Assessment and modification strategies for improved interlaminar properties of advanced FRP composites: A review

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Abstract

Demand for high strength and high toughness material with a light weight has always been a matter of concern. The specific properties of FRP composites make it a promising candidate for various structural applications. In the present article we highlight the strategies for obtaining FRP composites with enhanced interlaminar strength and toughness by various techniques. As strength of FRP composites are mostly limited by interlaminar properties, various ways to characterize the interfacial mechanical properties are narrated in the beginning. Further the ways to modify the matrix and reinforcement phases to obtain high strength and toughness are discussed. Effect of interleaving phase on mechanical characteristics is summarized. Various fiber architecture and their influences are also emphasized. Most of the strength characterization is discussed on the basis of flexural strength, interlaminar shear strength or tensile strength while the toughness is characterized through fracture toughness (stress intensity factor or critical strain energy release rate). Overall, this discussion gives a broad overview and technical viable routes to obtain a particular combination of strength and toughness.

Keywords: polymer composites, interlaminar shear strength, fracture toughness, compression after impact, nanofiller, z-pinning, interleaving

1. Introduction

Fibre reinforced composites are prime choice materials in various structural and high performance applications. Their unique properties make them superior than their metallic counterparts. Damage-tolerant design criteria complies the use of FRP composites with greater safety and reliability. The ability of structure for resistance against damage initiation and/or growth under certain mechanical loading is the damage resistance. Similarly the ability of structure for resisting sudden failure in presence of crack or other damages during their service life without any repairmen is known as the damage tolerance. Invisible damage under the upper surface layer of FRP composite can be obtained by low energy impact or low velocity impact. The damages which may result from mechanical loading or environmental variation can acts as precursor for further damages (particularly for moisture ingression) [1]–[3]. Economical overload can be resulted inevitably and hindrance in full potential of FRP composite may occur when damage tolerance is taken into consideration in designs. Novel materials and processing concepts helps in improving impact tolerance: Tougher matrix systems [4] , Planar woven laminates, Unidirectional or non-crimp fabrics (NCF), Mixed-woven fabric laminates, Selective interlayers [5] and hybrids, Three dimensional architecture [6], Stitching, Z-pinning [7], Protective layers. Present review highlights various test used to study the delamination resistance in fibrous polymeric composites. It also emphasizes on the various methodologies used to improve the delamination resistance in laminated composites.

2. Delamination resistance assessment in fibre reinforced polymer composites

Delamination is one of the most life limiting damage mode in laminated composite materials. During processing, handling or in-service conditions it can occur thus hampering the durability and structural integrity. The reliability of laminated composites is harmfully affected by delamination introduction at the time of processing or in-service environment. During processing delamination may exist as voids, discontinuity in the material. External events like Low velocity impact or residual stresses generated from moisture and temperature etc. may result delamination. Superior in-plane properties are exhibited by laminated composites but out of plane stress fields can be developed due to internal discontinuities even though the remote load applied externally is in plane as shown in figure 1.

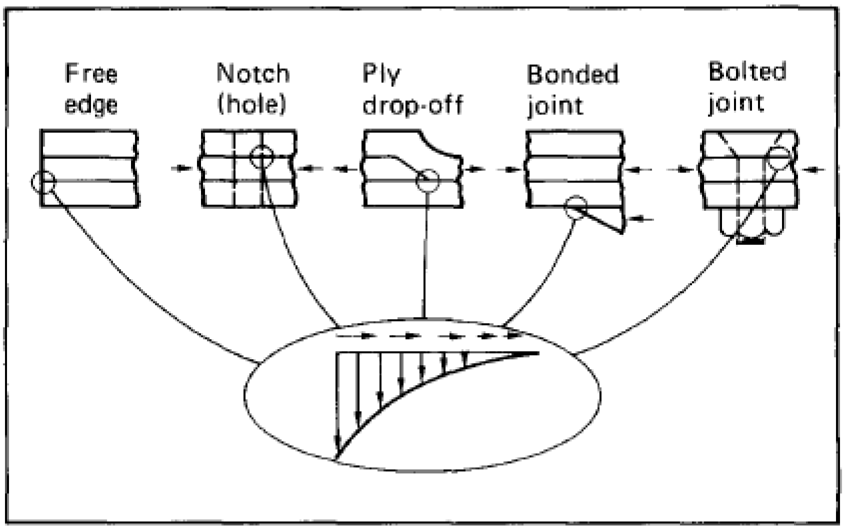


Fig. 1: Sources of out-of-plane stressing from load path discontinuities in structure [8].

2.1 Assessment of fracture toughness in FRP

The intensive stress field ahead of the delamination/crack tip is responsible for its growth. Extension or propagation of this existing delamination may eventually end up with a product with inferior mechanical strength. Delamination resistance is proven to be one of the major life limiting criterion for laminated composite materials, because of which the application of composites was earlier limited to secondary structural parts of aerospace industries where the loading conditions are well established and failure induced from loading is not life threatening [9].

In addition to delamination matrix cracking, debonding at matrix-fiber intrface, fiber fracture, fiber pullout etc. are some of the fracture modes in FRP composites [10]. Again there are several mechanisms which combinedly contribute towards the toughness of FRP composites. There may be a crack deflection which can occur for a tilting or twisting movement around the fiber. A pair of new superficial area is created, which apparently results in high fracture energy as observed in the debonding mechanism. In fiber-bridging mechanism, the unfractured interfacially slipped fibers establish a connection among both crack surfaces [11]. Environmental moisture plays an important role in determining the fracture behaviour of FRP composites during its service period as polymer matrix absorbs moisture. This becomes more important in case of natural fiber reinforced polymer composites [12].

Inherently, structural composite materials are subjected to 3-D loading. Thus the existing delamination will be subjected to various modes of crack propagation, i. crack opening or mode I, ii. forward shear or mode II and iii. anti-plane shear or mode III as shown in figure 2. In practice, delamination is always of mixed mode type as it is arrested between two consecutive plies. Based upon the fundamentals of classical fracture mechanics several tests have been standardized to study the resistance or tolerance power of the material under different fracture modes. The fundamental fracture mechanics concepts remain same for all modes. However, majority of the failure in materials takes place in mode I.

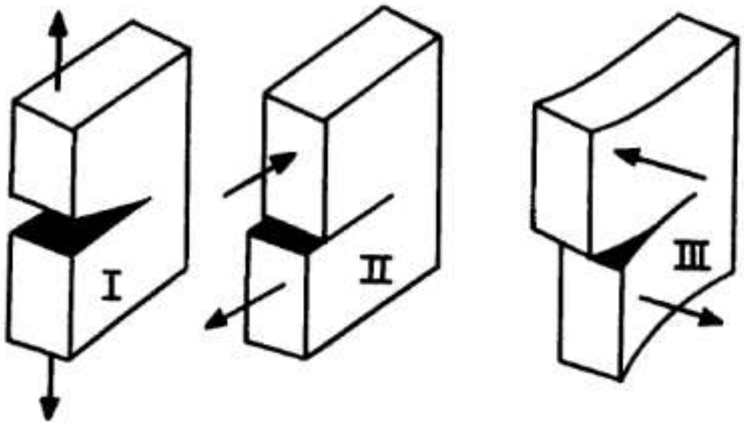
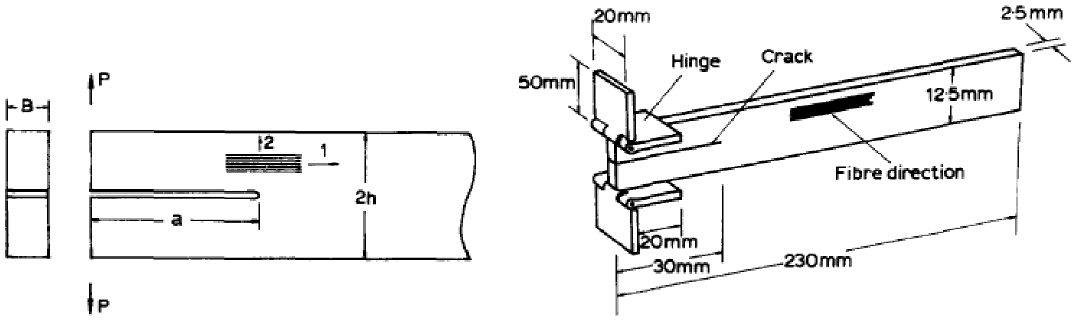


Fig. 2: Modes of interlaminar crack propagation: (a) Mode I opening mode; (b) Mode II sliding shear mode; (c) Mode III tearing mode [13]

2.1.1 Mode I fracture test

This mode of fracture testing has gained substantial attention as this is directly related to the opening up of the crack and the most commonly used experimental technique to carry out this is double cantilever beam (DCB) test, where the DCB specimen is loaded symmetrically under tension with a direction perpendicular to the plane of the crack. A typical DCB sample and testing technique (ASTM 5528 [14]) is shown in figure 3 [15]. A non-adhesive Teflon film is placed in the mid-plane of the laminate during fabrication which acts as delamination.



(a) (b)

Fig. 3: Mode I fracture testing; (a) A schematic of DCB specimen, (b) specimen dimensions and testing method. The hinges are pulled apart from each other during testing [15].

After obtaining the load-displacement curve (as shown in figure 4) the critical strain energy release rate (G_{IC}) which is a direct measure of fracture toughness can directly be evaluated from the strain energy contained in the test specimen or work done by the external loads as written in equation 1 [16].

$$G_{IC} = \frac{P^2}{2B}\frac{\partial C}{\partial a} \quad (1)$$

Where *P* is the critical load applied, *B* is the width of the beam, *C* (= δ/P) is the compliance and *a* is the crack length. The compliance is obtained from the slope of the loading/unloading line of the load-displacement curve.

2.1.2 Mode II fracture test

Interlaminar fracture toughness in the sliding shear mode is termed as mode II fracture, which is commonly determined by End-notched flexure (ENF) test. A three point bend specimen containing an embedded delamination at the mid plane of the laminate (where interplaner shear stress is maximum) is termed as ENF specimen . A typical ENF sample with loading direction is shown in figure 4.

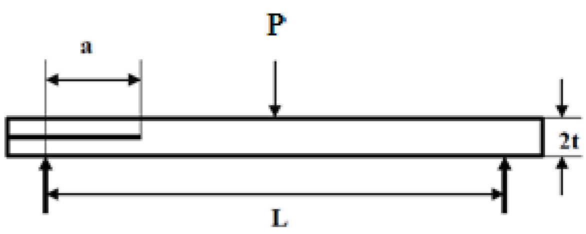


Fig. 4: Mode II fracture toughness testing using an ENF sample [17]

The critical strain energy release rate for mode II fracture (G_{IIC}) can be determined from equation 2 [13].

$$G_{IIC} = \frac{9a^2P\delta}{2B(2L^3+3a^3)} \quad (2)$$

Where *P* is the critical load applied, δ is the displacement, *a* is the crack length, *L* and *B* are the length and width of the beam respectively.

2.1.3 Mode III fracture test

Typically the mode III fracture is obtained by edge crack torsion (ECT) test. The test specimen and loading conditions are shown in figure 5. The Mode III fracture toughness is calculated by Irwin–Kies relation [18] mentioned below.

$$G_{IIIC} = \frac{mP^2}{2C(A-ma)^2} \quad (3)$$

where, C is the compliance $A = \frac{32\mu_{xy,0}h^3 b}{3cd^2}$, $m = \frac{32\mu_{xy,0}h^3}{3cd^2}(1 - \frac{\mu_{xy,1}}{4\mu_{xy,0}})$, $\mu_{xy,0}$ and $\mu_{xy,1}$ represent CLT torsional shear moduli of the uncracked and cracked parts of the specimen, respectively.

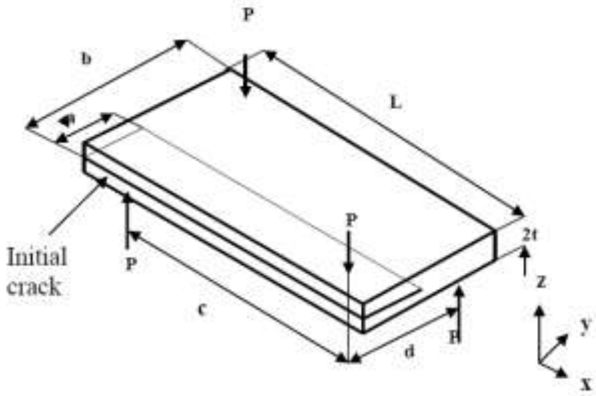


Fig. 5: Mode III fracture toughness testing using Edge crack torsion (ECT) specimen [17].

2.2 Compression after impact

Damages produced in FRP composites during processing, handling or in-service conditions may have a pronounced detrimental effect on their structural integrity and durability. Damages may present in the structure in form of discontinuity during processing or accidental dropping of heavy tools on the FRP composites or stress intensification at several designed holes, notches etc or may be because of low velocity impact during service. Such damages may be invisible or barely visible, but can deteriorate the composite strength significantly, especially in compression. Various aircraft industries carry out tests to determine the compressive strength of the FRP composite after a low velocity impact, termed as compression after impact (CAI) testing which is a measure of damage tolerating capacity of the composite [19] .

After giving a low velocity/energy impact as per ASTM D5628-07 [20], compression test is carried out according to ASTM D7137 M-07 [21] from which CAI strength is determined using equation 4 [22] .

$$P_c = \frac{8\pi^2 E t^3 G_{IIc}}{9(1-\nu^2)} \quad (4)$$

Where E is the elastic modulus, t is the thickness; v is the Poisson ratio of the laminate.

2.3 Interlaminar shear strength assessment of PMC

For the laminate composites the major failure mode is interlaminar shear failure. Interlaminar shear strength (ILSS) characterises the resistance against shear delamination. To measure the ILSS for laminated polymeric composites the following standards are commonly used: American Society for Testing and Materials D2344 [23] for short beam shear test (ASTM International, 2006) and D5379 [24] for V-notched (iosipescu) shear test (ASTM International, 2005).The short-beam specimen is simpler to manufacture and also consumes less amount of material as compared to the V-notched specimen. The specimen geometry and test configuration for a short beam specimen which is subjected to three point bending is shown in figure 6. The low span to thickness ratio (L/t= 4 or 5) reduces the bending stresses in a short beam shear test, hence the dominating parameter is through thickness shear stresses. And interlaminar shear failure is promoted at the neutral plane. The experimental result is interpreted by the Classical (mechanics of materials) beam theory (Timoshenko, 1972), in spite of the fact that in short beam specimen the actual stress state is complex because of low span to thickness ratio and induction of stress concentration at support and loading locations. It is presumed that in the unidirectional SBS specimen axial normal stress is varying linearly throughout the beam thickness and the variation of shear stress in the plane of loading is in parabolic manner and coming to maximum on the neutral plane. The Interlaminar shear strength for rectangular cross-sectioned beam is given below in equation 5 as:

$$ILSS = \frac{0.75\,F}{Bt} \tag{5}$$

where, F=maximum load, B=width of specimen and, t=thickness of specimen

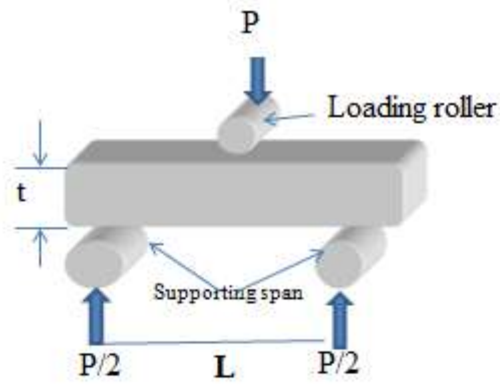


Fig. 6: Schematic of three point bending test

3. High strength and high toughness FRP composites

Damage-tolerant design criteria abide by the use of fibrous polymeric composites with greater safety and reliability. Damage resistance of any structure is defined by its ability to resist damage initiation and/or growth when subjected to specific mechanical loading conditions. Damage tolerance during the service life of the structure can be defined as the ability to resist catastrophic failure in the presence of cracks, or any other damage, without being repaired. Low velocity or low energy impact event can result in invisible damage beneath the upper surface layer of laminated composite. These damages can further stimulate the growth of other damages that may result from mechanical loading or environmental variation (especially moisture ingress) and may significantly result in stiffness loss. Designs which are based on the damage-tolerance consideration sometimes inevitably result in economical overload and limit the full potential of FRP composite. Damage tolerance can be enhanced by through thickness reinforcement, tougher matrix systems, three dimensional architecture, Z-pinning, control of fibre/polymer adhesion, insertion of interlaminar "interleave" layers, optimum laminate design, planar woven laminates, unidirectional or non-crimp fabrics (NCF), mixed-woven fabric laminates, and stitching. Some of the strategies to enhance the interlaminar damage resistance are described below;

3.1 Matrix modification

The in-plane mechanical properties of laminated FRP composites are generally governed by the fiber characteristics while the properties along the direction perpendicular to the fiber plane are dominated by the matrix phase. The most commonly used polymer matrix for structural applications is epoxy resin. Mechanical performance of FRP composites can significantly be improved by modifying the matrix with a tertiary component, of which nano dimensioned materials are of prime importance. Nano modification of matrix draws its importance because of the enormous high interfacial area created, which is responsible for stress transfer. Incorporation of rubber particles into polymer matrix has a beneficial impact on the toughness of the composite material, while at the same time its strength is hampered [4]. Several literatures are available showing the mechanical property enhancement by modification of the matrix with nano-fillers.

The most important nano-filler which has been drawing attention of polymer composite researchers is carbon nano tube (CNT). The unique properties of CNTs which researchers would like to replicate in the composite are its superior strength, ultra high conductivity, low density and exceptionally high aspect ratio and very high interfacial area. Addition of only 0.3% multi walled CNT (MWCNT) significantly improves the flexural strength and glass transition temperature [25] CNTs are incorporated into FRP composites by mixing it with the polymer matrix. Usually CNTs are mixed with epoxy before addition of the hardener. Once proper mixing is achieved hardener in then added to CNT/epoxy mixture and then this is further used for making fiber reinforced composites. The key factors which influence the mechanical performance of CNT/FRP composites are the degree of dispersion of CNTs in epoxy and the bonding between CNT and polymer. The degree of dispersion of CNTs in polymer depends on several factors, like length, extent of entanglement, volume fraction of CNTs and also on the matrix viscosity and tube/tube interaction. Agglomeration is expected to take place with a higher volume fraction of CNTs. Agglomeration of CNTs introduces many defect sites in the composite and limits its mechanical performance [26]. Poor dispersion eventually results in weakening of the composite [27]. Sonication, stirring and calendaring are some methods to obtain good dispersion of CNTs in polymer matrix [28]. The interfacial bonding between CNT and polymer is responsible for the stress transfer efficiency. A nice adhesion is desired for better effectiveness and exploitation of CNTs. Surface functionalization of CNTs is a good solution to achieve a perceptible reinforcement of CNTs in polymer in terms of achieving improved interfacial bonding. Functionalization is an effective way to for strong chemical bond between the CNT and polymer. A relatively low density chemical bonding (<1%) between the CNT and matrix polymer can increase the interfacial shear strength over an order of magnitude [29]. Amine functionalization [30] of CNTs is a well proven technology for nice interfacial adhesion. A CNT functionalization cycle is shown in figure 7.

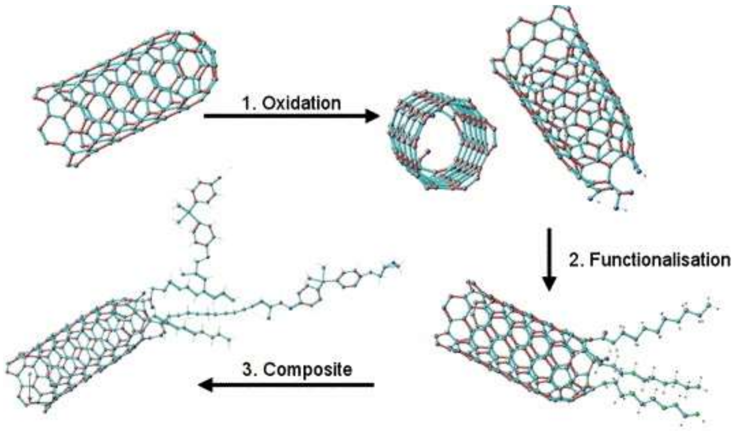


Fig. 7: Schematic of functionalization of CNT; 1. CNTs are oxidized, 2. Functionalization with desired functional group then, 3. Fabrication of composite using functionalized CNTs [31].

Initially the CNTs are oxidized (by dissolving in acid) to develop carboxylic end group (step 1), next the carboxylized CNTs are allowed to react with amines (step 2). Finally the amine functionalized CNTs are used to fabricate the composite (step 3) [28]. Similarly attempts have been made to functionalize CNTs with epoxide [32], silane [33] etc. to check its effect on the final properties of composites. Improvement in degree of dispersion and interfacial bonding is noticed in amine functionalized SWCNT/epoxy composites [34]. Further addition of 0.3% amine functionalized MWCNT in e-glass/epoxy composite is found to increase the flexural strength by around 40% and the glass transition temperature (Tg) has also been increased by around 10 °C [35]. Khare et al. have also shown the increased modulus and Tg because of amine functionalized CNTs in epoxy [36]. Significant enhancement in fracture toughness is also noticed in amine functionalized DWCNT/epoxy composites [37].

3.2 Fiber surface modification

Most of the properties of FRP composites are limited by the interface. Fiber surface modification is one of the methods to control the interfacial properties. Various fiber surface treatment techniques, reaction barrier coatings have been developed to strengthen the interface. Choice of the technique to be adopted is to be decided depending upon the compatibility and durability of the technique with the fiber type (composition and topology), matrix material. Coating is especially more profitable when fibers like glass are exposed to humid atmosphere where there is a thermodynamic tendency of the fiber to pick up water resulting a weak and porous surface. Silane coating on glass fiber surface has been proved to be extremely beneficial for having good interfacial bonding. One end of the silane coupling agent adheres with the fiber and at the other end forms a strong linkage with the polymer matrix. Several interfacial properties like ILSS, K_{IC} are found to be improved using silane coupling agent on glass fiber surface [38]. It has further been observed that a higher interfacial shear stress is transmitted in case of silane coating [39]. Electrochemical alternating anode and cathode treatment [40] of carbon fibers in various electrolytes like H_2SO_4 is proven to increase the surface grooves on carbon fibers which act as physical anchor hold between fiber and matrix resulting superior bonding at the interface.

Uniform dispersion of nanofillers in polymer during fabrication is still remains a challenge. Hence, recently interest on growing of nano fillers on the fiber surface has gained significant attention. Various techniques have been reported on the deposition of MWCNT on glass [41]/carbon[42] fibers. Kepple et al. have reported 50% enhancement in fracture toughness without any significant loss in structural stiffness in MWCNT grown carbon fiber epoxy reinforced composite [43]. Growth of carbon nanomaterial on glass fiber and its subsequent use for making GFRP shows tremendous increase in young's modulus. Carbon nanomaterial on the glass fiber acts as bridging element between glass and polymer [44].

Rubber is usually used in polymers and their composites to improve its fracture toughness behaviour. Several challenges like dispersion, miscibility etc. still persists for preparing rubber/epoxy composite. Another viable technique is to coat the prepreg surface with liquid reactive rubber. Gouda et al. [45] have reported the coating of a single carbon fiber prepreg with epoxy terminated butadiene nitrile rubber by automatic draw down prepreg coating machine which is placed at the mid-plane during prepreg stacking during composite fabrication. This modification resulted improvement in G_{IC} and G_{IIC} values by 140% and 32% respectively.

3.3 Effects of fibre architecture

Damage tolerance of any structure can be evaluated using in-plane tensile, compressive and shear tests [46]. Of these tests, Compression after impact (CAI) is one of the frequently employed tests. The extent of the damage has been described by different groups on the basis of area of the damage zone or width of the damage zone[47]. Delaminations caused by impact loading events propagate ordinarily perpendicular to the loading direction; this has provoked the utilization of damage width as being the key damage parameter [48]. It was shown that 3d weaves can altogether lessen the damage area. By reducing tow waviness in 3D weaves with the help of modified fibre architecture CAI values can be improved [49].

The widespread adoption and acceptability of 2D laminated composites in some critical structures in automobiles and aircraft also been limited by their low through thickness mechanical properties and inferior impact damage resistance when compared against their traditional metallic counterparts such as aluminium alloys and steel. Another important advantage of 3D woven composites is their low-velocity impact damage tolerance [50]–[53] and high ballistic impact damage resistance [54], which is the major problem, associated with 2D laminates in high performance structures. Chou et al. [51] suggested that the impact energy required to initiate damage in 3D woven carbon–bismaleimide composites is about 60% higher than in a 2D carbon–bismaleimide laminate. 3D composites offers high impact damage resistance and simultaneously they do not undergo reduction in their in-plane mechanical properties as compared to their 2D laminate counterparts [52], [55]–[58]. The high damage tolerance of 3D composites is resulted due to the through-thickness binder yarns. These yarns are able to arrest or retard the growth of delamination cracks generated under an impact loading. The binder yarns sometimes also results in increased tensile strain-to-failure values [6]. Their mode I interlaminar fracture toughness values have been reported as 6–20 times higher than the unidirectional carbon fibre reinforced epoxy laminates[59]. Despite of having these superior properties and potential benefits the 3D woven composites have failed to find many commercial applications. They have been tested or used in only a few specialised structures by the building, marine and aircraft industries, where the cost and/or performance of metals and traditional laminates have been unacceptable.

Issues impeding the full potential use of 3D woven composites:

- Expensive and difficult manufacturing process for quasi-isotropic 3D woven composites
- 3D woven laminates generally possess lower tension, compression, shear and torsion properties
- In-plane mechanical properties and failure mechanisms of 3D woven composites are not well understood
- Long term durability of 3D woven composites is not well explored

- Poor understanding of the architectural structure such as influence of weaving parameters on the preform architecture and composite properties

3.4 Z-pinning

There are some well explored strategies to enhance the delamination resistance and impact damage tolerance for textile laminates made using a dry fabric preform that contains the through-thickness reinforcement prior to resin infusion. These methods includes but are not limited to 3D weaving, braiding, and stitching [7], [60], [61]. More specialist techniques include tufting, embroidery, and zanchoring [60], [62], [63]. However, none of these techniques are suitable for the through-thickness reinforcement of prepreg laminates. Z-pinning is the only technique which is capable of reinforcing prepreg laminates in the through-thickness direction. z-Pins act as fine nails that lock the laminate plies together by a combination of friction and adhesion (Fig. 8). Initially in 1970s, thin metal rods were used to reinforce the laminates by using a labour-intensive manual process which is not practical for commercial production [64]. Tomashevkii et al. [65] developed an automated process for inserting thin wire fibres through laminates.

Aztex Inc. (Waltham,USA) developed a method named UAZ (Ultrasonically Assisted Z Fibre), for the rapid insertion of sufficiently large number of thin metal or fibrous pins [66]. UAZ is now the most widely used process for the z-pinning of laminates in large scale production [67], [68]. z-Pins are made using high strength and stiffness material such as steel, titanium alloy or fibrous carbon composite with a diameter of 0.2–1.0 mm. Z-pinning is very potential method of enhancing delamination resistance, joint strength, through-thickness properties and damage tolerance of prepreg laminates. The addition of very low volume fraction of z-pins can significantly enhance the properties. Depending on the impact energy level and laminate thickness, Zhang et al. [69] found that z-pinning reduced the impact damage area by 19–64%. Childress and Freitas[70] reported reductions of 30–50% in the amount of damage sustained under hailstone impacts. The reduction in damage is attributed to the bridging traction forces which are generated by the z-pins. However, Z-pinning is effective when the impact events are large enough to generate large damage zones. Z-pinning is also failed to increase the threshold impact energy to initiate damage and suppress very short delaminations under impact loading [71], [72]. But it is very interesting to note that the addition of z-pinning often results in higher post-impact properties[69], [73]–[75].

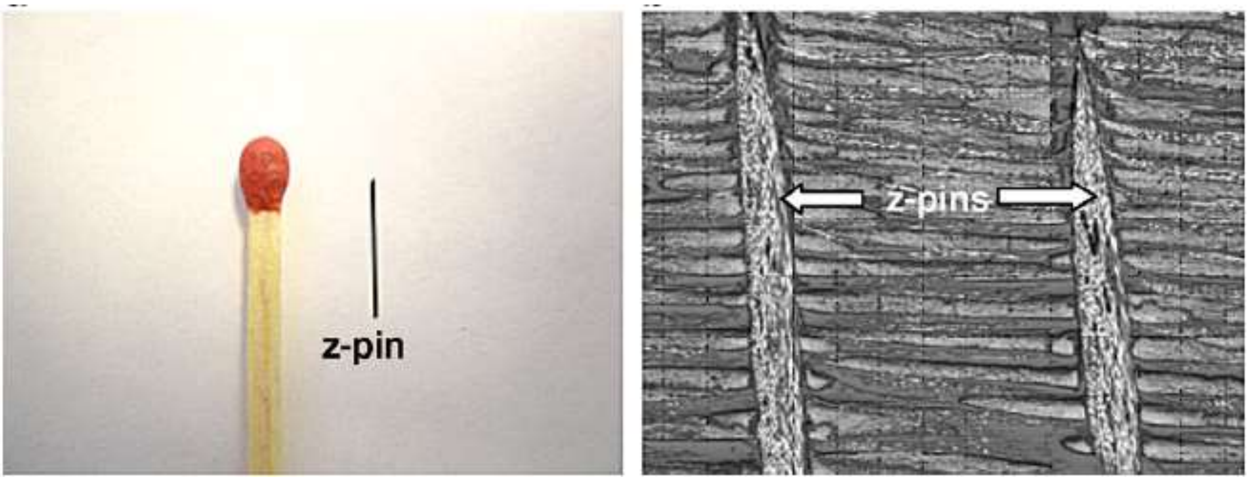


Fig. 8: (a) Photograph showing the size of a typical z-pin and (b) z-pins inside a prepreg composite [76].

3.5 Interleaving

Interleaving or adding a tough adhesive interlayer between laminate plies is one of the most promising method by which delamination resistance may be enhanced significantly without sacrificing the hot/wet performance of the composite material [77]–[79]. The restriction in crack front-yield zone due to the formation of narrow resin rich region between rigid elastic plies limits the translation of improved matrix toughness into improved composite toughness [77], [79]. About 25-fold increase of matrix toughness can only translates about four to eight times of toughness of composite [78], [80]. Interleaving allows more expansion of crack-tip yield zone between the composite plies [77], [79], [81]. However the problem associated with this technique is the weight penalty to structure because a tough layer of resin is introduced. Shear-yielding of the material around the crack tip can be attributed as the main mechanism responsible for toughness enhancement. Greater fracture energy due to the insertion of interleaving is resulted due to the formation larger height of the crack-tip yield zone.

A significant effect of interleaf thickness on fracture toughness was noticed. Initially a steep increase in fracture toughness was noticed with increase in interleaf thickness and followed by a saturation value after certain thickness [82]. The extent of interaction between the crack-tip yield zone and the rigid-composite plies decreases gradually with the increase in interleaf thickness; which is responsible for the transition from rising portion to a plateau. The thermoplastic-film material is supposed to be more effective than the thermoset film material in enhancing the fracture toughness because of a suitable combination of high strain to failure and high yield strength. The Optical micrographs of transverse sections for base laminates and epoxy-interleaved laminates, and method for measurement of resin-rich layer thickness is shown in figure 9. For modes I and II loadings, the effect of self-same epoxy interleaf is completely different. The mode II interlaminar properties can also be enhanced by self-matrix interleaf with conventional brittle epoxy which would be comparable to those of advanced systems with thermoplastic matrix or toughened interlayer.

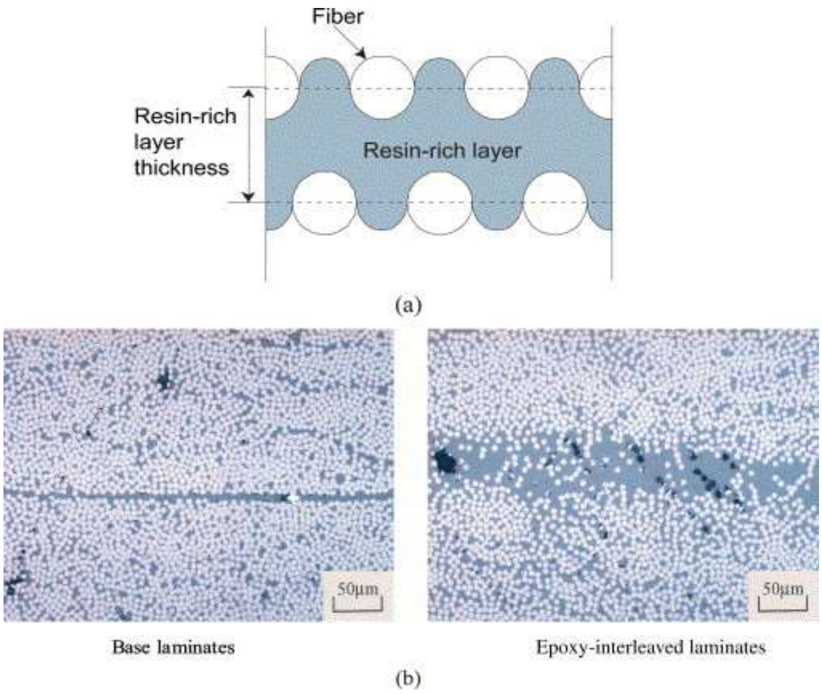


Fig. 9: Optical micrographs of transverse sections for base laminates and epoxy-interleaved laminates, and method for measurement of resin-rich layer thickness. (a) Method for measurement of resin-rich layer thickness. (b) Optical micrographs [5].

4 Concluding remarks

Poor interlaminar properties restrict the potential exploitation of FRP composites in various high performance applications. Exact characterization of these properties still remains a challenge, as it is directly influenced by the test conditions, precision of testing equipment, specimen geometry, manufacturing and handling defects. A design engineer must select an appropriate test methodology and laboratory testing conditions which simulate the equivalent in service loading and environmental conditionings. Further, there are some strategies which have been successfully applied to enhance the interlaminar properties of laminated composites. Mechanical performance of FRP composites in Z-direction can significantly be improved by modifying the matrix with a tertiary component, of which nano dimensioned materials are of prime importance.

The advantage of 3D woven composites is their high ballistic impact damage resistance and low-velocity impact damage tolerance, which have been a major problem with the use of 2D laminates in military aircraft structures. The only technique capable of reinforcing prepreg laminates in the through-thickness direction in large commercial quantities is z-pinning. Interleaving or adding a tough adhesive interlayer between plies is a method by which the delamination resistance of laminate may be enhanced many fold without sacrificing the hot/wet performance of composite

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