclic they results in cyclic stress variation at ply level which can be compared to a fatigue phenomenon. These cyclic stresses may results in various types of damage similar, to those observed in mechanical fatigue, like transverse matrix cracking, fibre/matrix debonding and delamination. These temperature variations become more deleterious in the presence of an oxidative environment which can cause matrix oxidation. Studies on oxidation phenomenon in thermoset epoxy polymers has been reported that the oxidation results in a loss of mass and a reduction in volume of the epoxy matrix, inducing shrinkage of the matrix with respect to the fibres [33-35]. Oxidation of epoxy and bismaleimide may results in formation of a low thickness oxidised layer on the free edges of the samples and during ageing the thickness of this layer grows quickly towards an asymptotic value, governed by the type material and temperature of ageing atmosphere [36]. Throughout thermal cycling tests, the observations of the free edges have shown three types of damages: debonding between fibres and matrix (Fig. 10(a)), matrix cracking (Fig. 10(b)), and permanent deformation of the matrix due to its shrinkage (Fig. 10(c)) [33].

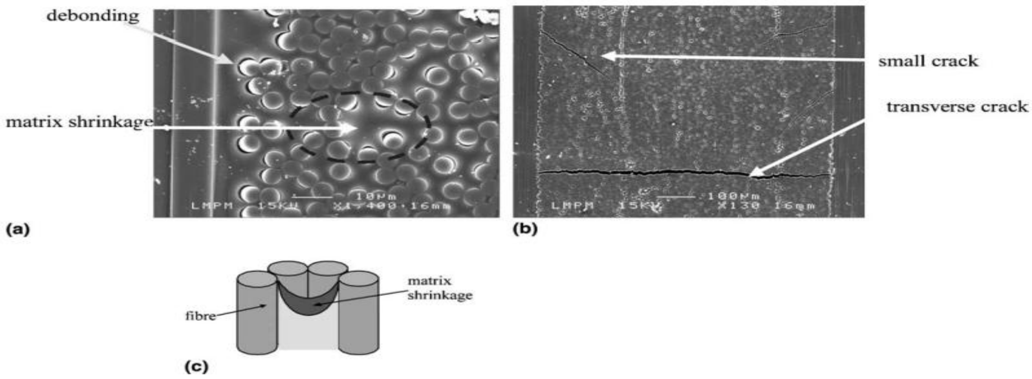

Fig. 10. Different types of damages. $[0_3/90_3]_S$ oxygen, 100 cycles [33].

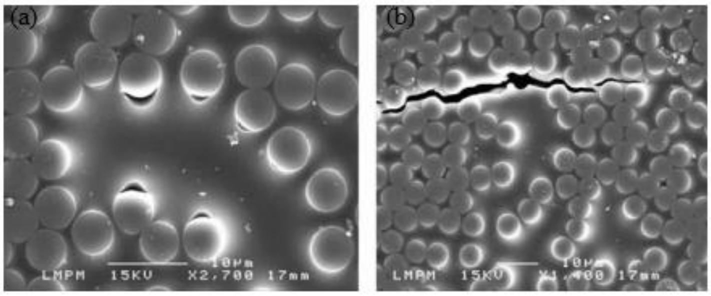

Fig.11. SEM observations of a $[0_3/90_3]_S$ specimen subjected to 100 thermal cycles in air [33].

As an example, Fig. 11 shows a SEM picture of the edge of the quasi-isotropic laminate $[45/0/-45/90]_S$ subjected to 500 thermal cycles in oxygen. In that figure, one can see a deep hole in the matrix, which is located at the interface between the central 90□ layer and a 45□ ply. In that case, the matrix contraction has induced numerous fibre/matrix debondings in the circumference of the hole. When the tests have been performed in oxidative environment, it appeared that, after 100 cycles, matrix shrinkage is already well developed. Consequently, fibre/matrix debonding, which seems to be connected with this type of damage, has been observed very early during the test. For example, in Fig. 11(a), some small fibre/matrix debondings are present in a $[0_3/90_3]_S$ specimen subjected to only 100 thermal cycles in air. Moreover, observations of the same specimen, at the same stage of the test, have shown short matrix cracks (Fig. 11(b)). It is shown that the onset of fibre-matrix debonding depends on the oxygen pressure and the increasing of oxygen pressure will accelerate the thermo oxidation phenomena by decreasing the time of the fibre-matrix debonding onset. When thermal cycling is performed in an oxidative atmosphere, there exists a coupling between thermal transverse stresses and oxidation which enhances the importance of the location of the layers with respect to the atmosphere [37]. A research programme entitled COMEDI was aimed to better identify the link between the physical mechanisms involved in thermo-oxidation phenomena: chemical shrinkage strain/stress, oxygen reaction diffusion, degradation at different scales and to provide tools for predicting the thermo-oxidation behaviour of composite materials under thermo-oxidative environments including damage onset [38].

3. Exposure to moisture and its effects on interfacial strength and stability

Fibre/matrix interface is believed to be an active pathway for the rapid diffusion of water into the polymer matrix composites. The diffusion can takes place due to capillary action that is also known as water wicking and is predominant in the composite systems in which wetting of the fibre by the matrix is incomplete [39]. Transport behavior of matrix voids and fibre/matrix interphase can have substantial effect on overall diffusivity of composite materials and higher value of diffusion coefficient for interphase (as high as 10-fold) than that of bulk matrix is suggested [40-41]. Induced moisture has detrimental effects on the performance of FRP composite materials [42]. Moisture inside polymer composite leads to matrix plasticization, chemical degradation and mechanical degradation [43]. Matrix plasticization has deleterious effects on matrix modulus. Chemical degradation includes hydrolysis of bond at interface. Mechanical degradation is a function of matrix swelling strain. During the excursion of FRP composites to water significant damage may occur in the form of interfacial microcracks [44-45]. These microcracks further accelerate the water accumulation and results in considerable weight change of FRP composites [46-47]. In the initial stages water can dissolve the interphase substances and further accumulation of water can replace these dissolved components. Moisture induced degradations in the composites can be suppressed by improving the wetting between the fibre and matrix, thus obstructing the diffusion path of the moisture [39, 48]. In GFRP composites, glass fibre absorbs negligible moisture as compared to the polymer matrix so it is the interface, which is solely responsible for the discrepancies in the amount of moisture absorbed by the composite and neat resin [49]. Effect of different volume fraction of fibre on the moisture absorption can be seen in fig. 12. Dependency between the volume fraction of E-glass fibers and the water weight gain was linear [50].

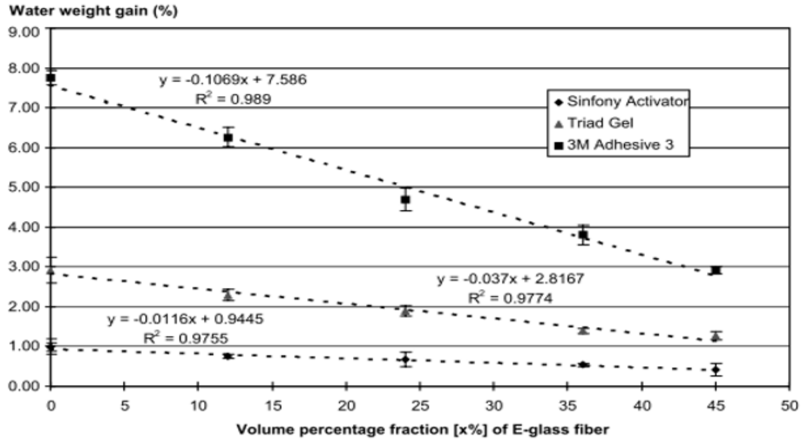

Fig.12. Water-weight gain (±SD) for the investigated materials with different volume fractions of E-glass fibers after 30 days of storage in water at 37 °C [50].

For Kevlar/epoxy composites it is observed that 1% absorbed moisture results in 5%, 4%, and 2% reduction in the compressive, interlaminar shear, and flexural strength, respectively [51]. Similar reductions in the tensile and interlaminar shear strength of carbon or glass-fibre-reinforced polyetherimide have also been reported [52]. Composites made up of different manufacturing techniques such as resin transfer molding (RTM) also studied for moisture induced degradations [53-54]. Numerous moisture absorption studies in polymer composites, observed that moisture uptake process follows the Fickian diffusion process, particularly in the initial linear uptake region [55-57]. Many other experimental investigations, however, found varying degree of non-Fickian moisture diffusion process [58-63]. Furthermore, the "Langmuir-type" model of diffusion [64], a time-varying diffusion coefficient model [65], was also presented. A study revealed that Langmuir and Fickian models could be statistically equivalent in some treatments and conditioning temperatures [66]. However, the Langmuir model should be favoured when studying adhesive or carbon/epoxy conditioned in anti-icing additive: it is a more accurate model and may capture the moisture uptake.

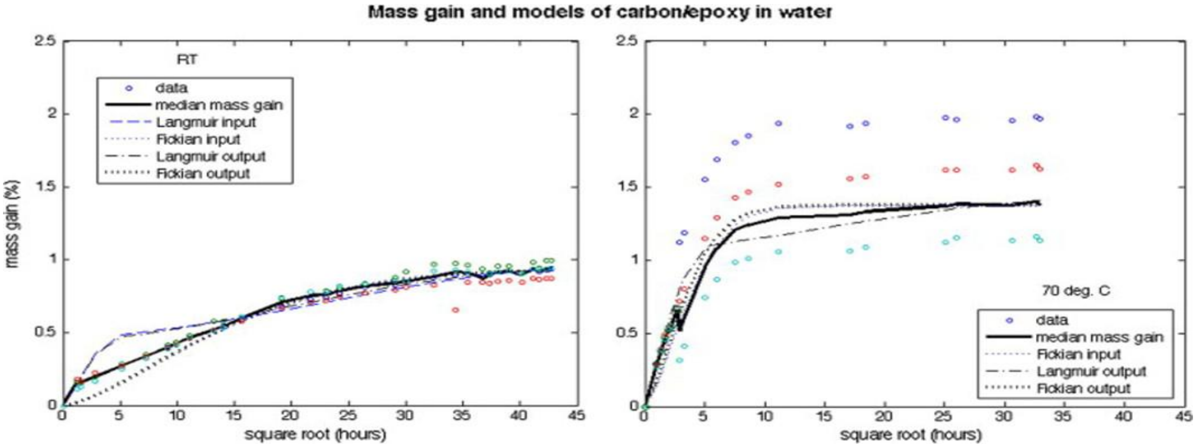

Fig.13. Application of Fickian and Langmuir models to gravimetric data of carbon/epoxy in 100% RH water, at room temperature (‘RT’) and 70 °C. ‘Model input’ is a model built on the median mass gain of the specimens. ‘Model output’ is a model built on the median of the output results of the specimens [66].

Long term moisture absorption leads to the degradation of mechanical properties [65-71] of FRP composites which significantly reduce the service life of FRP structures and components. Absorbed moisture can cause substantial changes in modulus, strength, and ultimate strain [69]. Reduction in strength and stiffness due to moisture absorption can be attributed to various damage mechanisms which can include matrix cracking, fibre–matrix debonding, and corrosion of fibres (especially in case of glass fibre). E-glass/vinyl ester composites submerged in fresh water for a period of about 2 years, shown 60% and 10% reductions in tensile strength and stiffness respectively [67]. Reduction in the interlaminar shear strength of aramid/epoxy composites by moisture absorption was also reported and the interlaminar shear strength of the aramid/epoxy composites for less sensitive environment depends on moisture concentration at the point of failure [68].

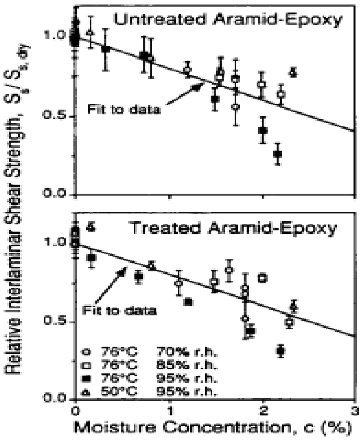

Fig.14. Relative interlaminar shear strength of untreated and treated aramid-epoxy composites subjected to the four environments shown by [68].

For short jute fibre/polylactide composites, after 24 h aging at 70 □C in saturated water vapour condition, the tensile strength of uncoated fibre/polylactide composite specimen was 85.4% of the specimens without aging, and after 72 h aging, deterioration in the tensile strength for both coated and uncoated specimens 30% of unaged specimens [70]. Ageing of graphite-fabric epoxy composites in boiling water even after a relatively short exposure of 46 h causes a large reduction in both shear and tensile strengths [12]. As clearly seen from fig.15, boiling water destroys the fibre matrix adhesion (bare fibres) and massive voids are formed in the matrix (as large as 20 µm).

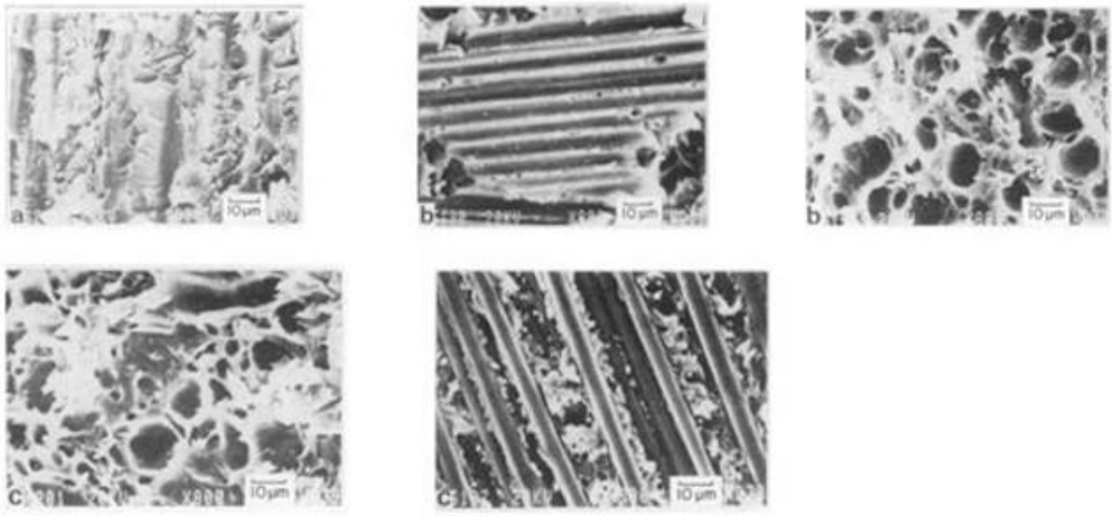

Fig.15. SEM micrograph of failure surfaces following immersion in boiling water for (a) 0h, (b) 46h and (c) 115h [72].

4. Hygrothermal behaviour and its effects on interfacial durability

Hygrothermal ageing refers to the synergetic ageing under moisture and temperature environment which can damage the polymer matrix [72-73]. Temperature induced damages can further accelerate the moisture diffusion [74]. Some investigations have considered the response of composite in hygrothermal environment and also subjected to a constant externally applied load [75-78]. For symmetric and anti-symmetric GFRP laminates, reductions in flexural stiffness were reported as 54% and 27% respectively, when exposed to 98% humid environment for 2000 h [73]. Hygrothermal degradation of a unidirectional glass fibre/epoxy composite by moisture sorption/desorption experiments and dynamic mechanical thermal analysis (DMTA) is also reported by [79]. Reduction in static and fatigue strength of carbon fibre/epoxy composite under hygrothermal conditioning has been investigated by [80]. Depending on the lay-up sequence, the maximum static bearing strength is reduced by 8% to 22% for woven laminates. Glass fibre (with solvent GF S and without solvent GF NS) and carbon fibre (with solvent CF S and without solvent CF NS) reinforced composite laminates were characterized in terms of water sorption and desorption [81]. Total amount of water absorbed for 1200 h exposure at 71 °C was 4–5% of the total laminate weigh and after 450 h desorption water content was approximately 3%. Water absorption and desorption behavior is shown in fig16 (a), and further its effect on flexural modulus is shown in fig.16 (b). Poor interfacial adhesion and change in failure mode due to moisture accumulation in the composite, is attributed as main cause of large reductions in flexural and interlaminar strength values [82-83].

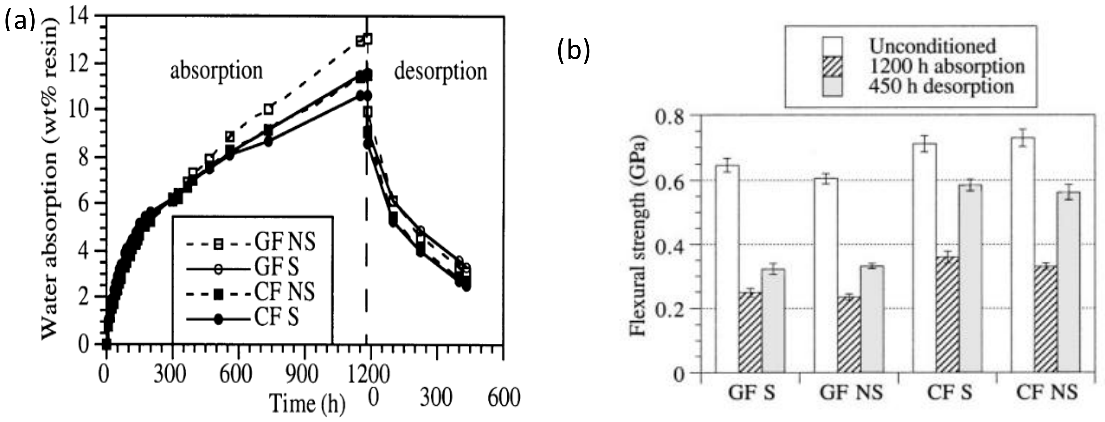

Fig.16. (a) Water absorption and desorption curves of laminates made from epoxy prepregs of various fibre reinforcement and solvent content, (b) Flexural strength for laminates made from epoxy prepregs of various fiber reinforcement and solvent content. Error bars shown are the standard deviation from five samples [81].

5. Effect of UV radiations on FRP's

Ultraviolet radiation has a wavelength between 290 and 400 nm, and the energy associated with these wavelengths is equivalent to the bond energy of the polymeric materials. Hence, these wavelengths can dissociate the molecule bonds in polymers and may lead to the degradation of the materials [84]. The degradation starts at outer surface of polymeric materials which is exposed to the UV light, if the light penetration is limited to surface only then it may results in surface discoloration only, and if the degradation is penetrated through the bulk of material then it can results in degradation in mechanical properties of the corresponding polymer materials [85]. Exposure to UV radiation causes hydrogen abstraction from the polymer molecules, which generate free radicals and these free radicals can initiate other reactions causing brittleness and subsequently lower the molecular weights and loss of thermal diffusivity and load bearing capacity [86-88]. The extent of degradation of the material under the exposure of UV radiation depends on the type of polymer and the duration of exposure [87, 89]. UV-radiations can cause either random chain scission or increase in cross-linking density in the polymers and consequently leads to variations in brittleness and reduction in material strength [88]. Reduction in interlaminar shear strength and the flexural properties of irradiated-composites (graphite/epoxy) were reported by [90], while no decrease in flexural properties of irradiated-composites under short term exposure is reported by [89], short term UV exposure resulted in changes in the surface morphology of the composites. Fritz Larsson [91] studied the effect of UV light on mechanical properties of kevlar 49 composites. Their results elucidated that the degradation depends on the thickness of composite. They postulated that only 0.13mm thickness specimens were found affected by UV exposure and their strength retained 60% after 1000h exposure. No degradation effect on 0.25mm and 0.50mm thickness laminates were observed. It is also observed that the damage due to UV radiations are higher when the composites are exposed to air than in near vacuum system [92]. Elastic modulus of a single kevlar fibre exposed to UV irradiation and water, increased 30% and decreased 15% compared to that of untreated ones respectively [93]. To measure the combined effects of humidity, temperature, mechanical stress, and UV exposure on the creep behaviour of polymers, new equipment has been demonstrated by [94]. Surface molecular characterisation of epoxy resin composites reinforced with E-glass (E), 3D glass (3D) and carbon fibre (CF) subjected to an intense UV and high temperature environment has been carried out using XPS and ToF-SIMS [95]. XPS results revealed that 3D glass reinforced composites exhibit more surface oxidation in comparison with E-glass and carbon fibre composites. Principal components analysis (PCA) of the ToF-SIMS positive ion spectra indicated that E-glass and 3D-glass reinforced composites suffered chain scission while carbon fibre composites suffered chain scission and cross-linking reactions under UV excursion.

6. Effect of neutron and γ-ray irradiation on FRP's

Exposure of composite materials in extreme radiation environments, however, may result in damage of the structure and microstructure. Especially, neutron irradiation has been noticed to cause delamination in stratified structures or debonding at fiber/polymer interfaces in organic composites. Irradiation can also change the electrical and optical properties of the graphite [96]. Excursion of carbon materials to ionizing radiation can modify the crystal lattice by displacement of atoms within the lattice or electronic excitation [97]. Lattice defects in carbon materials can produce a variety of effects and these defects can lead to the modifications in most physical properties including thermal and mechanical properties. Generally, it is observed that the mechanical properties of carbon materials have not been affected to any great extent by the electronic excitation. However, electrons ejected from atoms create the active sites that are sensitive to environment species and can accelerate other damage mechanisms, namely moisture uptake [97]. Irradiation with fast neutrons changes the value of interlaminar shear strength as observed in carbon/carbon composite [98]. Other studies showed that neutron irradiation can lead to increase the Young's modulus of carbon fibers due to an increase in shear modulus of the graphite parallel to the basal planes [99]. The extent of deformation in different composites materials due to irradiation depends on the type of fibers, their reinforcement direction in the carbon matrix and interaction between the carbon fibers and the matrix [100]. Pitch-based carbon fibers have more resistance to degradation under exposure to irradiation than PAN- based carbon fibers. Low doses of neutron irradiation may result in strengthening of graphite by ejecting atoms from graphene planes into interstitial positions while at high doses the ejection of atoms amounts to structural disorder and may account for strain-induced cracking which results in a decrease in the mechanical properties of carbon materials [101]. Investigation on the neutron irradiation effects on the mechanical properties of organic and carbon composite materials reported the improvement in flexural strength and modulus while no effect on deformation at break was observed but the flexural strength was distinctly affected [97]. This investigation also fetched interesting information about the improvement in ILSS of composite system. However, neutron irradiation damages the matrix (particularly carbon) but it improves the matrix–fibre interaction. Induction of compressive stresses on the graphite fibres by a slight shrink of matrix and/or swelling of the fibres can probably be attributed to the improvement of ILSS. When organic materials are subjected to neutron irradiation, the degradation is caused mainly by recoil particles, that are produced by neutron reactions such as elastic scattering, inelastic scattering, and nuclear reaction [102]. On the other hand γ-ray irradiation induced degradations are primarily due to secondary electrons generated by the interaction with photons. Investigations have been shown that as far as the E-glass and T-glass fabric composites are concerned, the dose dependence of the composite strength at 77 K is almost independent of the composite specifications such as the kind of glass fibres, type of fabric weave, the specimen thickness and the volume fraction of reinforced fibres [103].

7. Low earth orbit space environments and vacuum thermal cycling and their effects on FRP's

The LEO space environment constituents include high vacuum, ultraviolet (UV) radiation, thermal cycles, atomic oxygen (AO), electromagnetic radiation, charged particles, micrometeoroids, and man-made debris [104]. These environmental constituents can significantly degrade the material characteristics of polymers and polymer matrix composite (PMC) materials. Exposure of composite materials to the severe LEO space environment leads to the structural modification and mass loss by outgassing, thermal cycling can result in fatigue cracking, AO attack leads to the surface erosion, UV radiation can modify material properties and collisions with a high velocity micrometeoroids and man-made debris can leads to delamination in the laminated composites [104-105]. The outgassing of moisture and other volatile constituent can produce dimensional changes in composite components and also leads to contamination in adjacent spacecraft component [106-107]. The decrease in strength and stiffness of the graphite/epoxy composites after being exposed to thermal cycles were observed and this reduction was found to be in exponential proportion with increasing thermal cycles [104]. The loss in transverse flexural strength and stiffness were quicker as compared to other properties [105]. Matrix loss at the composite surface was attributed as the prime cause for the severe drop in transverse flexural properties. Effect of hypervelocity impact on carbon/epoxy composites in low earth space environment is also reported by [108]. Investigation on the effect of vacuum thermal cycling on the physical properties of unidirectional M40J/AG-80 composite revealed that increasing the thermal cycles, both the 90 and 0^0 tensile strengths decreases [109]. Initially, increase in bend strength is noticed but after 97 cycles it was decreased to a certain extent. The mass loss ratio during vacuum thermal cycling increases to a given value after 48 cycles and this mass loss is attributed to the volatilization of smaller molecules from the composite. The degradations in the properties of composites under vacuum thermal cycling is attributed to the formation of microvoids and interfacial sliding at the fibre/matrix interface [110]. Interface dominated properties, such as, compressive strength and ILSS, were remarkably reduced up to 15% [110].

8. Effect of nano-fillers on interface durability

The fundamental issue in damage resistance for laminated composite structures has been recognised as delamination [111]. Over the past three decades, researchers have demonstrated that there are two basic approaches to improve the delamination resistance of the FRP composites. First approach is based on through thickness reinforcement (3D fibre reinforcement e.g. stitching, z-pinning, waving, braiding, and knitting) [112], while second approach is to develop modified polymer resins with improved toughness. To overcome the brittle nature of thermosetting polymer matrix, Modification in the matrix resins by the dispersion of second phase has been drawn significant attention over the years. The second phase normally consists of micron-sized soft organic (rubber or thermoplastic) or inorganic rigid particles. Incorporation of these second phase particles (can also termed as fillers) may result in various toughening mechanisms such as crack deflection, crack pinning, micro-cracking, matrix shear yielding or shear banding, rubber cavitation and particle tearing (soft particles) or bridging (rigid particles) [113-114]. On the other hand, incorporation of soft particles suffers from drawbacks such as decrease in glass transition temperature (T_g) and even in stiffness and strength of the composites [115]. Incorporation of nanoparticles can decrease the initiation and growth of microcracking and can significantly enhance the damage tolerance of laminated composites. Presence of nanoparticle in the laminated composite can significantly contribute to prevent some more pronounced low-scale damage mechanisms such as fiber breakage, diffused intralaminar damage and diffused interlaminar damage [116]. Further, it is also apparent that introduction of micron-sized inorganic fillers into epoxy matrices do not result in much improvement in fracture toughness of the matrix [117]. Various most common micro-mechanical mechanisms, which are responsible for the improvement in fracture toughness in FRP composite systems with modified matrix resin by second phase dispersion, are (i) crack deflection, (ii) crack pinning, (iii) crack tip blunting (or crack tip deformation) (iv) localised inelastic matrix deformation and void nucleation/growth, (v) particle/fibre deformation or breaking at the crack tip, (vi) fibre pull-out, and (vii) particle/fibre debonding [115]. Various parameters which influence these mechanisms include volume fraction of particles, interfacial bonding, particle size, and shape [118]. For nanosilica reinforced materials increase in fracture toughness is attributed to the debonding of the nanosilica and subsequent plastic void growth [119]. The prime toughening mechanisms in highly exfoliated epoxy/clay nanocomposites is the formation of massive microvoids/cracks and the increase in the fracture surface area due to crack deflection [120]. In nanotube dispersed composites, the bridging mechanism conceals the nano-pores growth and crack propagation and improves the fracture toughness of the material [121], moreover, during nanotube pull-out significant increase in fracture energy can be attributed to the extraordinary high interface area of nanotubes [118]. Moreover, the inherent weak van der Waals interactions at the matrix/nanotube interfaces could result in interfacial slippage [122-123] which can result in poor load transfer from the matrix to the nanotubes and hinder the full potential of nanotube in attaining very high strength in composites [124]. Very low filler loadings of nanometre sized fillers are widely believed to significantly improve polymer mechanical properties by effective load transfer at filler–matrix interface. Incorporation of filler shows the improvement in flexural and compressive strength at higher temperatures this may be attributed to the additional supports provided by the nano particles to the reinforced fibre against kinking [125]. The global failure due to compressive loads can be delayed by the incorporation of nanotubes by bridging the inter fibre debonding and micro cracks [126]. Introduction of silica nanoparticles in the epoxy matrix can also improve the compressive strength and modulus of the composite [127]. The compressive strength of CNT dispersed CFRP were found increased as well as the deflection were decreased [128]. The nano Al- reinforced composite showed a higher elastic modulus and static and dynamic compressive strengths than micro Al-containing composite and epoxy due to enhanced cross-link density and nano Al-containing composite displayed significant strain hardening effect [129]. The dispersion of carbon nano-fibre (CNF) into the epoxy enhances the mechanical properties of composites and the incorporation of CNF into CFRP composites results in improvement in compressive strength [130]. Incorporation of small amount of fullerene also resulted in improvement of compressive strengths of $(0)_8$, and 16 ply laminates [131]. As the concentration of nanoparticle increases the modulus has been observed increasing and the increase in modulus is expected because the modulus of Al_2O_3, E = 360GPa is much greater than that of the epoxy matrix (3.2GPa) [132]. Up to certain volume fraction of nano-clay loading, elastic modulus and compressive strength and modulus of the resin were found increased and this increase seizes after certain volume fraction of loading [133].

9. Interface characterization

9.1 Atomic force microscopic (AFM) analysis

Atomic force microscopy (AFM) is able to infer interphase properties directly [134]. Among the various techniques utilised, the nanoindentation and the nanoscratch tests, originally designed to investigate the material surface properties for various purposes, is an effective and relatively straightforward way to assess interphase characteristics. The AFM, invented by Binning et al. [135], has become an increasingly popular tool for characterising surfaces and interphases of many different types of material systems. In addition to its conventional topographical imaging, recent developments have led to the utilisation of the AFM as a nanoindentation device with extremely small diamond tip [136]. Article regarding fibre/matrix interphase focuses on glass fibres sized by silane coupling agents [137].

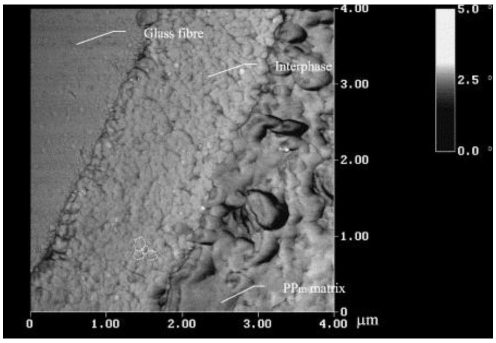

Fig.17. AFM phase images of interphase in γ-APS/PP–PPm composites. The dotted lines indicate the boundary between the particles [137].

Using AFM force modulation mode, Mai et al. [138] also observed a region of about 1 μm thick which is different from epoxy matrix and unsized glass fibres. Nanoindentation test was recently used to investigate the elastic modulus of the interphase region in MPS sized glass fibre/vinyl ester system [139]. Gao et al. [140] observed a distinct geometric interface between finished carbon fibre and epoxy resin in the topography and 3-D indentation contact stiffness map using AFM. For glass fibre/polyester composite with plasma polymer coated fibre, surface topography and phase distribution were also measured simultaneously using semicontact mode by [141]. Fig.18 demonstrated various topographical changes in AS4/VRM34 composite system detected with AFM, which were resulted due to exposure to hygrothermal environment.

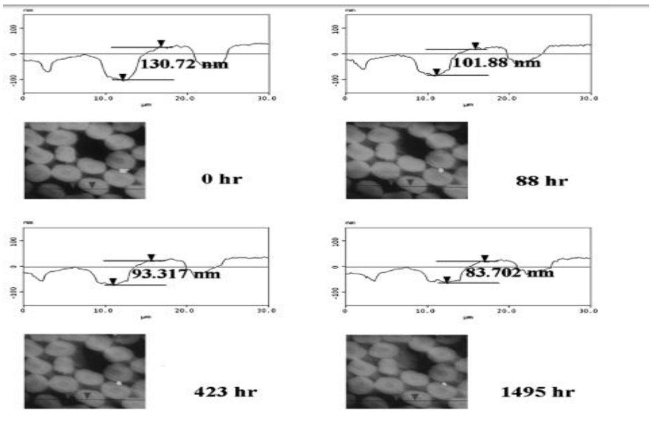

Fig.18. Topography change of AS4/VRM34 exposed to 100% RH for different periods of time. The vertical distance between the two selected points decreased from 130.7 nm before treatment to 83.7 nm after 1495 h of hygroscopic treatment at 100% RH [142].

9.2 Temperature modulated differential scanning calorimetry (TMDSC) analysis

TMDSC (Temperature modulated DSC), sometimes also referred as ADSC (Alternating DSC), has the supremacy over standard DSC that it enables better determination of the glass transition which is often accompanied by an exothermic curing reaction, and thus overshadowed [143]. The two phenomena, glass transition and cross-linking reaction can be separated by temperature-modulated DSC. The measurement principle of TMDSC is based on the superimposition of an oscillating temperature component on the usual temperature program with defined amplitude and period. The underlying heating rate, amplitude and period are the three parameters which must be selected for non-isothermal DSC. TMDSC investigations for epoxy used under non-isothermal and isothermal conditions are given in [144-147]. Determination of actual glass transition temperature and degree of curing for carbon-fibre epoxy prepreg samples pre-cured at 180 °C for different times is shown in fig19 (a).

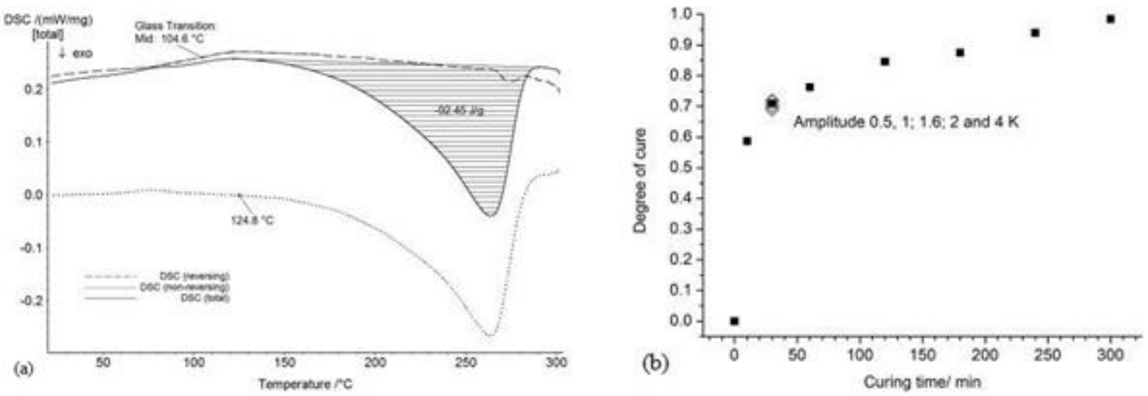

Fig. 19 (a). Temperature-modulated DSC, sample pre-cured for 10 min at 180 °C, underlying heating rate 10 K/min, modulation amplitude 1.6 K, modulation period 60 s, and (b) Degree of cure as function of curing time at 180 °C [143].

TMDSC measurements for carbon-fibre epoxy prepreg pre-cured at 140 °C were reported by [148]. The underlying heating rate was 5 K/min, the amplitude 0.5 K. The actual glass transition just at the onset of the post-curing reaction was clearly seen in the reversing heat flow signal (fig.20).

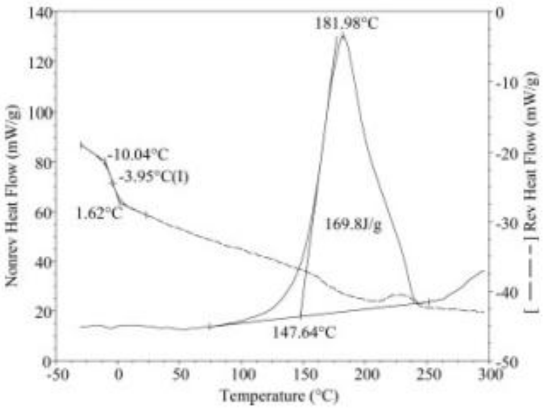

Fig.20. Reversing and nonreversing heat flow curves [148].

9.3 Fourier transfer infrared (FTIR) spectroscopy

When a beam of infrared (IR) radiation (wavelength between 800nm and 250 µm) is transmitted through a specimen, absorption versus frequency characteristics is obtained. The absorption or emission of radiation depends on the characteristic of interacting material and these radiations are related to the change in energy states (rotational or vibrational) of the material [2]. Some components or groups of atoms are absorbed in the IR at specific frequencies which yields the information about the molecular structure. The gradient in the structure of the epoxy resin from bulk matrix to bulk fibre as a result of the cure process at the fibre/matrix interfacial region was monitored by FTIR imaging [149].

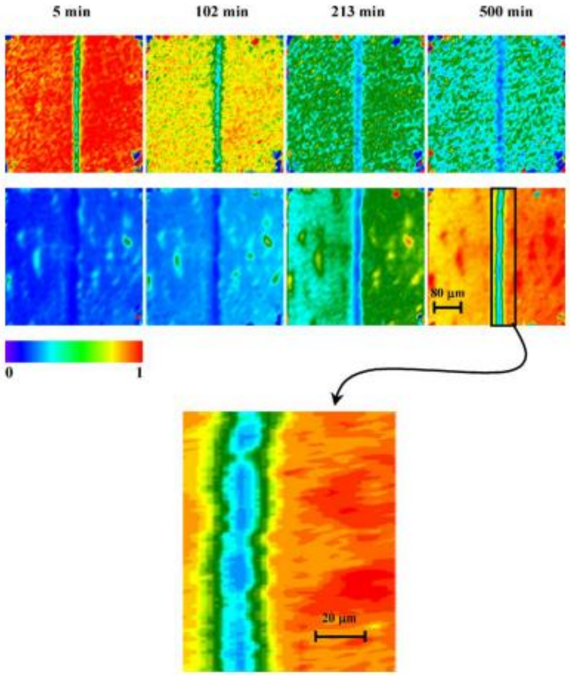

Fig. 21. Chemically specific images (IR absorption) of the amine groups, H–N–H (top), and hydroxyl groups, OH (middle), as a function of the curing time. The bar range from 1 to 0, indicating a relative absorbance scale [149].

There is a gradient of absorbance (colours) from the centre of the glass fibre to the bulk of the polymer yielding the information about the gradients in the chemical structure of the interphase [149]. The structure and properties of fibre/matrix interface depends on the coupling agents. The thickness of interphase region is accepted about 100 to 500 nm [150]. The curing process at interface may be slower than the bulk polymer phase [151]. The interfacial behavior of glass fibre/epoxy has been studied by Fourier transform infrared (FTIR) microspectroscopy [152–153]. A certain level of water concentration at interphase can catalyse a polymerization reaction. It is also oserved that under cycles of wet and dry environment change, the interfacial properties are rapidly degraded due to significant variation of the residual adsorbed water in the interphase region [152]. This variation might be the result of the diffusion of water within the epoxy film through the micro-void created by the debonding processes [154]. The FTIR spectrum of the cured bisphenol-A-based epoxy resin is shown in fig.22 as per [152]. The amino group of APS(y-aminopropyltriethoxysilan) establishes a chemical bond to an epoxide group of epoxy by a ring- opening reaction [155]. The siloxane bonds in the interphase improve the resistance to water penetration [156].

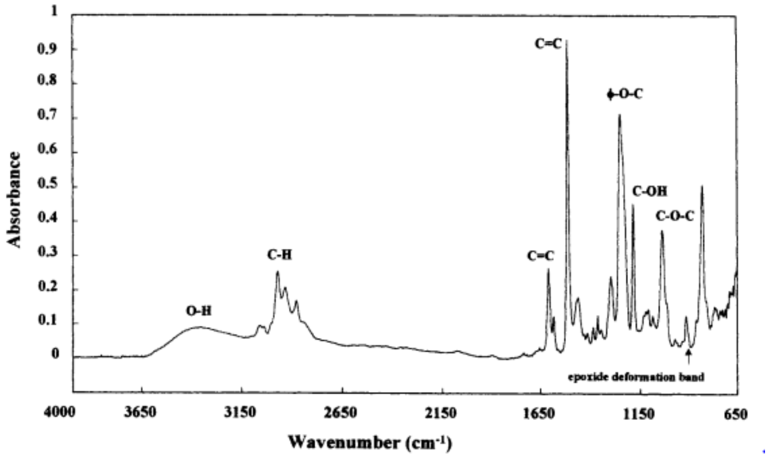

Fig.22. FTIR spectrum of bisphenol-A-based epoxy resin cured with tetraethylenepentamine [152].

9.4 Raman spectroscopy

Raman spectroscopy is one of the promising tool for the study of composite micromechanics, since it enables the point-to-point determination of stress and strain along the fibre/matrix interface in a variety of systems [157-160]. Raman spectroscopy has been extensively used for micromechanical studies of composite interfaces by many researchers [161–163].Moreover, the stresses and strains in the fibres and interface can be mapped at all levels of strain prior to overall catastrophic failure [164]. The micromechanical test methods give single-point values of interfacial stress obtained only through failure of the fibre/matrix interface, whereas the Raman technique can evaluate the variation of the interfacial shear stress along the fibre/matrix interface. The initial investigations were carried out on the polyethylene fibre/epoxy-resin system [165] followed by aramid fibre/epoxy [166] and carbon-fibre/epoxy systems [167]. The measured distributions of fibre strain along the fibre in pull-out specimens, and interfacial shear stresses for Kevlar 49/epoxy resin is shown in fig.23. as per [164].

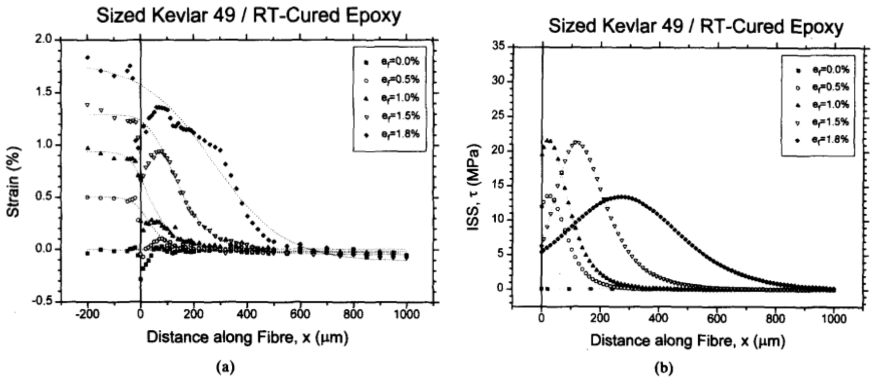

Fig.23. Variation of strain with distance along the fibre measured from the Raman band shifts for a sized Kevlar 49 fibre in a room-temperature cured block of epoxy resin at different fibre strain levels; (b) variation of interracial shear stress with distance along the fibre for the specimen in Fig. 23(a) derived from a relation given in [164].

Interfacial properties of carbon fibre/epoxy composite system by Raman spectroscopy is studied by [167]. The mechanical behaviour of dry samples, samples immersed in demineralised water, and sample immersed in seawater is shown in fig.24.

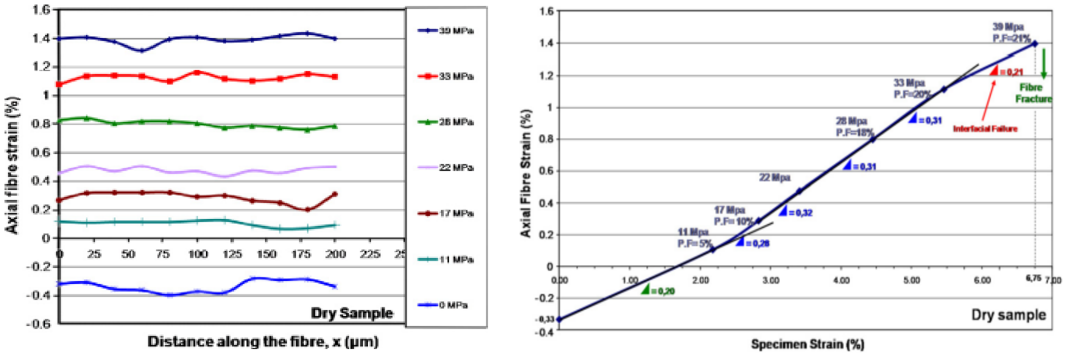

Fig.24 (a) Strain profile of dry sample for different stresses and (b) axial fibre strain versus specimen strain for dry sample [167].

10. Comparisons of environmental conditionings and interface evaluation techniques

10.1 Environmental conditionings

Differential coefficient of thermal expansion between fibre and matrix resin in a composite may lead to residual thermal stresses at the fibre/matrix interface, and is a prime cause of thermal shock. The behavior of the interfacial contact between fibre and matrix is strongly influenced by the presence and nature of residual stresses. It should be emphasised that the freeze-thaw exposure causes matrix microcracking in resin-rich regions which most often leads to local zones of weakness. These local zones of weakness may change the fracture/ failure mechanisms in the loading process. Susceptibility to de-lamination are one of the inherent weaknesses of laminated composite materials.

Thermal fatigue may induce gross matrix cracking because of large misfit strain. The subsequent damage could usually be weaker interface and/or delamination. The failure mechanisms commonly attributed to fatigue are matrix cracking, fibre/matrix debonding and delamination. Differential coefficients of thermal expansion would modify the local stress threshold required for interfacial debonding which may eventually lead to nucleation of delamination. It should also be understood that the transport of moisture in to the body of the composite, which depends on the free volume available in the body of the epoxy matrix also depends on the segmental mobility of the polymer chains. The segmental mobility, on the other hand, is affected by the degree of unsaturation, cross linking and the degree of crystallinity. The glass transition temperature T_g is greatly influenced by the transport of moisture. The net effect of moisture is deterioration of matrix dominated properties such as compressive strength, ILSS, fatigue resistance and impact resistance influencing long-term durability and performance of composite.

The behavior of water diffusion in epoxy networks could be confined into relatively free water, while the other could be attributed to bound water. On the contrary, in the early stage of water ingression, absorbed water molecules forming double hydrogen bonds may cause an increase of glass transition temperature T_g, but after a long period the sorption of water will lead prevalent plasticizing effect and thereby reduced T_g temperature [168]. Prior cryogenic exposure might introduce matrix cracking and/or interfacial debonding which may result in greater percentage of absorbed water in a shorter time. The physical properties of polymer materials depend severely on frequencies of excitation.

At low temperature the polymer matrices become brittle and do not allow relaxation of residual stresses or stress concentrations to take place. 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 crackings and interfacial debondings. Cryogenic conditioning stimulates the formation of rows of cups due to coalesce of transverse microcracks that originate longitudinal cracks along the fibre. 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. Long-term exposure at elevated temperature also enhances cross-linking by post-curing mechanisms. This increases the laminate’s stiffness thereby reducing the fracture toughness.

Thermal conditioning is likely to change the chemistry at the fibre/matrix interface either by forming an interpenetrating network and/or by further possible crosslinking in the epoxy network. Most forms of high-energy radiation are damaging to polymers because of the relatively low energies required to cause chemical damage. Scission often causes a lowering of the polymer viscosity and softening temperature and reduction of mechanical strength, and it may also lead, in some cases, to an increase in the degree of crystallinity. Exposure of thermoset resin composites to ultra-violet radiation can promote additional cross-linking in the surface resin which may result in surface microcracks. Cross-linking, on the other hand, leads to an increase in strength and ductility up to some limiting cross-link density beyond which the strength is again reduced and the polymer embrittled. These are therefore opposing effects which nevertheless occur simultaneously. But the long-term effect of irradiation is almost always serious embrittlement of the polymer. Internal stresses are also developed which, in the presence of an external stress and an aggressive environment, may result in rapid disintegration.

10.2 Interface evaluation techniques

Scanning force microscopy (Also known as AFM) provides high resolution both in width and heightat the surface of a substrate and single polymer moleculess adsorbed on a solid surface may be resolved. The most unique and valuable information not accessible by other methods of nanoindentation techniques- initially seen as ultra low load indentation tests- is the quantitive characterization of material properties and structure manipulation on the nanometer scale. Therefore it should be possible to measure modulus profile around the reinforcement that will prove important information for understanding the micromechanism of composite performance. Hygroscopic and thermal treatments subsequently resulting the swelling of polymer matrix by moisture absorption, and matrix shrinkage by further polymerization at elevated temperature. The sheath-core structure may be captured in both height and phase contrast AFM images. Thus AFM images reveals interfacial susceptibility to environments, implying that degradtion and failures likely initiate at the interface [142]. The surfaces and interfaces of polymer matrices play an important role in the properties and applications of polymeric composites. The advanced characterization techniques are compared with each other with reference to the information that can be gained, and also with reference to applicability to polymer surface and interface analysis.Accurate T_g calculations require stable baselines before and after the transition and the curing exotherm interferes with the upper base line. One alternative to the measurement of T_g, is temperature modulated DSC (TMDSC). TMDSC utilizes a modulated temperature ramp. The basis for the modulation signals and evaluation, including the phase lag, is derived from electrical signal modulation in the electronics and telecommunications field. TMDSC mathematically de-convolutes the response into two types of signals, an in-phase and an out-of-phase response to the modulations, as well as producing an average heat flow. The advantages of TMDSC include improved resolution and sensitivity and the ability to separate overlapping phenomena. Using thermal analysis techniques, average macroscopic properties of the multiphase materials can be determined as a function of time and temperature. Raman spectroscopy has proved to be a very powerful method for the study of composite micromechanics, since it enables the point-to-point determination of stress and strain along the fibre/matrix interface in a variety of systems, Moreover, the stresses and strains in the fibres and interface can be mapped at all levels of strain prior to overall catastrophic failure. The Raman technique enables determination of the variation of the interracial shear stress along the fibre/matrix interface, whereas the micromechanical test methods give single-point values obtained only through failure of the fibre/matrix interface. The problems with the infrared spectroscopic method for microstructure analysis have been identified as (a)accuracy of the value for the extinction coefficients, (b) imprecision at high absorbance values, (c) path length (selecting and reproducing an appropriate one) and (d) accidental degeneracies. Points (a) to (c) are not associated with Raman spectroscopy and this makes the Raman technique advantageous. In addition, this method can be applied to single-fibre test geometries as well as to single fibres in practical composites under both tensile and compressive loading conditions.

11. Comments and a possible outcrop

The interface of composite materials plays an important role to sustain the structural integrity of the system. Thereby, its function is critical and decissive in stress transmissibility under loading. The health of interphase/interface determines the reliability and durability of the composite systems in the service life. It has only been during the last few decades that applications of FRPs have become so rapidly growing that the tailoring the well-bonded and durable interfaces has become a curious concern. Many years of investigation have been concentrated in characterizing the molecular structure of the interface rgion and its relation to mechanical and chemical stabilty. The interface degradtion has been found to be the most detrimental on the properties and performances of FRPs. Most of the environments are having deleterious and deterimental effects on its character and chemistry of the interphase. The microcharacterization techniques are essentially imperative to explore the full potential of the most promisingmaterial of the present century.

The uncontrolled and non-uniform degradations at micro- and macro-levels manisfested in the interphase because of different environmental conditions during service life.These may restrain its uses in the short term and also in the long term reliability of the material. The predicted mechanical behaviour may alter during service life because of changes in the nature of interface. Any changes in the interface might have a substantial implications on its performances.

The precise mode of failure is a function of the status of environmentally conditioned interfaces and time of exposure, thus complicating the prediction of its performances and behavior. The interface is the most highly stressed region of composite materials. The present review highlights the different degree of damages and degradations under different enviromental conditionings. The important roles of interface necessitates a critical and comprehensive understanding of environmentally conditioned interfaces in FRP composite systems.

It is reasonably assumed, the molecular structure here is dynamic in nature at the interfacial area, which is different from the bulk polymer matrix. the changes occuring at the interface are highly sensitive and susceptible to degradations under different environmental conditionings. Since the interphase is a region of chemical inhomogeneity, thus it provide an easy path of the system for becoming more susceptible to thermal, chemical, thermochemical and mechanochemical degradtions. Sometimes migration and or attraction of polar adherents of low molecular weight impurities from the bulk thermoset polymers onto adherents manifests a weak boundary layer of high crosslink density. This microstructural gradient might promote failure intiation or crack propagation through this weak layer of manifested boundary [169].

Interfacial durabilty is a primary factor because environments to which the FRP composite is exposed can degrade interfacial adhesion as well as properties of the materials as a whole.The development of glass, carbon and aramid organic fibres reinforced polymeric composites is the begining of an era of new light weight and durable structural composite materials.

An urgent need exists here to assess and evaluate the chemistry and the character of the region by the advanced resolving techniques, unless otherwise the full potential of FRP may not be realized and explored in service life. The emphasis has to be laid in engineering the interfaces with more accuracy and reliability in exploring technological viability of FRPs. Here an attempt has been initiated to compile and comprehend scattered literature in focusing the impoartance of understanding the interfaces with micro-techniques and adavanced tools. The article has also stressed on interfacial susceptibility to environmental variants and their deleterious effects on interfacial strength and stabilty. The micro changes in the interfacial health may manifest a substantial variation in properties and performanes of FRPs.

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