Fatigue and Fracture Toughness of Epoxy Nanocomposites

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The fatigue and failure mechanisms of epoxy composites have been researched extensively because of their commercial importance in fields demanding materials with high specific strength. Particulate, sheets, short and long fibers with dimensions in the micrometer and nanometer range are the major fillers which have been studied for enhancing the fatigue resistance of epoxies. The nano and micro scale dimensions of the fillers give rise to unexpected and fascinating mechanical properties, often superior to the matrix including fracture toughness and fatigue crack propagation resistance. Such properties are dependent on each other (e.g., the fatigue properties of the polymer composites have been found to be strongly influenced by its toughness). This article is a review of the various developments in this field and the underlying mechanisms which are responsible for performance improvements in such composites.

INTRODUCTION

Fatigue is a mode of progressive failure in solids under cyclic loading at stresses lower than the material's ultimate tensile stress.[1] Due to the increasing use of polymers and their composites in engineering applications, especially the aerospace industry, the fatigue properties of composites have inspired much work.[2–5] The characterization of material behavior under cyclic loading is done either by fatigue life (*S-N*) measurement or by studying the fatigue crack propagation (FCP) rate in the material. The growth of a crack in the stable region under cyclic loading (Figure 1) is governed by the Paris law and is given by $\frac{da}{dN} = C(\Delta K)^n$.[7] According to the Paris law, the crack propagation rate per cycle (*da/dN*) is directly proportional to the stress intensity factor range ΔK and two constants, *C* and *n*, which depend on the testing parameters including moisture, temperature, loading frequency, and the stress ratio.[8] The faster the rate of crack propagation, the lower the fatigue resistance. Smaller values of the Paris exponent signify high material resistance to FCP. The Paris exponent, and hence the fatigue properties of the material, have been found to be strongly influenced by their fracture toughness. An increase in toughness of the matrix has been associated with an increase in FCP resistance of the material.[9,10]

How would you…

…describe the overall significance of this paper?

The mechanical properties of epoxy nanocomposites have been extensively researched because of their commercial importance in fields demanding materials with high specific strength. Various fillers like nano-ceramic, nano-rubber, carbon nanotubes, and nano-clay sheets have been studied for enhancing the fatigue resistance and fracture toughness of epoxy composites. This article is a review of the significant developments to enhance fracture toughness and fatigue resistance of epoxy nano-composites.

…describe this work to a materials science and engineering professional with no experience in your technical specialty?

Thermoset polymers like epoxy are important for the aerospace and automobile industry due to their high specific strength. However, they lack damage tolerance, a critical attribute for advanced applications. Introduction of a second phase in the epoxy matrix may improve the mechanical properties, especially fracture toughness and fatigue resistance. Epoxy nanocomposites utilizing carbon nanotubes, nano-ceramics and nano-rubber exhibit superior properties compared to the matrix.

…describe this work to a layperson?

Epoxy composites have greatly influenced the aerospace and automobile industry by allowing new designs and innovations. Two important material properties critical for advanced applications are high fracture toughness and resistance to cyclic loading. Epoxy has poor crack propagation resistance because of low ductility and hence second phase nanoparticles are introduced in the epoxy matrix for improvements. This article describes how fillers of various geometries and chemical nature affect the matrix.

The S-N curve is another classical approach used for studying fatigue behavior of a material. The curve gives an estimate of the material's fatigue life under controlled amplitude of cyclic stress. Hysteresis loss measurements are also utilized to determine the resistance of polymers to crack initiation and crazing.

The fatigue process has been traditionally divided into three stages: crack initiation, crack propagation, and final failure.[11] Surface flaws and inclusions are the most common sites for fatigue crack initiation. In most engineering materials cracks are inherently present on the component surface. Another area prone to crack generation is the second phase-matrix interface. Due to high local stress concentration and the discontinuity in mechanical properties at the particle-matrix interface crack initiation becomes easy. In polymer matrix composites (PMC), the failure mechanisms are not as well understood/defined as in metals. In the failure of a PMC multiple mechanisms might contribute, such as matrix crazing, shear yielding, delamination,

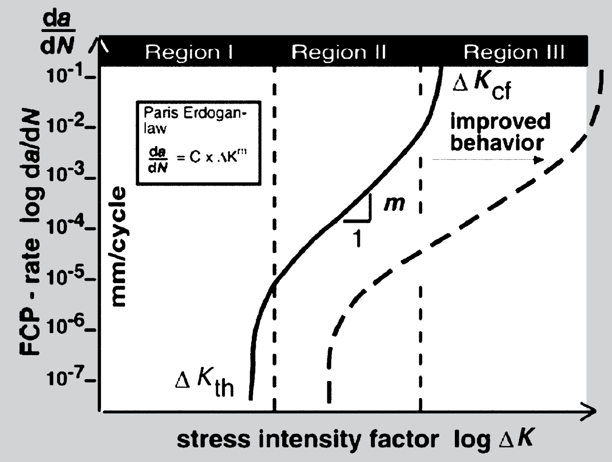

Figure 1. An FCP diagram for a neat matrix in comparison to a modified and improved system.[6]

fiber breakage, debonding, plastic void growth, and matrix cracking.[12] Some scanning electron micrographs to convey a broad picture of failures in polymer composites are shown in Figure 2.

See the sidebar on page 52 for a description of polymer failure modes.

THERMOSETTING EPOXIES

Epoxy resin (two or more groups of epoxide per molecule) and a curing agent comprise an epoxy system. Epoxy composites are used for aircraft, automobiles, ship-building, resin casting, slide bearings, and many other applications because of their good chemical and corrosion resistance, high specific strength, and multiple curing options.[2] Despite these advantages epoxy lacks a crucial attribute: damage tolerance. Offering a fracture energy of less than 0.3 kJ/m^2, they can be classified as highly brittle.[18] As specified by Johnston,[19] the fracture energy for a resin to be used in aircraft structures should lie in the range of 1.9–3 kJ/m^2. Epoxy possess aromatic rings, which increase the polymer chain stiffness and has high cross link density; hence the plastic deformation in front of the crack tip is highly localized. This extremely localized plastic deformation causes little absorption of energy leading to catastrophic brittle failure. Enhancement in strength and stiffness of the polymer matrix can be obtained by increasing the cross-link density, but it also increases the brittleness of the polymer leading to reduced toughness.[20] In order to control the toughness and hence the fatigue of thermoset polymers, studies have been done on the introduction of a second phase in them. Since the toughening mechanism in thermoset polymers is not a well-understood phenomenon, it led to the study of various kinds of fillers to obtain optimum mechanical properties of the composite. Some of the second phases that have been studied are micro- and nano-size particulates like rubber (e.g., carboxyl terminated butadiene acrylonitrile (CTBN)),[21,22] thermoplastics (e.g., polyethersulphone),[23–26] ceramic particles (e.g., Al_2O_3),[27] some reactive diluents;[28] long and short fibers including carbon nanotubes;[29,30] laminates of fibers[31,32] in different orientations, layered silicate membranes,[33,34] and their combinations.[35,36]

FILLER PROPERTIES AFFECTING TOUGHNESS AND FATIGUE

The use of fillers like elastomers with lower modulus than that of the matrix results in composites with increased toughness[37] due to high ductility, but modulus of the composite decreases,[18] whereas for inorganic fillers the modulus of the composite is observed to be more than that of the polymer matrix.[38,39] The size of the fillers also plays a central role. Use of nano-fillers (NF) has proved more effective than micro-filler (MF) in enhancing the strength of the polymer matrix, without compromising ductility. The size of the NF (a few tens of nm in diameter) being smaller than the micro-sized filler reduces the stress concentrations in comparison to MF (a few tens of µm in diameter).[40] The high stress concentration at the surface makes MF more prone to cracking as compared to NF.

Another advantage of having nano-sized fillers is that for the same volume fraction of fillers added, the particle density will be higher for NF than for MF. Therefore, the distance between two neighboring particles will be

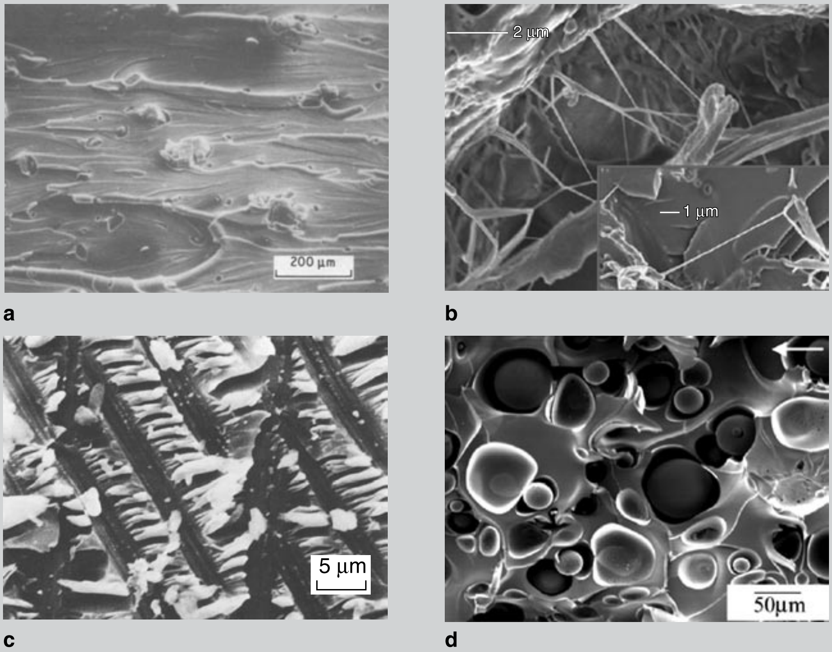

Figure 2. Scanning electron micrographs of common mechanisms contributing to polymer composite failure (a) shear yielding,[13] (b) crazing,[14] (c) fiber delamination fracture surface,[15] and (d) particle pull out and plastic void growth.[16]

BASIC FAILURE MODES IN POLYMERS

Depending upon the chemistry and the curing agent used, the failure mode of the polymer matrix could be either ductile or brittle. The ductile mode is often identified by shear yielding. An increase in brittle nature of the polymer is seen as a shift from shear yielding to micro-voiding followed by crazing. In case of networked polymers like epoxy highly brittle failure without crazing is common.

Shear Yielding

Shear yielding is an energy absorption mechanism associated with polymer failure. It occurs when localized plastic flow starts in response to an applied stress at approximately 45° to the applied load. Such plastic flow might spread shear bands in the whole sample (Figure 2a) absorbing a significant quantity of energy or might lead to localized yielding resulting in isolated shear bands.

Crazing

Crazing is another common failure mode that is observed in glass and amorphous thermoplastic polymers.[17] During crazing, microcracks form under tensile load and are held together by polymer fibrils called crazes (Figure 2b). Formation and plastic deformation of such crazes involves absorption of energy, which leads to enhanced toughness. When the applied stress is high enough to cause failure of the fibrils, the microcracks start growing.

smaller for nano-sized fillers, which is an important parameter in crack bowing and pinning. Lack of transparency is another issue associated with micrometer-sized fillers in polymer composites.[41] Transparency of the composite is improved for nano-fillers as their size is less than the wavelength of light, especially when a good dispersion is achieved.[42] The presence of fillers affects the crystallinity, mobility, and other structural aspects of polymer chains.[5]

Fillers also act as nucleating sites for crystallization of polymer chains.[43,44] The effectiveness of load transfer between the polymer and the filler is a function of wettability and adherence.[45,46] The two plots in Figure 3 demonstrate the difference in the static mechanical and fatigue properties of the neat epoxy, Al_2O_3 reinforced epoxy, and APTES (3-aminopropyltriethoxysilane) modified Al_2O_3 reinforced epoxy. The surface modification of fillers improves their dispersion, which could also be attained by physical means like ultrasonication.[49,50]

Another significant filler property is the aspect ratio.[51] Layered silicates, with thickness in nanometers and length and width in micrometers, and carbon nanotubes, with diameter in nanometers and length in micrometers, have much higher aspect ratios than particulates. This leads to a more efficient load transfer and the increased toughness of the composite.[52–54]

PARTICULATE–POLYMER COMPOSITE

Rubber – Thermoset

Around 1971, the Sultan and McGarry group initiated research on the effect of rubber in thermoset polymers.[55–58] Reactive functional elastomers (e.g,. CTBN (carboxyl terminated Butadiene),[21,59–61] HTBN (hydroxyl terminated Butadiene),[62] ATBN (amine terminated Butadiene),[63,64] VTBN (Venyl terminated Butadiene),[65] and ETBN (epoxy terminated Butadiene)[66,67]) increased the fracture toughness of the polymer matrix when added between 5–20% weight fraction.[18]

To obtain rubber dispersion in epoxy, rubber is dissolved in epoxy resin followed by curing with appropriate hardener. After curing, a dispersed phase of rubber in epoxy matrix is observed. The degree of phase separation and the dispersion size can be controlled by controlling curing parameters and filler volume fraction.[18,68] Elastomer addition by either phase separation at adequate temperature or through addition in the form of fine solid powder was found to improve the ductility of the thermoset, increasing its toughness to around 2–4 kJ/m^2.[18] Shown in Figure 4a is a scanning electron micrograph of the dispersed phase of nano-rubber in epoxy. Treatment of rubber with silane coupling agents, plasma oxidation, and acid treatment has been found to enhance interfacial interaction, leading to an increase in fracture toughness.[70–72]

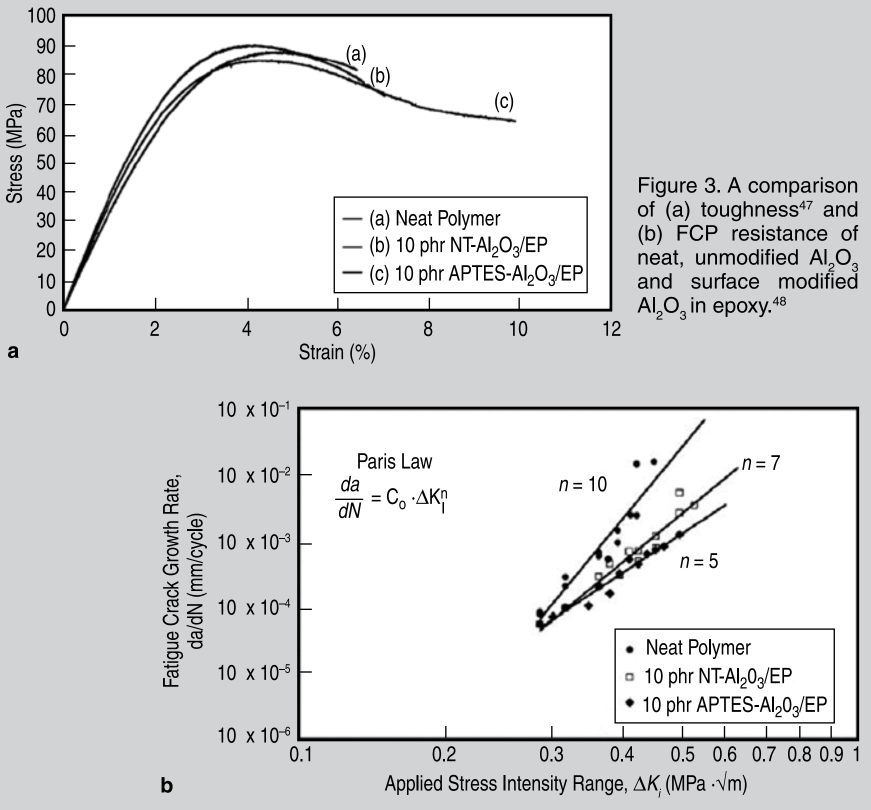

Figure 3. A comparison of (a) toughness[47] and (b) FCP resistance of neat, unmodified Al_2O_3 and surface modified Al_2O_3 in epoxy.[48]

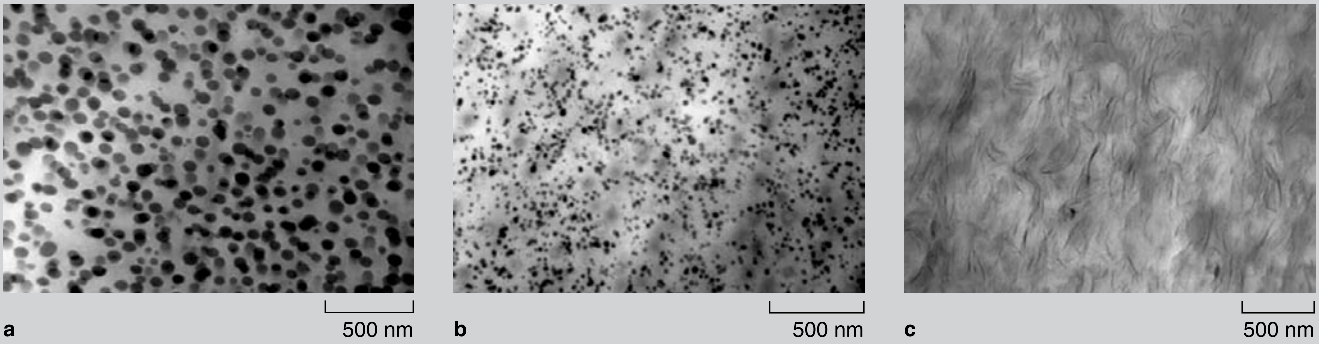

Figure 4. Transmission electron micrographs of dispersed phases: (a) nano-rubber, (b) nano-silica, and (c) organoclay C30B in nylon-6 matrix.[69]

The crack propagation velocity in rubber-reinforced polymers has been measured[73] and it was observed that crack blunting in the rubber phase of the composite significantly decreased the crack propagation velocity. In the presence of rubber particles the crack tip blunts due to localized shear yielding around it. Figure 5a is a plot of FCP rate in rubber reinforced epoxy composite with increasing filler content.

The plot shows improvement in the fatigue resistance of the composite with increasing rubber phase fraction. Fatigue property studies of elastomer-epoxy composites have shown the early initiation of crazes around the rubber particles, proving useful in the late life of the material by improving the toughness of the polymer matrix via microcrazing, cavitation, and shear yielding.[74,76] The rubber phase undergoes significant strain and finally acts as a ligament in the polymer craze.[77] However, this ductility is achieved at the cost of modulus, strength, and impact resistance of the matrix.[18,71]

Ceramic – Thermoset

The reinforcement of epoxy using ceramic particles with materials such as glass beads,[27,78] silica,[79–81] and alumina,[49,82] from micrometer to nanometer size, is found to increase the toughness of the matrix without compromising its rigidity. Surface-coated inorganic fillers have been found to improve mechanical properties of the composite under both tensile and cyclic load.[49,83] In Figure 4b a scanning electron micrograph of the dispersed phase of nano-silica in epoxy matrix is shown. The fatigue studies of ceramic-filled polymer have shown significant improvement,[50,83] increasing K_{IC} from ~0.5 $MPa^{1/2}$ to 0.88 $MPa^{1/2}$ with ~ 20.2 wt.% of nano SiO_2 fillers, with an increase in elastic modulus from 2.96 GPa to 3.85 GPa.[10]

Numerous phenomena are associated with the toughness increase in particulate-reinforced composites, some of which are crack deflection, crack pinning, and debonding followed by plastic void growth. Crack deflection is the process of tilting and twisting of cracks in the matrix around the filler particles, as shown schematically in Figure 6a and b. During the deflection process the crack tip propagates under mixed I and II mode and the fracture surface roughens (Figure 6c) as an outcome of increase in fracture toughness.[85–87]

Theoretical models for such deflection studies have been analyzed by Faber and Evans.[84] Crack pinning is a process similar to pinning of dislocations by impurity or second phase particles in the matrix. First proposed by Lange,[88] the process describes the bending of the crack front in the presence of pinning elements, which obstruct its smooth motion. The crack pinning is studied by observing the bowing of the crack front,

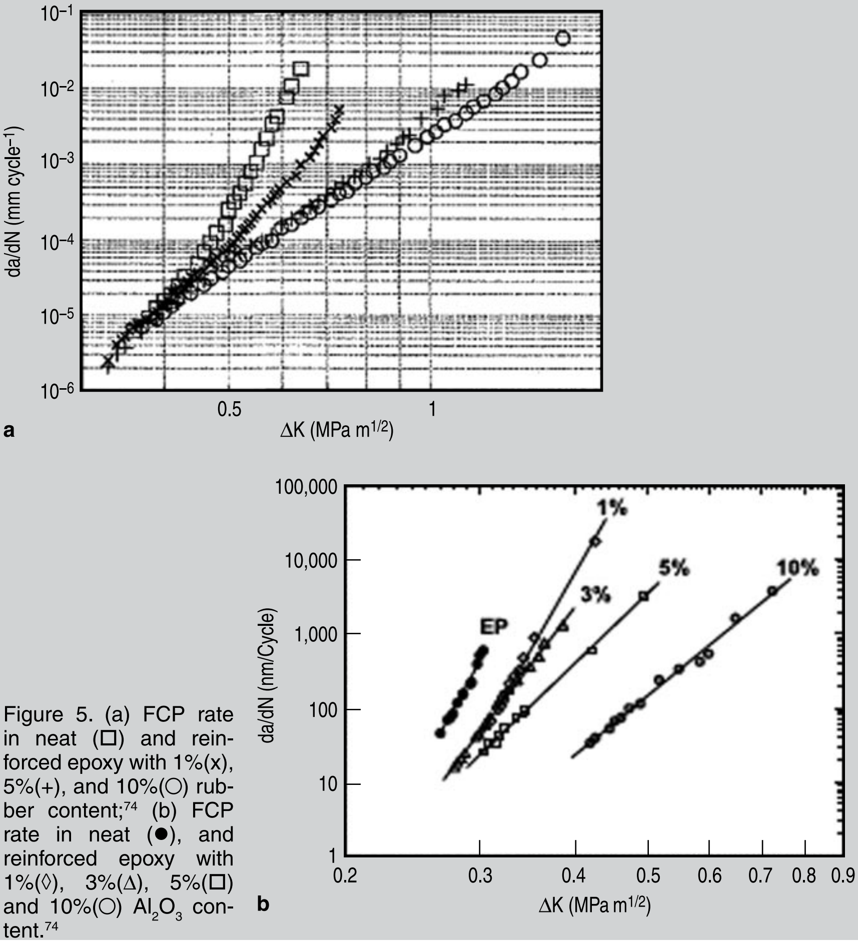

Figure 5. (a) FCP rate in neat (□) and reinforced epoxy with 1%(x), 5%(+), and 10%(○) rubber content;[74] (b) FCP rate in neat (●), and reinforced epoxy with 1%(◊), 3%(Δ), 5%(□) and 10%(○) Al_2O_3 content.[74]

as shown schematically in Figure 7a. Crack pinning is observed only when the filler size is greater than the crack-opening displacement; hence it is an effective pinning mechanism mostly for micrometer size fillers for epoxy matrix whose crack opening size has been calculated to be ~1.7 µm.[85] The crack front bows in between the particles, leaving behind tail-like structures (Figure 7b).

Particle debonding and local plastic void growth is another phenomenon contributing to the fracture toughness increase of the polymer matrix infiltrated with micro- and nano-fillers (Figure 8). The debonding of the filler relaxes the stress state at the crack tip and causes deformation of polymer matrix by void growth process.[85]

Plastic void growth of the polymer has been reported to be the major cause of toughening for nano-sized SiO_2 and Al_2O_3 particles due to enhanced shear yielding of the polymer. Functionalized nano-Al_2O_3 fillers which had better adhesion with the epoxy matrix than untreated fillers, were found to have 39% higher strain to break as compared to the neat polymer, whereas unmodified nano-Al_2O_3 fillers showed only 6% increase at 10 phr (parts per hundred) filler concentration. It was realized that the plastic void growth mechanism is

FATIGUE BEHAVIOR IN COMPOSITES

Clay Nanosheet Polymers

Exfoliated clay sheet reinforced polymers have been considered for improved fatigue resistance of polymers. When the intercalation of clay layers through polymer chains is not possible, phase separation occurs and a micro-composite instead of nano-composite is obtained, making the dispersion of nano-clay in the polymer critical for composite properties. Dispersion of clay nano-sheet in polymer is difficult due to the hydrophilic nature of clays and hydrophobic nature of polymers. The dispersion barrier is overcome using organic surfactants like vinylbenzyldimethyldodecylammonium chloride (VDAC), which makes the clay surface organophillic.[89] Forcing polymer chains through the exfoliated layers of clay sheets (a few nm thick) leads to a finely dispersed composite (Figure 4c).[34,90–92] The high aspect ratio of exfoliated clay layers provides large interfacial contact area with the matrix.[93] Studies on the mechanical properties including fatigue of such nano-layer reinforced composites have shown improvement in neat and traditional fiber reinforced polymers. An addition of 5 wt.% nano silicate clay in polypropylene has been found to increase fatigue strength coefficient (true stress which causes failure in one reversal) by 13.3% with respect to the neat polymer and at the same time resulting in an increment in modulus and yield strength by 90% and 5%, respectively.[94] The stiffness and toughness of nano-clay epoxy composite has been reported to increase with an increase in filler content.[95] The fracture surfaces of such composites have been found to be much rougher than plain epoxy, indicating higher energy absorbtion by the system prior to fracture. Crack deflection has been implied by the presence of steps and microcracking on the fracture surface.[96] The fracture toughness and FCP resistance of the composite have been found to increase by chemical modification of clay sheets like surface treatment of the clay layers with 3-aminopropyltriethoxysilane or long chain alkylammonium salt and using physical means like forcing polymer in between clay layers using a twin screw extruder.[97,98]

Nanofibers

Nanofibers are whiskers with diameters in the range of a few hundred nanometers and lengths of a few hundred micrometers. Vapor grown carbon nanofibers (VGCNFs) obtained from chemical vapor deposition of hydrocarbons, have been used to reinforce the epoxy matrix due to its excellent mechanical properties.[99] Vapor grown carbon nanofibers consist of a few-nanometer-diameter carbon tubes surrounded by concentric circles of carbon layers increasing its outer diameter to around 50–200 nm.

Dispersion of the VGCNFs is difficult to achieve as the fibers get twisted and intertwined. Using surface treatments like functionalization and plasma treatment, better dispersion and interfacial ad-

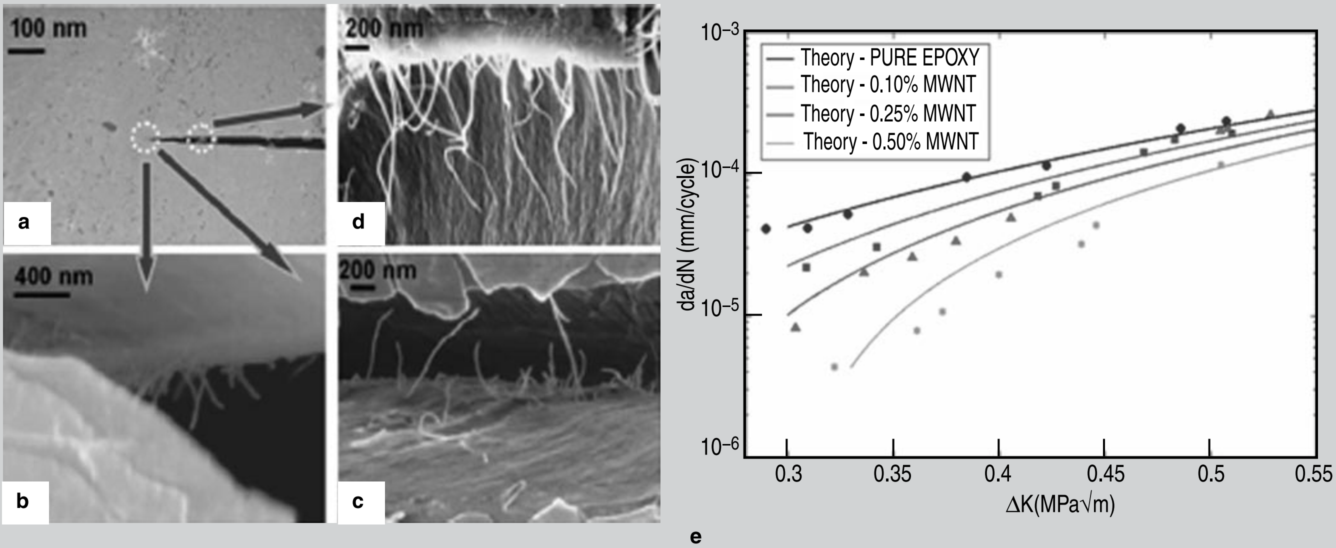

Figure A. (a) Scanning electron micrograph of the side view of the fatigue crack. The microstructure of the sample in the vicinity of the crack is shown. (b) Close to the crack tip, fiber bridging zone is shown, where the nanotubes are pulled out of the matrix but are effectively bridging the crack interface. (c) At a small distance behind the crack tip, some nanotubes are bridging the crack and some are pulled out of the matrix. (d) Far behind the crack tip, nanotubes are completely pulled out of the matrix. (e) Lowering of FCP rate in MWNT reinforced epoxy with increasing weight fraction of MWNT.[29]

the main mechanism resulting in the rise in toughness.[47,48] Figure 5b is a plot of FCP in Al_2O_3 epoxy composite with varying volume fraction of filler. See the sidebar for fatigue behavior in various composites.

THREE-PHASE COMPOSITES

Oriented fiber reinforced composites with excellent longitudinal properties have poor transverse properties due to lack of fibers in the thickness direction.[105] Lack of fibers through the thickness of the composite also leads to poor fatigue behavior. Weaving of fibers in the thickness direction (i.e., stitched composites) can be used to improve the transverse properties of laminated composites but only at the cost of longitudinal properties.[106,107] Another approach to improve the properties of these traditional composites is by using nanofillers like CNTs to improve the interlaminar strength of the composite.[108] The CNTs could either be randomly distributed or vertically oriented on the fibers.[109–111] The effect of functionalization of the CNTs in such three phase composites was observed to further enhance the transverse and longitudinal toughness of traditional epoxy/fiber composites.[112,113]

hesion between the polymer matrix and carbon nano-fibers (CNF) is achieved.[100] Since random dispersion of VGCF leads to isotropic properties in the composite, to obtain desired alignment extrusion[101] and magnetic field[102] are employed. Vapor grown carbon nanofibers have resulted in an increase in the fracture toughness of epoxy with increasing fiber content.[103] The fatigue life and the fatigue strength of nanofiber-reinforced epoxy were also found to improve substantially on introduction of ~2% VGCF.[104] The increase in fracture toughness is attributed to fiber debonding and the pull out mechanism.

Carbon Nanotube Polymers

Carbon nanotubes have been demonstrated to increase the fatigue life of PMCs. The fatigue crack propagation velocity is significantly reduced through the action of crack bridging by the CNTs and the subsequent dissipation of energy that occurs due to the frictional pull out of the bridging CNT fibers as shown in Figure Aa–d. In the low stress intensity factor amplitude regime a decrease in the crack propagation rate by over ten-fold is reported,[30] with strong dependence on the weight fraction of CNTs. Figure Ae shows the increase in resistance to fatigue crack propagation with an increase in the weight fraction of multiwalled carbon nanotubes (MWNTs) in the epoxy matrix. The amount of CNT required for such a reduction in FCP rate is less than 1% which is small in comparison to the amount of particulate nano-fillers (~5–10%).

For the case of CNT fillers, a substantial reduction in the fatigue suppression with increasing ΔK (Figure Ae) is observed. This is because in the case of CNTs the dominant toughening and fatigue crack suppression mechanism is crack bridging. The fatigue crack is bridged by high aspect ratio nanotubes generating a fiber-bridging zone in the wake of the crack tip. As the crack advances energy is dissipated by the frictional pull-out of the bridging nanotubes from the epoxy matrix which slows the crack propagation speed. However this crack bridging effect loses effectiveness at high ΔK due to progressive shrinkage in the size of the fiber-bridging zone as ΔK is increased.[29] The fact that such behavior is not observed in nanoparticle filled epoxy composites indicates that crack bridging phenomena are not playing a dominant role in the fracture and fatigue of nanoparticle filled polymer systems. Reducing the CNT diameter and increasing its length has been shown to increase the effectiveness (Figure B) of the crack bridging mechanism.[30]

Functionalizing CNT with amido-amine groups has also been shown to enhance the epoxy's resistance to fatigue crack propagation by initiating craze formation (Figure 2b) in the epoxy.[14] The origin of the crazing behavior was traced to a significant amount of unreacted epoxy that was kinetically trapped in the crosslinked matrix structure that is formed at the CNT/epoxy interface. Such local heterogeneity in the curing may be caused by a variety of factors such as, for example, the fact that the chemistry may be modified locally due to the presence of amido-amine groups. Epoxy chain alignment, which is known to influence the cross-linking density, may also be modified locally due to the presence of these functional groups. Heterogeneous cross-linking results in localized pockets of enhanced molecular mobility;[14] the correlated evolution of such contiguous mobile regions under mechanical loading leads to crazing which substantially boosts the toughness and the resistance to fatigue crack propagation of the baseline epoxy.

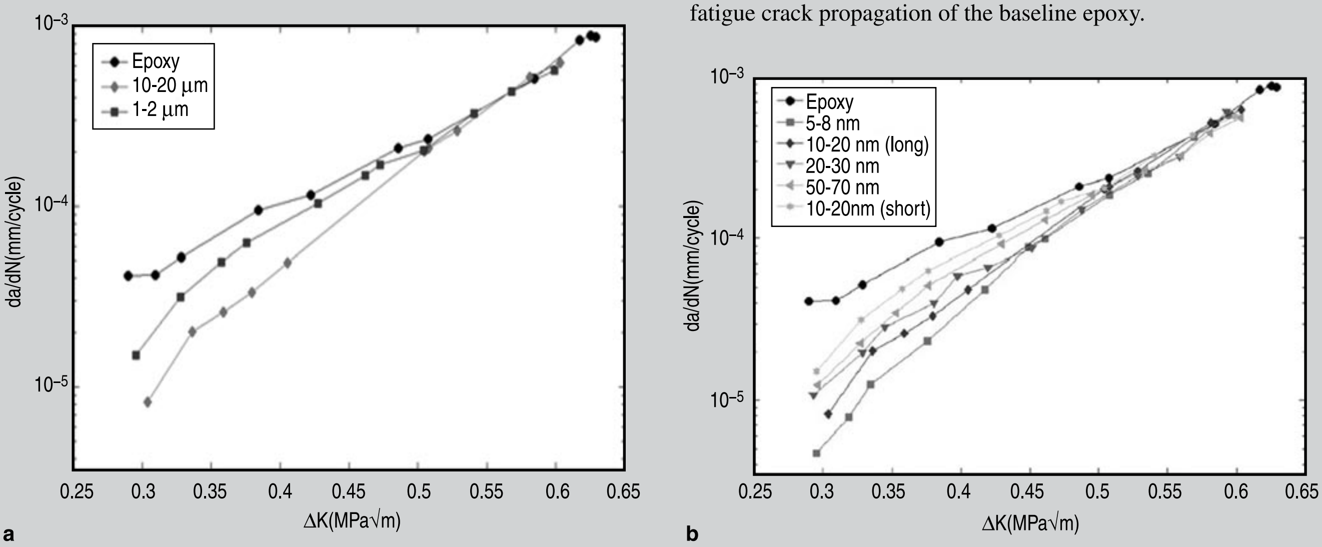

Figure B. (a) Effect of nanotube diameter on fatigue suppression performance; (b) effect of nanotube length on fatigue suppression performance.[30]

CONCLUSION

Fatigue life improvements in epoxy composites have been studied and researched for a wide variety of second-phase particles. Different kinds of fillers have different ways of obstructing FCP. Particulate fibers obstruct the fatigue crack by crack deflection, crack pinning, debonding, and plastic void growth whereas short fibers undergo crack bridging and crack trapping.

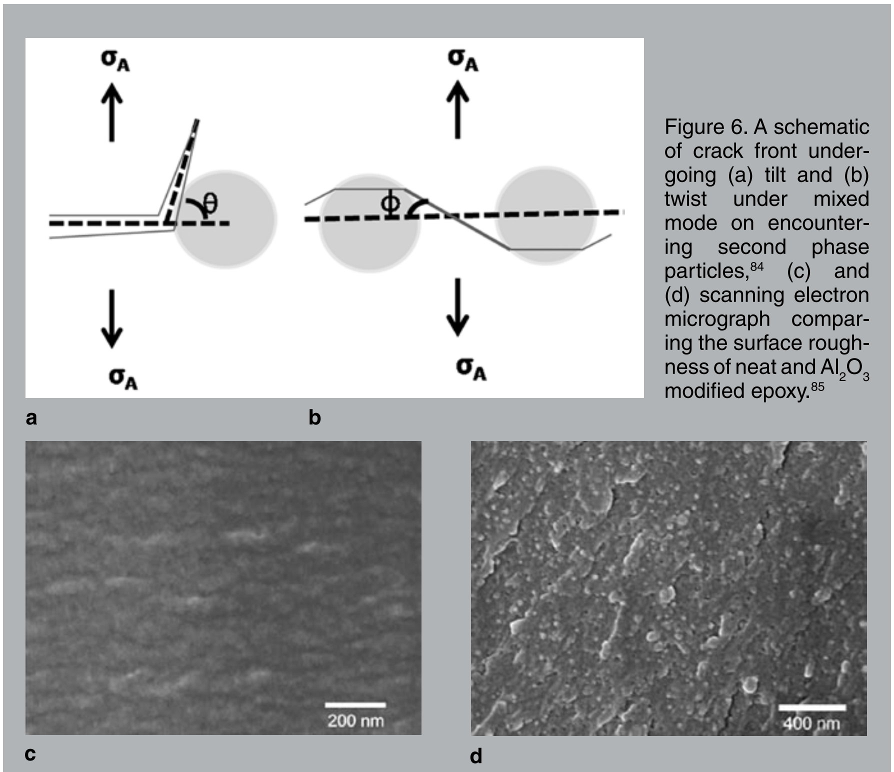

Figure 6. A schematic of crack front undergoing (a) tilt and (b) twist under mixed mode on encountering second phase particles,[84] (c) and (d) scanning electron micrograph comparing the surface roughness of neat and Al_2O_3 modified epoxy.[85]

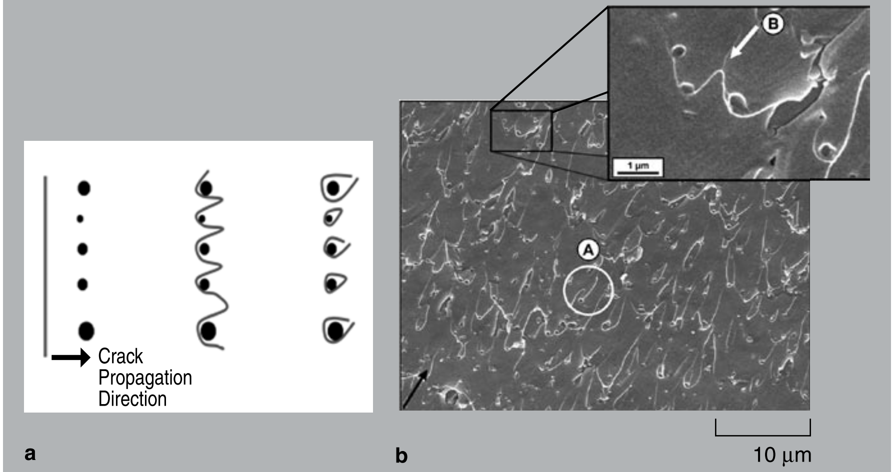

Figure 7. (a) A schematic of second phase particles pinning the crack front, leaving behind tail-like structure.[41] (b) Scanning electron micrograph illustrating the fracture surface of epoxy reinforced with TiO_2 nanoparticles, demonstrating the tail-like structures.[75]

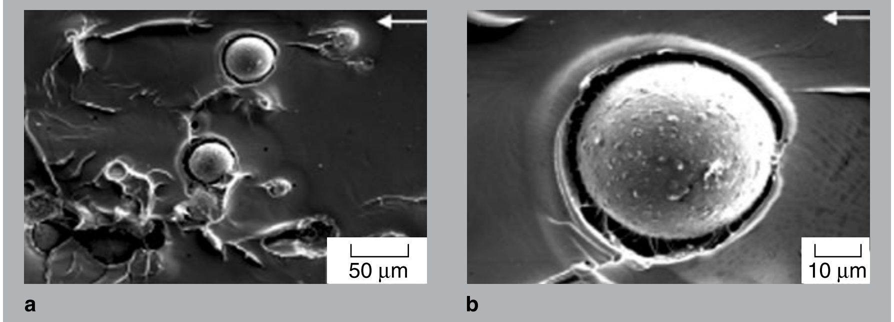

Figure 8. (a) and (b) Scanning electron micrographs illustrating the fracture surface of glass-particle epoxy matrix after debonding.[16]

Rubber composites degrade the original stiffness of the epoxy matrix whereas inorganic particles are not as efficient as rubber in enhancing the toughness of the composite. High-aspect-ratio fibers such as carbon nanotubes are able to significantly enhance the epoxy's fatigue crack propagation resistance at relatively low weight fractions (below 0.5%), but they lose their effectiveness at high stress intensity factor amplitudes. Graphene is another emerging nano-material and shows promise to enhance fracture and fatigue properties of polymers[114] at low loading fractions due to its high specific surface area, two-dimensional sheet geometry, strong filler-matrix adhesion, and the outstanding mechanical properties of the sp^2 carbon bonding network in graphene.[115] Due to the increasing interest of researchers in graphene composites, in-depth study of the fracture and fatigue properties of grapheme-based composite materials is clearly warranted.

In addition, theoretical/computational modeling of fracture and fatigue in nanocomposites is still in its infancy. Improved models for toughness in nanocomposites and validation with experimental data are essential for development of nanocomposite polymers with optimized strength, stiffness, fracture, and fatigue properties.

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