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REVIEWS

Fracture and Fatigue Behavior of Polymer Nanocomposites—A Review

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Abstract | Fiber reinforced polymer (FRP) composites are widely used in structural applications, mainly due to their high specific strength and stiffness. These composites experience several types of static and fatigue loads in service. For a safe and durable structure, high fracture toughness and enhanced fatigue life are prominent requirements of these composite materials. Efforts have been made in recent times to improve the fracture toughness and fatigue properties of FRP composites by incorporation of second phase fillers in the epoxy matrix. Addition of nano sized fillers to the epoxy has led to the development of a new class of materials—polymer nanocomposites. The presence of nano fillers has been shown to improve the fracture toughness and fatigue life of bulk epoxies as well as FRPs with nano-modified epoxy matrix. The type of nano filler, its shape, size, volume fraction and dispersion in the epoxy have all been shown to influence these properties significantly. In this review, an overview on the effect of nano fillers on the fracture toughness and fatigue life of bulk epoxies and FRPs is presented. The mechanisms proposed for observed improvements in these properties and the empirical method of prediction of fatigue life of nanocomposites subjected to spectrum fatigue loads simulating service loads are also discussed.

Keywords: *fracture toughness, fatigue, nanocomposite, toughening mechanisms*

1 Introduction

Fibre reinforced plastic (FRP) **composite** materials are widely used in structural applications such as airframe, wind turbine, ship hull etc., due to their high **specific strength** and specific stiffness. They are fast replacing conventional aluminium alloys in airframe applications. Any candidate material for structural application should possess good mechanical properties in addition to other requirements such as creep and corrosion resistance depending on the specific applications. The engineering structural FRPs generally consist of continuous carbon or glass fibres reinforcement in a thermosetting epoxy polymeric material. The overall mechanical properties of FRP composite, thus, depend on the properties of its constituent materials, i.e., fiber and matrix and the interfacial bonding characters between them. The epoxy polymer, being an amorphous and highly cross-linked material, is relatively brittle and possess low strength as compared to fibers. Also, it exhibits relatively poor resistance to crack initiation and growth. Properties of the epoxy material, thus, affect the overall matrix dominated mechanical properties of FRP composites.

The demand for advanced materials with improved mechanical properties for structural applications has recently led to the development of FRPs containing second phase nanofillers in the epoxy matrix. These polymer **nanocomposites** have been shown to exhibit improved mechanical, thermal, electrical and optical properties[1–7] depending on the type, size and volume fraction of nano filler used. Nanocomposites have been introduced in various applications such as airframes, automobiles, gas barrier films, surface coatings, flame-retardant cables, etc.

Composite: A substance comprising two or more materials, insoluble in one another, combined to form a useful engineering material possessing certain properties not possessed by the constituents.

Specific strength: It is the ratio of strength to density. Structural material possesses high specific strength so that it is lighter as well as stronger.

Nanocomposite: Composite in which at least one of the dimensions of filler material is of the order of nanometers.

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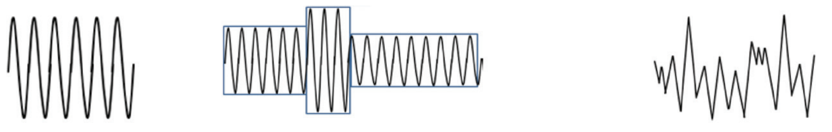
Considerable improvements in several mechanical properties of polymer composites such as tensile, compressive, shear, flexure, fracture toughness, fatigue etc. have been obtained by the addition of nano fillers. The effects of nanofillers on the fracture toughness and fatigue properties of composites will be dealt with more in detail later. Incorporation of various types of hard ceramic nano particles such as SiO_2, SiC, Al_2O_3 and TiO_2 have been shown to improve the strength and stiffness of polymer composites.[8–15] The presence of low amounts of single walled carbon nano tubes (SWCNT) and multi walled carbon nano tubes (MWCNT) has been observed to enhance the matrix-dominated interlaminar shear strength, tensile strength and modulus of composites.[3,4,16–18] Many studies have demonstrated that a significant increase in the interfacial shear strength could be obtained by the addition of CNTs.[19,20] Carbon nanofibers (CNF) with high aspect ratio as a filler in polymer has been observed to improve several mechanical properties. For e.g., the incorporation of 2 wt. % of CNF in a carbon fiber composite (CFC) increases the tensile and flexural strengths.[21] Iwahori et al.[22] reported an improvement on compressive strength of composite laminates by CNF. Joshi et al.[23] showed that CNF alter the interface behavior of the carbon fiber and the phenolic matrix, leading to an increment in mechanical properties.

Modification of epoxies with layered fillers such as clay, graphite nanoplatelet (GNP) and fullerene have all been observed to enhance the mechanical properties of epoxies and FRPs.[24–28] Use of nanoclay in polymers has been reported to improve both the modulus and yield strength.[24,29–32] Kornmann et al.[33] found that layered silicates improved the interfacial bonding between the matrix and glass fibers, and consequently the flexural strength of the composite. Similar results were obtained using modified montmorillonites in carbon fiber and glass fiber based composites.[34,35] Zhou et al.[36] showed that by adding nanoclays into the phenolic matrix, the flexural properties of composites could be enhanced. GNP based nanocomposites[25,26] have been shown to exhibit improved modulus, compressive strength and in-plane shear properties.

Structural composite components experience various types of static and fatigue loads in service. Fatigue loads may broadly be classified into three categories as shown in Figure 1. The various parameters associated with fatigue are shown in Figure 2. Based on the stress ratio (See Figure 2(b)), the fatigue loads can also be classified as Tension-Tension (T-T) ($0 \le R \le 1$), Tension-Compression (T-C) ($-\infty < R < 0$) and Compression-Compression (C-C) ($1 < R < \infty$) type fatigue. Due to accidental and/or prolonged exposure to fatigue loads, several types of internal damages such as matrix cracks, disbonds and delamination develop in the composites.[37–40] In the presence of such damages, the static load carrying capability of the material reduces. Further, these damages may also grow sub-critically under cyclic fatigue loads. Both



(a) Constant amplitude

(b) Block loads

(c) Spectrum/Random/Variable amplitude

Figure 1: A schematic of general classification of cyclic fatigue loads.

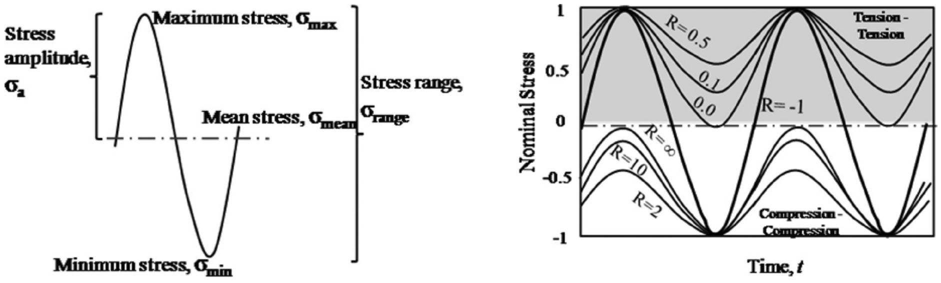


Figure 2: A schematic of variables in fatigue of materials.

these conditions may finally lead to premature and catastrophic failure of structures.

The maximum load bearing capability of a component, in presence of damage(s), is determined by its **fracture toughness**, whereas, the durability of the structural component is determined by its **fatigue** life. Thus, both of these properties are linked in some form in determining the safety and durability of the structure. Hence, it is necessary that composite material possess high fracture toughness and enhanced fatigue life. Recent research work on polymer nanocomposites has shown that they are highly promising structural materials, and exhibit enormously improved fracture and fatigue properties. This paper reviews these recent developments.

2 Fabrication of Nanocomposites

Various types of nanofillers have been used to fabricate polymer nanocomposites. These can be broadly classified based on their shapes or dimensions as (i) Particulate or 0-D fillers, (ii) Fibrous or 1-D fillers, and (iii) Layered or 2-D fillers. Commonly used hard spherical ceramic nanoparticles are silica (SiO_2), alumina (Al_2O_3), ZrO_2, SiC, $Si_3 N_4$, TiO_2, ZnO. Particle size in the range of 10 to 100 nm diameter, and loading up to 20 wt.% is generally dispersed in the epoxy resin. Fibrous fillers such as SWCNT, MWCNT and CNF have been extensively used to produce composites with improved mechanical properties. Layered fillers used include Montmorillonite clays[41] with sheet-structure, graphene, graphite nano platelets (GNP), fullerene etc.

There are several widely used methods for fabrication of FRP composites viz., wet lay-up, pultrusion, resin transfer molding (RTM), resin film infusion (RFI) etc. Details on these processes may be found elsewhere.[42] However, not all these methods are conducive at present for fabrication of nanocomposites. In general, nanocomposites are produced by resin transfer moulding techniques, because of ease of mixing required quantity of nano fillers in the epoxy resin in liquid state.[1,7] Initially, the required amount of nano filler is dispersed in the resin to produce epoxy nanocomposite. Further, such nano modified epoxy resins are infused into a fiber/cloth lay-up set-up under vacuum to produce FRP composites.

There are still many difficulties experienced in production of nanocomposites. Of these the two major difficulties are (i) non-uniform dispersion of nano filler in the epoxy resin, and (ii) high viscosity of the nano modified resin. In thermosetting FRP nanocomposites, the dispersion of nano fillers in the epoxy is carried out in the liquid resin before infusion to form FRP. It is required to obtain a high level of uniform dispersion at this stage to avoid agglomeration in the final FRP.[43–45] Several mechanical and chemical methods are used to accomplish dispersion of nano fillers in resins.[46–51] Nanoclays are dispersed by in situ intercalative polymerization technique.[52–54]

Thermosetting liquid resins containing nanofillers are commonly more viscous than their neat counterparts. The high viscosity may create difficulties in the processing that can lead to a poor quality FRP laminates. Non-uniform dispersion of fillers in the laminate, agglomeration, and a poor impregnation of the fibers are some of the most common problems due to high viscosity.[55] The increase in viscosity depends on many factors such as filler morphology, filler nature, compatibility of filler with the matrix and weight or volume percent. It is necessary, therefore, to optimise the nano filler loading for a given epoxy resin before it is further processed to manufacture FRP.

3 Mechanical Testing

3.1 *Fracture toughness testing*

There are no exclusive test standards to determine fracture toughness and fatigue performance of polymer nanocomposites. The standard test methods and procedures employed for testing of plastics and FRP composites are also used for nanocomposites. The fracture toughness testing and evaluation of nanocomposite is determined at both bulk epoxy level and at FRP level.

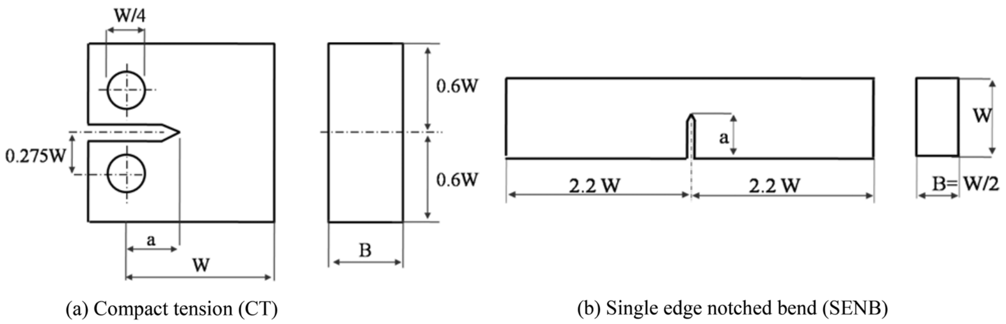
3.1.1 Bulk epoxy nanocomposite: The fracture toughness of bulk epoxy nanocomposite is determined generally by using the compact tension (CT) or single edge notched bend (SENB) specimen under three point or four point bending arrangement (Figure 3).[56] The notched test specimen is pre-cracked by tapping with blade to produce a sharp crack. Further, the specimen is subjected to monotonically increasing load until failure. The load-displacement data obtained is then used to estimate the fracture toughness of the material.

3.1.2 FRP nanocomposite: The delamination in FRP composite may be subjected to three different modes of failure as shown in Figure 4. Although, the mixed mode conditions generally prevail in service, the studies are made on pure mode failures, and then a failure criterion is employed to predict the mixed mode failures.

The typical specimens used for determination of fracture toughness under various modes are shown in Figure 5. The details of the specimen

Fracture toughness: Energy required to fracture a material in the presence of a defect. It is a property of the material. A generic term for measure of resistance to extension of a crack/delamination.

Fatigue: The process of progressive localized permanent structural change occurring in a material subjected to conditions that produce fluctuating stresses and strains at some point or points and that may culminate in cracks or complete fracture after a sufficient number of fluctuations.



(a) Compact tension (CT)

(b) Single edge notched bend (SENB)

Figure 3: Schematic of standard test specimens used for fracture toughness evaluation of bulk epoxy nanocomposite.

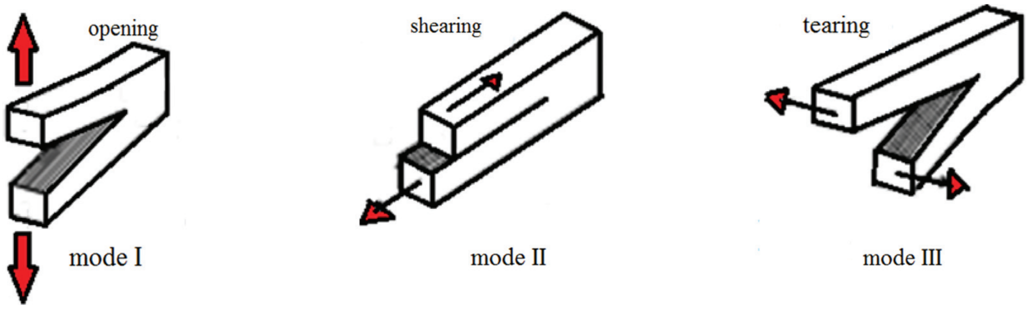


Figure 4: Modes of failure.

size, testing procedures and analysis of results to determine fracture toughness can be found in their respective ASTM test standards.[57–59] In all these specimens, the delamination is simulated by the insertion of a non-adherent thin film such as teflon tape during fabrication of specimens. An insert film thickness of 13 microns or lower is generally preferred. Test procedure involves the application of monotonically increasing load until failure to obtain the load displacement data, which is then analysed to estimate fracture toughness.

3.2 *Fatigue testing*

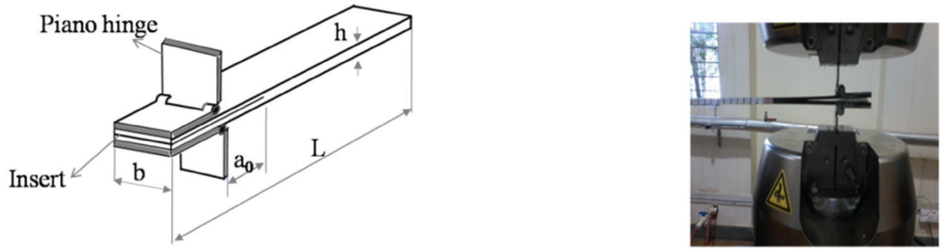
3.2.1 Bulk epoxy nanocomposites: Fatigue tests on bulk epoxy nanocomposites are carried out using dog-bone type test specimen.[60] These specimens are generally cut and prepared from the bulk epoxy nanocompsites fabricated after dispersion of nano filler in the liquid resin and cured. The surface preparations of specimens play a major role in fatigue life and hence careful and consistent surface finish is required to be maintained in these tests. The specimens are subjected to cyclic fatigue loads (Figure 1), and the number of cycles or blocks required for failure is determined.

3.2.2 FRP nanocomposite: The tensile fatigue (T-T) tests on FRP composites is carried out[61] using constant rectangular cross-sectioned specimens with end tabs (Figure 6). The edges are polished to remove any flaws to avoid delamination starting from such flaws. No standards for fatigue testing under T-C and C-C loading conditions are available, at present. However, the modified version of static compression test specimen geometry with tabs[62] is generally employed in fatigue tests containing compressive loads. A gage length of 10–15 mm is used as trade-off between a length short enough to avoid Euler buckling and long enough to introduce uniform compressive load in the gage section area.

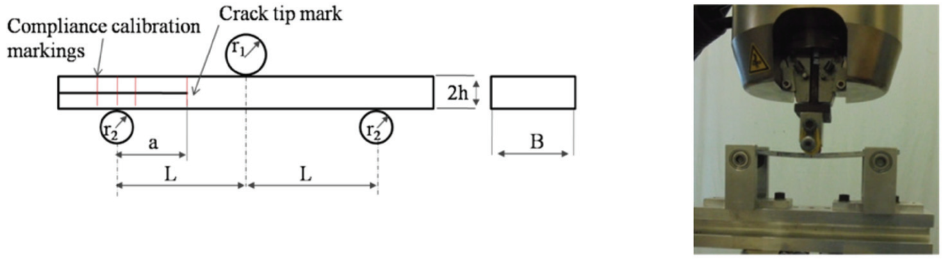
3.3 *Fatigue crack/delamination growth rate testing*

The studies on the progressive fatigue damage accumulation in the composites suggest that crack/delamination growth behaviour in epoxy/FRP is one of the determining factors in the total fatigue life of composites. The incorporation of nano fillers alters the crack/delamination growth rates. Thus, the damage tolerance capability of a material is altered with the addition of nano fillers. In order to study these effects, the crack/delamination growth behaviour of nanocomposites is investigated.

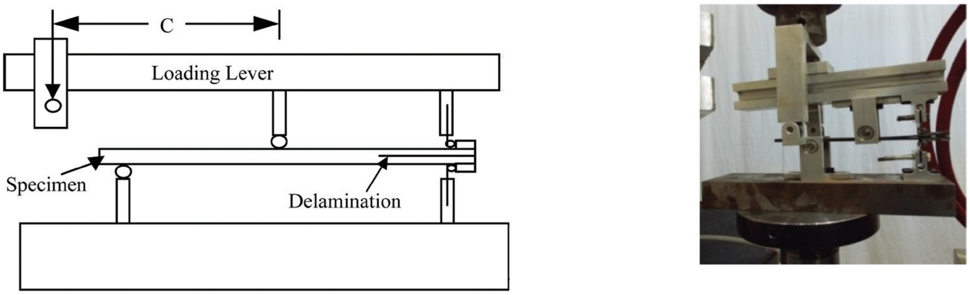
The fatigue crack growth rate in bulk epoxy nanocomposites is determined following ASTM



(a) Double cantilever beam (DCB) specimen for Mode I delamination toughness

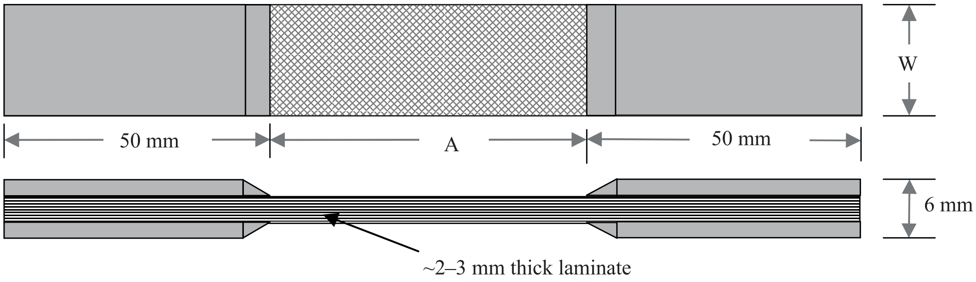


(b) End notch flexural (ENF) specimen for mode II delamination toughness



(c) Mixed mode fracture toughness

Figure 5: Fracture toughness specimens and photographs of the test set-up.



(a) For spectrum fatigue; A = 15–25 mm, W = 12.5 mm
(b) For constant amplitude Tension-Tension (T-T) fatigue : A = 100–150 mm, W = 25 mm
(c) For constant amplitude Tension-Compression (T-C) and Compression-Compression (C-C) fatigue;
A = 10–15 mm, W = 12.5 mm

Figure 6: A schematic diagram showing the dimensions of the fatigue test specimens.

test standard specifications.[63] Similar to fracture mechanics test specimens (Figure 3), either CT or SENB specimens are used. Compliance and/or optical methods are used to monitor crack length during fatigue test. Initially, the specimen is pre-cracked under fatigue loads to produce a sharp crack ahead of notch. Then, the decreasing ΔK test is conducted to obtain growth rates in the Paris and near-threshold regime. Further, the constant amplitude loads are applied to obtain the a-N data, which then is analysed to obtain growth rates in Paris and high ΔK regimes. The delamination growth behaviour in FRPs is studies using specimens containing artificial delamination as shown in Section 3.1.2.

4 Fracture Toughness of Nanocomposites

Lamina: A subunit of a laminate consisting of one or more adjacent plies of the same material with identical orientation.

Laminate: Any fiber- or fabric-reinforced composite consisting of laminae (plies) with one or more orientations with respect to some reference direction.

Delamination: Separation of plies in a laminate. This may be local or may cover a large area in the laminate.

Engineering FRP composite is a laminated material where several different **lamina** are stacked one over the other with each layer being oriented in required direction to produce a thick **laminate**. **Delamination**, is a typical damage observed in these composites. The presence of delamination damage reduces load carrying capability of the material/component. However, by improving the toughness of the material, the load carrying ability in presence of such defect could be raised. Efforts have been made in the recent past to improve the fracture toughness of the epoxy as well as that of FRP by introducing nano fillers into the resin. Fracture toughness of nanocomposite has been evaluated both at bulk epoxy and FRP level to study the improvements obtained and the possible mechanisms for such observed phenomenon.

4.1 *Bulk epoxy nanocomposite*

Traditionally, rubber micro particles have been used to toughen thermosetting epoxies.[64] While soft rubber particles improve the toughness of epoxies, they also result in reducing the strength and stiffness of the composite. Further, the micron sized particles result in only moderate improvements in toughness.[2] Additional drawbacks of using rubber particles include reduction in glass transistion temperature and increase in the viscosity of resin. However, with advent of use of nano particles, various types of hard nano fillers are employed to dramatically enhance the toughness of polymers with or without additional benefit of increasing the strength and stiffness.[12]

Kinloch et al.[65–69] have extensively studied fracture toughness of silica nano particle modified epoxies. Hard spherical nanosilica particles of about 20 nm size dispersed uniformly in thermosetting epoxy resins has been shown to enhance the toughness by about 2 to 4 times. The increase in toughness was observed to increase with loading of nanofiller up to about 20 wt.%.

To take advantages of both soft rubber micro particles and hard silica nano particles, many investgators have used both these particles to modify epoxies and produce a hybrid composite with enormously improved toughness.[66,70,71] However, these hybrid particulate nanocomposites do not display any synergistic effect on toughness. Liang et al.[71] observed that adding small amount of nano silica particles into rubber toughened epoxy further improved the fracture toughness to a level that could not be achieved by increasing rubber content alone. They also observed that nanosilica particles clustered at high rubber content to result in reducing the toughening effect.

Adachi et al.[72] added silica particles of diameters ranging from 1.56 μm to 240 nm, and volume fractions up to 35% to an epoxy resin. They observed that toughness increase was linear with respect to reciprocal of the product of the square root of the mean distance between the particle surfaces. However, some studies have shown that while toughness increased steadily with concentration of silica nanoparticles, the particle size does not appear to have any significant effect.[71,73–75] For e.g., Dittanet et al.[74] used silica nanoparticles of size 23 nm, 74 nm, and 170 nm, and observed that the fracture toughness and fracture energy improved significantly with the addition of silica nanoparticles, but the effect of particle size on fracture toughness was negligible. The role of nano vs. micro filler particle size-scale on fracture behavior of silica-filled epoxy was examined by Jajam et al.[76] who observed the fracture toughness enhancement in case of nano filled relative to micro-particle filled epoxy.

Other types of ceramic nano particles also have been shown to improve toughness of epoxies. Wetzel et al.[12] carried out a comprehensive study on nanocomposites containing varying amounts of either TiO_2 or Al_2O_3, and found that the toughness is enhanced by these particles. Interestingly, Zhao et al.[11] used nanoscale alumina filled epoxy and reported no significant improvement in fracture toughness or fracture energy. Chisolm et al.[10] investigated matrix properties by introducing micro and nanosized SiC fillers, and showed that by adding 1.5 wt.% into an epoxy, about 20–30% increase in mechanical properties could be obtained.

Many studies have been made to investigate the effect of fibrous fillers on improving toughness of epoxies. Addition of low amounts of CNTs have been reported to enhance the toughness by up to 50%.[16,17] Yu et al.[77] observed that addition of 1wt.% and 3 wt.% of MWCNTs to an epoxy increases the toughness by 29% and 62% respectively. Chandrasekaran et al.[78] studied the effect of addition of different types of carbon nano-fillers on fracture toughness of epoxy nanocomposites. They used thermally reduced graphene oxide (TRGO), GNP and MWCNT, and showed that toughening effect of TRGO was most significant, resulting in 40% increase in toughness by addition of 0.5 wt% of filler. The enhancements in toughness were 25% for GNP and 8% for MWCNT. Bortz et al.[79] added 0.5% and 1 wt.% of a helical-ribbon CNF to an epoxy, and observed that toughness increased by 66% and 78%, respectively.

Fracture toughness enhancement by dispersion of layered fillers in epoxy has been reported by many investigators.[8,80–82] Zerda et al.[83] showed that the fracture behaviour was improved in the intercalated system with respect to the exfoliated configuration. They observed that the toughening mechanism was due to the spacing of regions of the intercalated filler that allowed the creation of additional surface areas for crack propagation. Interestingly, it has also been observed that silicates may be detrimental to toughness of epoxy due to the formation of microvoids originated by the debonding of clay platelets which coalesce and form larger cracks causing embrittlement.[84] Rafiee et al.[26] characterized the mechanical properties of fullerene/epoxy nanocomposites containing 0.1 to 1.0 wt.% fullerene. The fracture toughness of the epoxy polymer was significantly enhanced. They showed that the other types of nanoparticle fillers such as silica, alumina, and titania nanoparticles require up to an order of magnitude higher weight fraction to achieve comparable enhancement in properties.

More recently, the hybrid modified epoxy composites wherein two or more different type or sized fillers are added, have been developed to further improve toughness of composites. Nano and micro sized silica particles,[72] nano silica and nano rubber,[85] nano silica and micron rubber,[66,70,71] nano silica and MWCNT,[86] CNT and GNP[87] combinations have been employed to dramatically improve fracture toughness.

Several different mechanisms have been proposed by various authors for the observed improvements in toughness of epoxies by nano fillers. Many studies have identified that there are two toughening mechanisms operative in the silica nano particle modified epoxies[66,74,88] i.e., (i) localised shear bands initiated by the stress concentrations around the periphery of the silica nanoparticles, and (ii) debonding of the silica nanoparticles, followed by subsequent plastic void growth of the epoxy polymer. Dittanet et al.[74] showed that shear banding mechanism is the dominant while the particle debonding and plastic void growth are minor mechanisms. Rosso et al.[89] observed that the nanoparticles caused a high deflection of the crack growth, whereas Zhang et al.[90] observed that the nanoparticle induced dimples are likely to cause energy dissipation. Ma et al.[8] proposed the initiation and development of a thin dilatation zone and nano-voids as the dominant toughening mechanisms in epoxy nanocomposites. Wetzel et al.,[12] in TiO_2or Al_2O_3 nano particle reinforced epoxy, found that the toughness is enhanced by various mechanisms such as crack deflection, plastic deformation, and crack pinning.

In fibrous type nano particle filled epoxies such as CNTs and CNF, the toughness improvement is attributed to extra energy spent in nano-tube or CNF pull-out during fracture.[91] Also, the nano tubes have been observed to suppress the propagation of crack by bridging mechanisms, thereby leading to increase the toughness of epoxy.[17] In layered nano filler/epoxy composites, crack deflection, formation of nanovoids and promotion of shear yielding of matrix has been explained as dominant mechanism for enhanced toughness.[92]

Analytical and finite element modeling efforts have been made to verify experimental observations on improvements in toughness of epoxies by nano fillers.[93] Wagner et al.[94] quantified nanocomposite toughness through an analysis of nanotubes using energy dissipation model for pull-out. Salviato et al.[95] used a multiscale model to assess the toughness improvements by the formation of localised plastic shear bands that is initiated by the stress concentrations around nanoparticles. They have shown that the elastic properties of the interphase affect the stress field rising around particles and the energy dissipation at the nanoscale. Zamanian et al.[75] also quantitatively modelled the toughening mechanisms and observed an excellent agreement with experimental results. Quaresimin et al.[96] used a multi-scale modelling strategy to assess the fracture toughness of particle reinforced nanocomposite. The model includes damaging mechanisms such as nanoparticle debonding, plastic yielding of nanovoids and plastic shear banding of the polymer. Further, their analytical framework considers the influence of an interphase around nanoparticles, and show good agreement with experimental results.

4.2 *FRP nanocomposite*

The delamination fracture toguhness of FRP composites with nano modified epoxy matrix has been studied by several researchers. In general, the delamination toughness of FRP is higher than that of corresponding bulk epoxy. Kinloch et al. observed considerable improvements in both Mode I and Mode II fracture toughness of a glass fiber/epoxy composite by introducing silica nano particles in the epoxy matrix.[66,68,97] They also showed that hybrid epoxy matrix of GFRP containing both silica nano particles and rubber micro particles exhibit further enhhanced toughness. Similarly, carbon fiber/epoxy with silica nano particle modified epoxy matrix also exhibits improved toughness.[98] Tsai et al.[99] investigated the interlaminar fracture toughness of GFRP composite consisting of the silica nanoparticles and two types of rubber particles in the epoxy matrix. They observed that inclusion of silica nanoparticles together with the core shell rubber particle can appreciably increase the fracture toughness of the GFRP up to 82%, whereas the GFRP with the epoxy matrix modified by CTBN rubber particles and silica nanoparticles improve toughness by about 48%. Zeng et al.[100] investigated the Mode I interlaminar fracture toughness of CFC laminates, and interestingly observed that nano-rubber is more effective than nano-silica in toughness improvements. In all these studies, the cavitation of rubber particles/void growth and debonding of nano-silica from epoxy matrix have been identified as responsible mechanisms for the improved interlaminar toughness of FRP composites. Chisholm et al.[10] introduced nanosized SiC particle 1.5%–3.0 wt.% into SC-15 in a carbon fiber composite and observed enhanced toughness.

Fibrous fillers such as CNTs and CNFs also has been shown to enhance the delamination toughness of FRP composites. Fenner et al.[101] fabricated a woven CFC containing well dispersed CNTs in the epoxy matrix resulting in toughness improvements by about 180%. Arai et al.[102] reported an increase of 50% to the initiation delamination fracture toughness and 20% increase at the final fracture toughness in CFRP with carbon nano-fibre interlayer. The results of improved toughness in FRPs obtained by Wang et al.[29] and Siddiqui et al.[103] underline the role of layered silicate in the enhancement of the interlaminar fracture toughness.

It is observed that the bulk toughness of nanoparticle filled epoxies cannot be fully transferred to the interlaminar toughness of composite laminates due to constraint effect imposed by the fibres.[100] Tang et al.[104] recently reviewed the toughness improvements in FRP nanocomposites and observed that the transfer efficiency from epoxy to FRP decrease with increasing nano filler content in the epoxy matrix of FRP.

5 Constant Amplitude Fatigue of Nanocomposites

Although the pattern of cyclic loads on structural components may vary (see Figure 1), the service loads are mostly spectrum in nature. Analysis of fatigue behaviour of a composite under spectrum loads is carried out from the knowledge of its behaviour under constant amplitude loads. While the total fatigue life approach (stress-life curves) is used for pristine composites, the growth behaviour of damage in composite under fatigue loads is analysed to determine the damage tolerance behaviour of the material.

5.1 *Bulk epoxy nanocomposite*

The fatigue life of bulk epoxy nanocomposite has been observed to be higher than their neat counterpart. The magnitude of life enhancement depends on the type of epoxy and the nano filler. Considerable improvements in fatigue life have been shown by addition of silica nano particles in the epoxies. The presence of 10 wt.% silica nanoparticles in a DGEBA epoxy polymer has been shown to improve the fatigue life by 3–4 times.[105,106] Further, presence of rubber particles in addition to silica nano particles enhance the fatigue life much more than the enhancement observed due to presence of either of these particles alone.[85,106–108] The energy dissipating mechanisms of rubber particle cavitation/plastic deformation, nano particle debonding-void formation and plastic deformation of voids are observed to enhance the fatigue life in these epoxies.

Fibrous nanofillers have been observed to tremendously improve the fatigue life of epoxies. Yu et al.[77] added 0.5 wt.% MWCNT to an epoxy and observed an enhancement in fatigue life by about 9–10 times. Loos et al.[109] incorporated small amounts of CNTs to an epoxy to show that fatigue life is increased by over 1500% due to crack bridging and pull-out mechanisms. Ren et al.[110] added SWCNT to an epoxy and observed about two times improvement in fatigue life. Bortz et al.[79] added 0.5 wt.% of a helical-ribbon CNF to an epoxy and observed fatigue life improvement by 180%. They have also seen that increasing the CNF to 1 wt.% increases the fatigue life linearly and by about 365%. Zhou et al.[21] studied a nanocomposite of SC-15 epoxy resin and CNF upto 3 wt.%. They have seen that the fatigue life improvement exhibits a peak at about 2 wt.%. Use of clays to enhance the fatigue life has also been attempted by several investigators. Zhou et al.[24] studied 5 wt.%

silicate-clay filled polypropylene nanocomposite and showed that the nanocomposite exhibits the highest fatigue performance.

Fatigue studies on hybrid nanocomposites have been taken up recently. Presence of both silica and rubber particles enhance the fatigue life of epoxy by about 10 times.[107,111] Shokrieh et al.[112] added grapheme nanosheets and CNF and observed a remarkable improvement in flexural fatigue life of epoxy resin. Experimental observations show that addition of low amounts of graphene or CNF alone enhance the flexural fatigue life by about 27 and 24 times whereas presence of both these nano fillers increase the fatigue life by about 37 times.

5.2 *FRP nanocomposite*

Glass fiber/epoxy composite with modified epoxy matrix containing silica nano particles has been investigated by several authors. Addition of 10 wt.% silica nano particles has been shown to improve the fatigue life by 3–4 times.[105,107,113] Boger et al.[86] investigated the fatigue properties of a GFRP modified with 0.3 wt.% of nanoparticles (fumed silica SiO_2 and multi-wall carbon nanotubes (MWCNT)). The addition of nanoparticles leads to increases in the high cycle fatigue life by several orders of magnitude. Chisholm et al.[10] introduced 1.5%–3.0% nano sized SiC particle into SC-15 epoxy matrix of a CFC, and observed flexural fatigue behaviour to be superior to that of the neat system. Various mechanisms such as suppressed matrix cracking, reduced crack growth rates, delayed initiation of delamination etc. have been suggested to enhance fatigue life in FRP composites.

Fenner et al.[101] fabricated a woven CFC with well dispersed carbon nanotubes in the epoxy matrix, and observed over an order of magnitude increase in shear fatigue life. Zhou et al.[21] observed a significant improvement in fatigue strength of a CFC nanocomposite having SC-15 epoxy matrix modified with CNF. Knoll et al.[114] investigated the influence of MWCNT and graphene in CFC. The fatigue life increased significantly for both types of carbon nanoparticles, being most pronounced for graphene at high fatigue loads. They identified enormous plastic deformation of the matrix due to the nanoparticles as the energy absorption mechanism leading to improved fatigue life. Interestingly, Borrego et al.[115] used nanoclay and MWCNT in GFRP composite and observed that fatigue strength decrease due to nanoparticles agglomerates.

Presence of nanoclay in the epoxy matrix has been shown to enahnce fatigue life of CFC composites.[27,28] Zhou et al.[24] observed significant improvements in fatigue life of CFC with 2 wt% nanoclay. Khan et al.[27] showed that nanoclay serves to suppress and delay delamination damage growth, and eventual failure by improving the fiber/matrix interfacial bond and through the formation of nanoclay-induced dimples in CFC.

6 Fatigue Crack/Delamination Growth Behavior of Nanocomposites

Addition of silcia nano partices has been observed to reduce fatigue crack growth rate (FCGR) of epoxy composite by over an order of magnitude.[116–118] Further, presence of ruber particles in addition to silica nano particles in the epoxy can reduce the FCGR enormously.[111,117] Liu et al.[117] also observed that addition of nanosilica particles upto 12 wt.% increase threshold stress intensity range, ΔK_{th}, whereas similar amounts of rubber nanoparticles alone did not show any such effect. They observed a synergistic effect on the fatigue threshold when both silica and rubber nanoparticles were added into epoxy. Kothmann et al.[119] used silica nanoparticles up to 25 wt% in an anhydride cured epoxy resin, and observed that FCP behaviour is improved in all three regimes of fatigue crack propagation. Particle debonding, in combination with subsequent plastic void growth and shear yielding of the matrix, are identified as major energy dissipating mechanisms in all three regimes of FCP.

Wetzel et al.[12] made a comprehensive study on a series of nanocomposites containing varying amounts of TiO_2 and Al_2O_3 nanoparticles. They observed significant reduction in fatigue crack growth rates, and the reduction is attributed to various fracture mechanisms such as crack deflection, plastic deformation, and crack pinning. Similarly, Zhao et al.,[11] in their study on alumina nano particle modified epoxy, attributed improved fatigue crack propagation resistance to mechanisms such as particle matrix debonding, plastic void growth, and plastic deformation of the matrix around the well-bonded nanoparticles.

Addition of small volume fractions of MWCNTs to the matrix of GFRP reduces cyclic delamination crack propagation rates significantly.[120,121] Grimmer et al.[121] showed that fatigue life of GFRP composite increases by a factor of 2 to 3 in presence of the CNTs. They observed that the energy dissipating mechanisms of crack bridging, nanotube fracture, and nanotube pull-out at the delamination crack front reduce the propagation rate. The relative proportion of CNT pull-out to CNT fracture is, however, shown to be dependent on the applied cyclic strain energy. Fenner et al.[101] also observed a reduction in crack growth speed by a factor of 2 in a CFC with well dispersed CNTs. 0.3 wt% CNTs in the epoxy of a CFC was observed to reduce crack speed by about 69%.[122]

Use of fullerene to reduce the fatigue crack growth rate of an epoxy polymer has been demonstrated by Rafiee et al.[26] The material's resistance to fatigue crack propagation was significantly improved by addition of relatively low nanofiller contents of 0.1 to 1%. They also observed that other forms of nanoparticle fillers such as silica, alumina, and titania nanoparticles require up to an order of magnitude higher weight fraction to achieve comparable enhancement in properties.

7 Variable Amplitude/Spectrum Fatigue of Nanocomposites

The structural components experience variable amplitude fatigue loads in service.[123,124] Also, the magnitude and sequence of loads may vary between specific periods of operation, even if the structure is operated under similar loading and environmental conditions. The structural composites, thus, have to withstand such loads safely for the entire operational life of the structure. Although improvements in constant amplitude fatigue life have been observed in nanocomposites, the presence of **load sequence effects** may lead to adverse or much better fatigue life under spectrum loads. It is of interest to note that load sequence effects on the fatigue life of FRP composites have been investigated by several authors.[123,125–131] While some studies have shown that a high-low sequence lead to a lower fatigue life compared to a low-high sequence, the opposite trend has also been observed by several investigators.[125–127,131] There are also studies which suggest that no load sequence effects exist in composites.[128,129] In view of these contrasting behaviours in composites, it is necessary to study such effects in nanocomposites, and develop models to predict fatigue life under spectrum loads. Such an effort would assist in defining the safe life of structural component and study the damage tolerance behaviour of nanocomposites.

Load sequence effect: The alteration or change in fatigue damage accumulated in a composite due to change in the relative position of load cycle(s) in a variable amplitude load (load path alteration).

Investigations on the fatigue life of nanocomposites under spectrum loads are very limited. Jen et al.[132] investigated the 0.5 wt.% MWCNT modified epoxy subjected to two stage block loads. They observed that fatigue life under high-low sequence and low-high sequence was different, suggesting the presence of load sequence effects in this nanocomposite. It was further confirmed by showing that prediction of second stage fatigue life by non-linear damage accumulation was better than linear or Miners rule.

Manjunatha et al. studied the effect of high-low (decreasing) and low-high (increasing) sequence on the fatigue life of a GFRP nanocomposite containing silica nano particles and rubber micro particles in the epoxy matrix.[133] The fatigue life of the GFRP nanocomposite was shown to be higher than that of the corresponding GFRP neat composite by a factor of about 3.9 and 2.6 under increasing and decreasing three-step block load sequences, respectively. Thus, they concluded that there is evidence of load sequence effect in the GFRP nanocomposite.

The effect of addition of silica nano particles in the epoxy matrix of a GFRP composite on the spectrum fatigue life has been investigated in detail.[134–136] A fatigue life enhancement of about four times has been observed under standard WISPERX, Helix-32 and mini-FALSTAFF loads sequences. The suppression of matrix cracks, reduced crack growth rates and delayed initiation of delamination have all been attributed to such improved fatigue life in GFRP nanocomposite.

The current available fatigue prediction models can be classified into three major categories, viz., empirical, phenomenological and physics based damage models. Empirical models rely on experimental data (stress levels, stress ratio or frequency) without considering the inherent damage mechanisms. These have been adopted in the past with limited success and typically require a huge test matrix for better predictive accuracy. Phenomenological models use experimentally measurable phenomena like residual stiffness or strength as a damage matrix as against simple nonphysical quantities used in empirical models. In physics based damage models, one or more appropriately chosen damage variables are introduced to account for deterioration of composite properties. The macroscopic mechanical property degradation is correlated to underlying damage mechanisms through sound physical modelling. Though there are models that evolved as simple design tools, no robust model is available to accurately predict the response under fatigue loads.

The modeling and prediction of fatigue life under spectrum loads in polymer composites has been reviewed by Post et al.[123] The general approach to the prediction of the fatigue life by empirical model is shown schematically in Figure 7.[123,137] The prediction procedure involves several sequential steps, i.e., (i) the separation of individual load cycles in the spectrum sequence by any counting method such as rainflow counting,[138] (ii) the determination of the cycles to failure, N_f, for each of the counted load-cycles using a constant life diagram (CLD) of the material as shown in

Figure 8, (iii) the calculation of the damage fraction for each of the counted load cycles, and (iv) the determination of the total fatigue damage per load block by summation of the damage fraction. The material is assumed to fail when the total damage fraction reaches 1.0 and, hence, the fatigue life under the spectrum load-sequence is equal to the reciprocal of the total damage estimated per load block. Following this procedure, Manjunatha et al.[137] estimated the fatigue life of a nanocomposite under spectrum loads, and observed a good agreement between the experimental and the

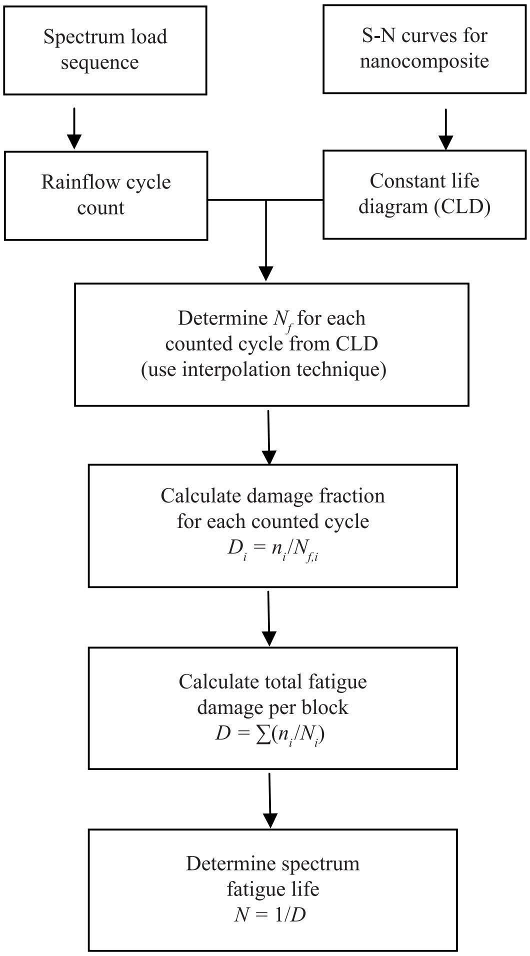


Figure 7: Flowchart for prediction of fatigue life under spectrum loads.[137]

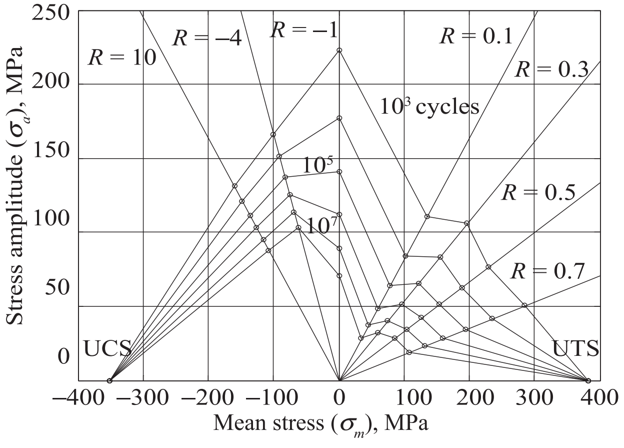


Figure 8: A typical CLD for a GFRP nanocomposite.[137]

predicted fatigue lives. Shokrieh et al.[139] derived a micro-mechanics based model and predicted the stiffness degradation behavior of a nanocomposite successfully. However, further work in modeling needs to be carried out to predict the fatigue lives of nanocomposites.

8 Summary and Concluding Remarks

Fiber reinforced polymer composites with nano filler modified epoxy matrix exhibit improved fracture toughness and enhanced fatigue life. They appear to be the promising structural materials of future with improved damage tolerance capabilities. However, the use of nanocomposites in service still needs many issues to be sorted out.

1. Structural engineering polymer composites are used in the form of FRPs. Significant improvements in fatigue and fracture properties have been observed by the addition of nano fillers in bulk epoxies. However, the enhancement factors observed in epoxy levels are not translated to FRPs completely. The possible reasons being (i) the difference in mechanisms of improvements, (ii) processing methods resulting in difference in distribution of nano fillers at epoxy and FRP levels, etc. Hence, studies need to be carried out to determine the possible extent of improvements in FRPs than in epoxies alone.
2. Service loads are spectrum in nature. FRP composites have been shown to be both sensitive and insensitive to load sequence effects, depending on the type of fibers and epoxies. In addition to these, the nano filler may also affect the load sequence mechanisms. The enhancement factor observed in constant amplitude fatigue life in FRP nanocomposites may not necessarily be observed in spectrum fatigue loads. It could either be decreased/increased or unaltered depending on specific filler/epoxy/fiber interaction mechanisms.
3. Although many types of fillers are used to improve the mechanical properties of FRPs, the specific filler type, size, shape and volume fraction to obtain maximum improvements in fracture toughness and fatigue life has not been established to yield commercial grade FRPs. It is necessary to investigate these issues to get industrial grade nanocomposite prepregs with optimally improved mechanical properties.
4. Hybrid composites containing two or more different types of nano fillers have been shown to enormously improve fatigue and fracture properties. Thus, further work is required in this regard for development of hybrid composites to take advantage of different types of fillers and their synergistic effects.
5. Processing methods to obtain uniform distribution of nano fillers and the control of viscosity of nano modified resins is still a major issue to be sorted out before they could be used industrially.
6. While it is desirable to have dramatic improvements in specific mechanical properties such as fatigue and fracture properties, the nano modification of epoxies should not be detrimental to other mechanical properties of the composites. Studies are required to evaluate other mechanical properties, especially those under hot-wet conditions to determine the suitability of FRP nanocomposites for structural applications.[140]
7. Fatigue life prediction of nanocomposites using micro-mechanics models, stiffness or strength based models, and empirical models need to be developed further to improve prediction accuracies.

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