



Review

A review of recent research on mechanics of multifunctional composite materials and structures

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ABSTRACT

In response to the marked increase in research activity and publications in multifunctional materials and structures in the last few years, this article is an attempt to identify the topics that are most relevant to multifunctional composite materials and structures and review representative journal publications that are related to those topics. Articles covering developments in both multiple structural functions and integrated structural and non-structural functions since 2000 are emphasized. Structural functions include mechanical properties like strength, stiffness, fracture toughness, and damping, while non-structural functions include electrical and/or thermal conductivity, sensing and actuation, energy harvesting/storage, self-healing capability, electromagnetic interference (EMI) shielding, recyclability and biodegradability. Many of these recent developments are associated with polymeric composite materials and corresponding advances in nanomaterials and nanostructures, as are many of the articles reviewed. The article concludes with a discussion of recent applications of multifunctional materials and structures, such as morphing aircraft wings, structurally integrated electronic components, biomedical nanoparticles for dispensing drugs and diagnostics, and optically transparent impact absorbing structures. Several suggestions regarding future research needs are also presented.

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1. Introduction

The number of publications dealing with various aspects of the mechanics of multifunctional materials and structures has in-

creased markedly in recent years. Fig. 1 shows how the number of English language refereed journal articles in multifunctional materials and structures has steadily increased since 2000, based on data collected from the Engineering Village© web-based information service. Along with the increase in the number of publications in this area comes a need for a comprehensive review article,

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Nomenclature

A	surface area of spherical particle	SE	EMI shielding effectiveness
C_D	drag coefficient	t_E	flight endurance time
C_L	lift coefficient	U_e	electrical (dielectric) energy density
E_B	nominal stored battery energy	V	volume of spherical particle
E_i	incident electric field	W_B	battery subsystem weight
E_t	transmitted electric field	W_{PL}	payload subsystem weight
H_i	incident magnetic field	W_{PR}	propulsion subsystem weight
H_t	transmitted electric field	W_S	structure subsystem weight
k_s	piezoelectric coupling coefficient for sensing	W_m	mechanical (strain) energy density
k_a	piezoelectric coupling coefficient for actuation	α	conductivity exponent
k_c	electrical conductivity of composite	η	crack healing efficiency
k_f	electrical or thermal conductivity of filler	η_B	efficiency factor for battery
k_m	electrical or thermal conductivity of matrix	η_P	propeller efficiency
$K_{Ic_{healed}}$	Mode I fracture toughness for healed specimen	ρ	air density
$K_{Ic_{virgin}}$	Mode I fracture toughness for virgin specimen	φ	concentration of carbon nanotubes
$P_{c_{healed}}$	critical fracture load for healed Mode I fracture specimen	φ_c	critical concentration of carbon nanotubes, or percolation threshold
$P_{c_{virgin}}$	critical fracture load for virgin Mode I fracture specimen		
S	wing planform area		

and the objective of this paper is to address this need. The emphasis of the publications surveyed will be on the mechanics aspects, although the multidisciplinary nature of the topic will lead to the inclusion of some publications on relevant disciplines such as materials science, thermodynamics, and electronics. In addition, the vast majority of the surveyed articles deal with polymer composites, and by definition, a multifunctional material must be a composite. Due to the large number of articles involved, and the lack of electronic access to many conference proceedings, the emphasis of this review is on the more accessible refereed journal articles. It was not practical to cover all of these articles, and since some articles had already been covered by previous related review articles, an attempt was made to select representative articles in each of the relevant categories. According to Fig. 1, most of the relevant articles have been published since 2000, so that is the focus of this review.

The increased interest in multifunctional materials and structures is driven by the need for the development of new materials and structures that simultaneously perform (a) multiple structural functions, (b) combined non-structural and structural functions, or (c) both. One example of a multifunctional structure of type (a) would be a composite structure that has high strength, high stiffness, high fracture toughness and high damping. An example of

type (b) would be a load-bearing structure that has the capability of providing its own noise and vibration control, self-repair, thermal insulation, and energy harvesting/storage, whereas an example of type (c) would be a structure combining the functions of both type (a) and type (b). Most of the recent developments in multifunctional materials and structures tend to be of type (b).

Multifunctional materials are necessarily composite materials, and the strong growth in the use of composites has been greatly influenced by multifunctional design requirements. The traditional approach to the development of structures is to address the load-carrying function and other functional requirements separately, resulting in a suboptimal load-bearing structure with add-on attachments which perform the non-structural functions with the penalty of added weight. Recently, however, there has been increased interest in the development of load-bearing materials and structures which have integral non-load-bearing functions, guided by recent discoveries about how multifunctional biological systems work.

Due to the interdisciplinary nature of multifunctional materials and structures, and the need to avoid duplication in the current review, it is appropriate to cite several relevant previous review articles. For example, Baur and Silverman [1] reviewed the challenges and opportunities in multifunctional nanocomposite aerospace structures, while Ye et al. [2] reviewed developments in the application of artificial intelligence to functionalize composite airframes. By definition, a multifunctional material must be a composite, and it is becoming increasingly apparent that nanostructured composites can produce and/or enhance multifunctionality in ways that conventional composites could not. For example, Thostenson et al. [3] and Chou et al. [4] reviewed recent advances related to the science and technology of carbon nanotubes and their composites; Breuer and Sundararaj [5] reviewed recent studies on polymer/carbon nanotube composites; Li et al. [6] surveyed the recent advances related to the use of carbon nanotubes and their composites as sensors and actuators, while Gibson et al. [7] reviewed recent publications dealing with vibrations of carbon nanotubes and their composites, and Sun et al. [8] reviewed articles dealing with various types of energy absorption in nanocomposites. With the addition of very small amounts of carbon nanotubes, non-conducting polymers and polymer composites can be transformed to conducting materials, thus enhancing their multifunctionality. Accordingly, Bauhofer and Kovacs [9] have re-

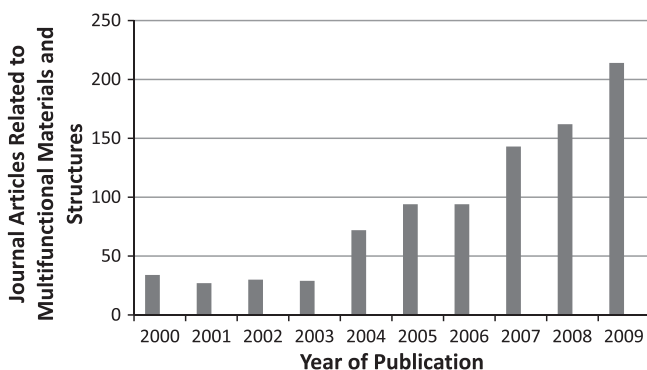


Fig. 1. Recent English language refereed journal publications related to multifunctional materials and structures. Data collected from Engineering Village® web-based information service.

viewed relevant research on electrical percolation in carbon nanotube polymer composites. Modeling and analysis of functionally graded materials (FGM) have been reviewed by Birman and Byrd [10]. The field of structural health monitoring (SHM) is highly relevant here, and several review articles have appeared recently. Montalvao et al. [11] reviewed vibration-based SHM of composite materials, while a similar review with emphasis on composite delamination identification had been published earlier by Zou et al. [12]. Recent developments in self-healing polymeric materials were reviewed by Wu et al. [13]. Articles on energy harvesting for sensor networks in SHM were reviewed by Park et al. [14]. Piezoelectric materials are often utilized for energy harvesting, and publications on this topic have been reviewed by Sodano et al. [15], Anton and Sodano [16], and Cook-Chennault et al. [17]. Closely related to SHM is the study of shape memory polymers (SMP), and reviews of recent advances in SMP have been published by Ratna and Karger-Kocsis [18]. Gibson et al. [19] edited the Proceedings of the 2008 SAMPE Fall Technical Conference entitled “Multifunctional Materials: Working Smarter Together”. Lau et al. [20] have archived selected papers from the 2008 International Conference on Multifunctional Materials and Structures (MFMS 08), which was held in Hong Kong.

2. Multiple structural functions

2.1. Composite structural materials

Among the most important structural functions that a system can provide are stiffness, strength, fracture toughness, ductility, fatigue strength, energy absorption, damping, and thermal stability. Although structural weight is not a function, it is an extremely important design consideration which has driven more designs towards lightweight composite materials in recent years. With conventional structural materials, it has been difficult to achieve simultaneous improvement in multiple structural functions, but the increasing use of composite materials has been driven in part by the potential for such improvements. For example, it has been shown that simultaneous improvements in vibration damping and fracture toughness in composite laminates are made possible by incorporating polymeric interleaves between the composite laminae [21]. However, this is only true if the interleaf thickness is less than a critical value – further increases in interleaf thickness cause the fracture toughness to drop off while the damping keeps increasing.

The use of nanoreinforcements in polymer composites has produced unprecedented improvements in mechanical properties of the composites. Koratkar et al. [22] measured greater than 1000% increases (Fig. 2) in the loss modulus of polycarbonate (PC) without significant reductions in the storage modulus when the PC was enhanced by 2 wt.% of single-walled carbon nanotubes (SWNTs). It was hypothesized that frictional sliding at the SWNT/PC interfaces was the reason for the enhanced energy dissipation. This hypothesis is supported by the analysis of Zhou et al. [23], who developed a model for the frictional sliding damping mechanism based on interfacial “stick-slip” frictional motion between the nanotubes and the polymer matrix. Rajoria and Jalili [24] reported that multi-walled carbon nanotubes (MWNTs) were more effective than SWNTs in improving damping of epoxy, but there was no significant effect on the storage modulus. Another way to incorporate the improved damping associated with nanotube reinforcement is to embed nano-enhanced polymer film sub-layers within a multifunctional composite laminate [25,26].

By mixing silica microparticles and epoxy in the right proportions, it is possible to simultaneously increase strength and modulus of the resulting composite while reducing its coefficient of

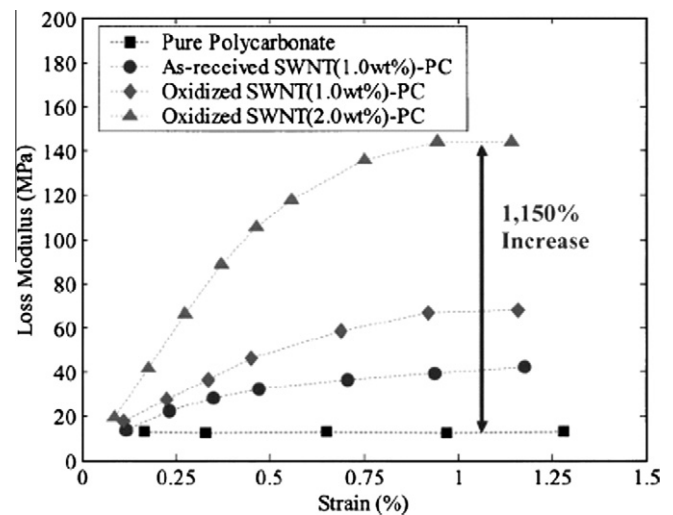


Fig. 2. Loss moduli for pure PC and several SWNT/PC nanocomposites at different strain levels. Reprinted with permission from [22]. Copyright 2005, American Institute of Physics.

thermal expansion (CTE) [27]. These are all desirable changes, but if the volume fraction of silica is increased too much, the strength will start to drop due to particle agglomeration, poor particle dispersion and reduced silica/epoxy interfacial strength. Even with composites, it is not always possible to simultaneously improve several properties – in some cases, modifications to composites lead to major improvements in some properties while causing minor reductions in other properties. For example, the incorporation of rubber microparticles in the epoxy matrix of a glass fiber reinforced epoxy composite improved the tensile fatigue life of the composite by a factor of three while causing only a 5.2% reduction in the tensile strength and a 12.7% reduction in the elastic modulus [28].

2.2. Hybrid multiscale structural composite materials

There are increasing reports in the literature that significant improvements of multiple structural functions can be achieved with new hybrid multiscale composites which incorporate nanoscale reinforcements as well as conventional micron scale fiber or particle reinforcements. For example, while fiber-dominated properties (i.e., longitudinal tensile strength and elastic modulus) of conventional unidirectional polymer composites with micron size fiber reinforcements are excellent, the corresponding matrix-dominated transverse tensile strength and longitudinal compressive strength properties are often poor. However, these traditionally poor properties can be significantly improved by (a) replacing the neat resin polymer matrix with a nanocomposite matrix (see Fig. 3 from Vlasveld et al. [29]), and/or by (b) growing nanoreinforcements like carbon nanotubes on the surface of the fibers (see Fig. 4 from Zhao et al. [30]).

In one example of approach (a), Uddin and Sun [31] reported that when a silica nanoparticle-enhanced epoxy was used as the matrix material in a unidirectional E-glass/epoxy composite, the longitudinal compressive strength and modulus were both significantly improved. Minimization of particle agglomeration and resulting improved dispersion of silica nanoparticles in the epoxy matrix due to the use of a sol-gel process based on the use of organosilicasol (colloidal silica in organic solvent) is believed to be the primary reason for the improvements. More recent research by the same authors extended the approach to hybrid multiscale composites containing not only the silica nanoparticles from the sol-gel process but alumina nanoparticles and carbon nanofibers

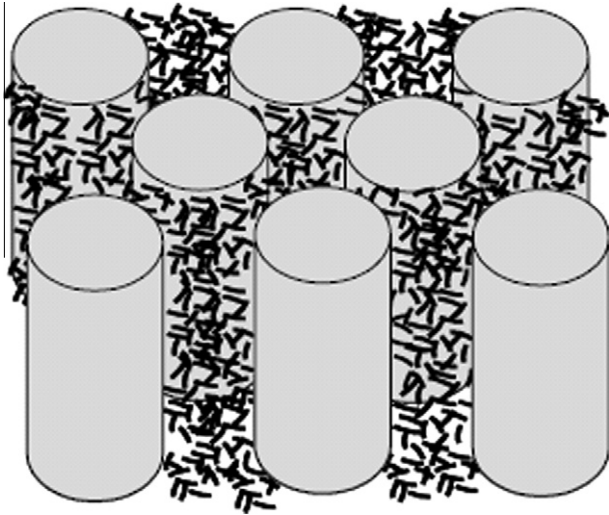


Fig. 3. Nanoparticle reinforcement of the matrix in a unidirectional fiber composite. Reprinted from [29] with permission from Elsevier.

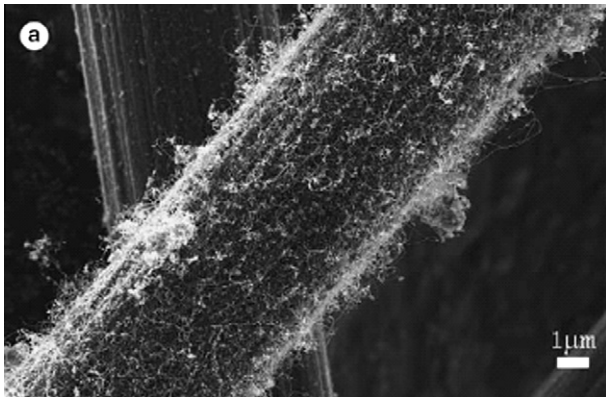


Fig. 4. Multi-walled carbon nanotubes grown on the surface of carbon fibers. Reprinted from [30] with permission from Elsevier.

(CNF) in an epoxy matrix [32]. As shown in Figs. 5–7, simultaneous improvements of at least 30% in modulus, strength and strain at break are possible with several types of these hybrid nanocomposites. Similarly, Liu et al. [33] and Zhang et al. [34] found that Young's modulus, tensile strength and fracture toughness of epoxy all simultaneously improved with the addition of sol-gel-formed nanosilica particles, and that the dispersion of the particles was excellent. Manjunatha et al. [35] observed that the addition of 10 wt.% sol-gel-formed nanosilica to the epoxy matrix resulted in simultaneous improvements of 4.4% in tensile strength, 7.4% in tensile modulus and a factor of 2–3 in tensile fatigue life of a glass fabric-reinforced epoxy composite. The presence of the nanoparticles was believed to suppress matrix cracking and reduce delamination growth rate, thus improving the fatigue life. Since hybrid multiscale composites typically have reinforcement sizes ranging from the micron scale to the nano scale, it is essential to understand the effects of particle size on the resulting composite properties. Important observations regarding such effects were reported by Cho et al. [36], who measured modulus and strength of vinyl ester polymer matrix composites containing spherical alumina particles or glass beads, with particle sizes ranging from 0.5 mm down to 15 nm. It was found that the Young's modulus was not affected by varying particle sizes in the micron range, but as the particle size was reduced in the nano range, the Young's modulus increased with decreasing particle size. The tensile strength increased with

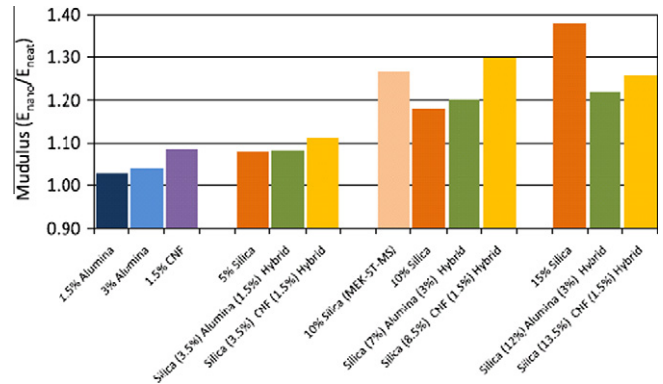


Fig. 5. Flexural moduli of different nanocomposites at various particle loadings. Reprinted from [32] with permission from Elsevier.

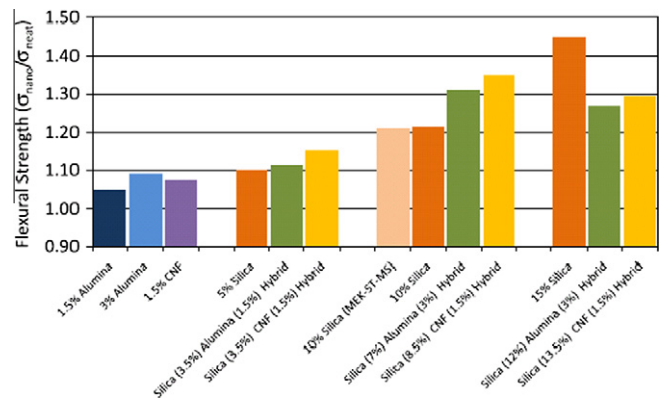


Fig. 6. Flexural strengths of different nanocomposites at various particle loadings. Reprinted from [32] with permission from Elsevier.

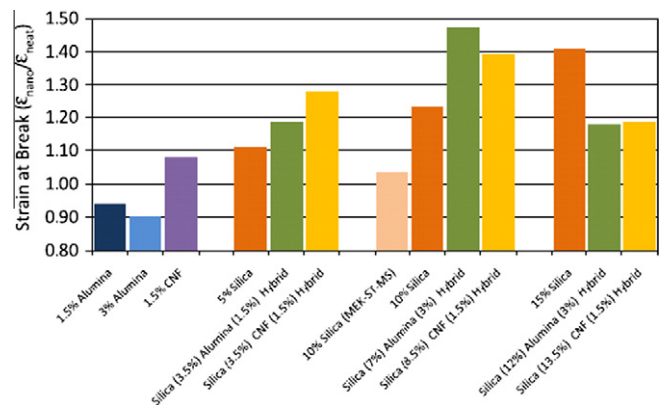


Fig. 7. Flexural strains at break of different nanocomposites at various particle loadings. Reprinted from [32] with permission from Elsevier.

decreasing particle sizes in both micron and nano ranges as long as particle agglomeration was avoided. Cho and Sun [37] later used molecular dynamics simulation to show that if the polymer–nanoparticle interaction strength is greater than the polymer–polymer interaction strength, the polymer density near the polymer–nanoparticle interface and the Young's modulus of the nanocomposite both increase significantly with reduced particle size. More research is needed about particle size effects on both structural and non-structural properties of nanocomposites and hybrid multiscale composites. This is particularly true for analytical modeling, since most of the publications to date involve experimental work.

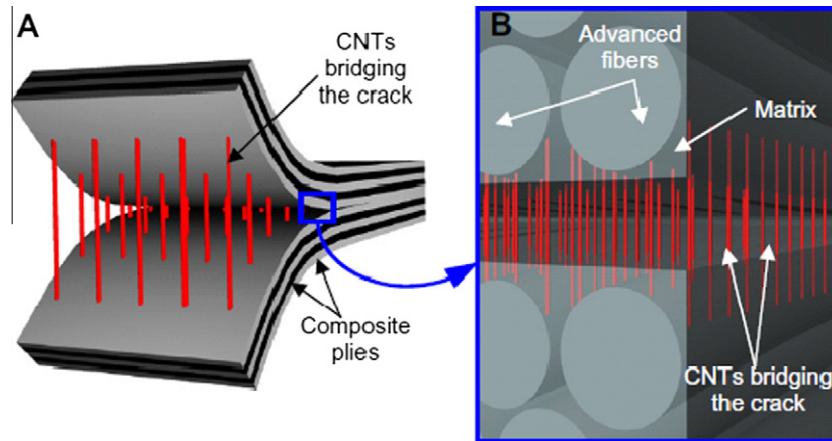


Fig. 8. Use of aligned CNT forests to strengthen interlaminar region in composite laminates. Reprinted from [41] with permission from Elsevier.

Approach (b) which involves the growth of nanotubes on the surfaces of micron-sized fibers has also been the subject of numerous investigations. Thostenson et al. [38] grew carbon nanotubes (CNTs) on the surface of carbon fibers using chemical vapor deposition (CVD), then conducted single fiber fragmentation tests of the modified carbon fibers in an epoxy matrix to determine the fiber/matrix interfacial shear strength. It was found that the interfacial shear strength of the modified carbon fibers was 15% greater than that of the baseline carbon fibers. Veedu et al. [39] also used CVD to grow aligned CNT forests perpendicular to the surface of 2D woven SiC fabric cloth consisting of micron size SiC fibers. The fabrics were then infiltrated with epoxy resin and stacked to form a 3D composite. Compared with the baseline composite, the 3D composite was found to exhibit simultaneous and significant improvements in the Mode I and Mode II fracture toughnesses, the flexural modulus, the flexural strength, the flexural toughness, the coefficient of thermal expansion, the thermal conductivity and the electrical conductivity. This is a true multifunctional composite combining structural and non-structural functions, and will be discussed further in the next section. Further studies and applications of aligned CNT forests to conventional fiber composites have been reported by Wardle and his colleagues [40–44], who focused on the use of the aligned CNT forests to improve interlaminar strength and toughness. These are major concerns about conventional composite laminates because of the weak matrix resin-rich regions that exist between the composite laminae. As shown in Fig. 8, vertically aligned CNT forests can bridge and strengthen this interlaminar region [41]. More specifically, the authors reported that the CNT modified interfaces increased the Mode I interlaminar fracture toughness of aerospace grade carbon/epoxy laminates by a factor of 1.5–2.5 and the corresponding Mode II value by a factor of 3. Analytical modeling of fracture toughness of the CNT-modified laminates based on the crack closure technique for fiber bridging was reported later in [43]. The so-called “fuzzy fiber” (CNTs grown on carbon fibers) concept applied to composite laminates can provide both interlaminar and intralaminar reinforcement as illustrated in Fig. 9 [44].

3. Integrated structural and non-structural functions

As indicated in the previous section, the development of nanocomposites and hybrid multiscale composites containing both conventional micron level reinforcements and nano level reinforcements has made it possible to achieve simultaneous improvements in not only multiple structural functions, but multiple non-structural functions as well. This section focuses on several

important non-structural functions, including electrical and/or thermal conductivity, sensing and actuation, energy harvesting/storage, self-healing capability, electromagnetic interference (EMI) shielding, recyclability and biodegradability.

3.1. Electrical and/or thermal conductivity

Among the most important non-structural functions that a structure may need are electrical and thermal conductivity, but the most widely used composites have polymer matrix materials, which are typically poor conductors. One very important application of polymer composites where electrical conductivity is required is in aircraft structures, where non-conducting structures may be damaged by lightning strikes. Here, conductive polymer nanocomposites are being investigated as possible replacements for non-conducting polymer matrix materials. This would eliminate the need for add-on metallic conductors, which are too heavy and may be difficult to repair [45]. Enhanced thermal conductivity of composites is important for cooling of electronic circuits and propulsion systems. The structural advantages of nanocomposites have already been summarized in the previous section, and there is abundant evidence in the literature of simultaneous improvements in mechanical and electrical properties of nanocomposites [46–49].

It turns out that very small concentrations of carbon nanotubes or other conducting nanoreinforcements in polymers lead to disproportionately large improvements in the electrical conductivity of the nanocomposite. For example, Fig. 10 shows that the electrical conductivity of CNT/epoxy nanocomposites increases by nearly 6 decades when the CNT concentration is increased by only 2 decades [9]. The “percolation threshold”, ϕ_c , which is the CNT concentration in the polymer that characterizes the insulator–conductor transition, is only 0.04 wt.% in this case. Percolation theory accurately describes this transition by equation

$$k_c = (\phi - \phi_c)^\alpha \quad (1)$$

Sandler et al. [50] reported ultra-low percolation thresholds as low as 0.0025 wt.% for aligned MWNT/epoxy nanocomposites. The percolation threshold for CNTs in polymer matrix materials is so low because the extremely high aspect ratios of CNTs make it relatively easy for a contiguous conducting path or percolation network to form along the tangled CNTs in the insulating polymer matrix. Fig. 11 from Li et al. [51] shows how the percolation threshold decreases with increasing CNT aspect ratio. Since processing typically breaks up CNTs into shorter lengths, it is important to develop processes which preserve the high aspect ratios of CNTs, thus

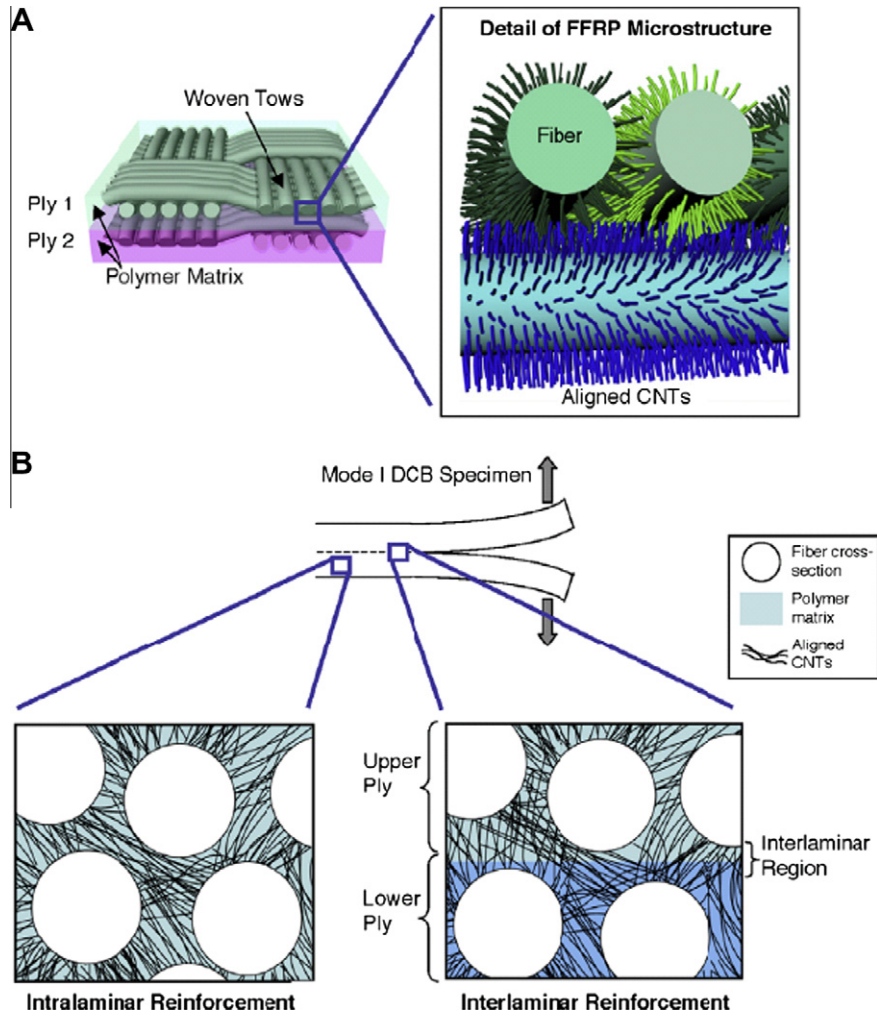


Fig. 9. Illustration of fuzzy fiber reinforced plastic (FFRP). (A) Radially aligned CNTs grown on advanced fiber cloth (B) CNT intralaminar and interlaminar reinforcement. Reprinted from [44] with permission from Elsevier.

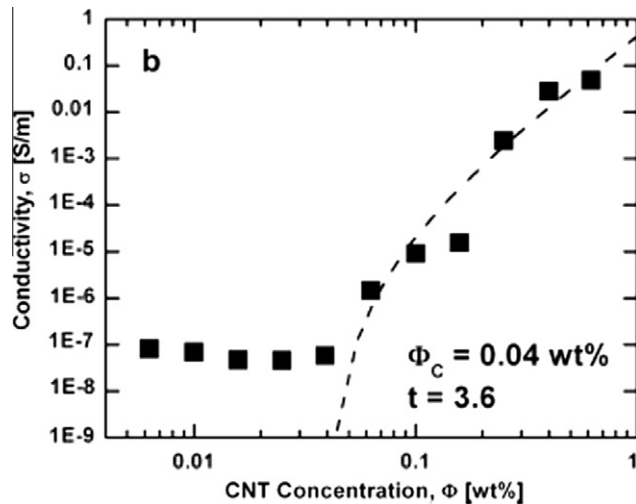


Fig. 10. Electrical conductivity of CNT/epoxy nanocomposites at various CNT concentrations. Percolation threshold is 0.04 wt%. Reprinted from [9] with permission from Elsevier.

insuring the desired low percolation thresholds. Thostenson et al. [52] reported that a 3-roll mill process induces intense shear mixing of a CNT/vinyl ester nanocomposite while preserving the high aspect ratios of the CNTs. Photomicrographs show that CNTs are wavy, but most analytical models are based on the assumption that

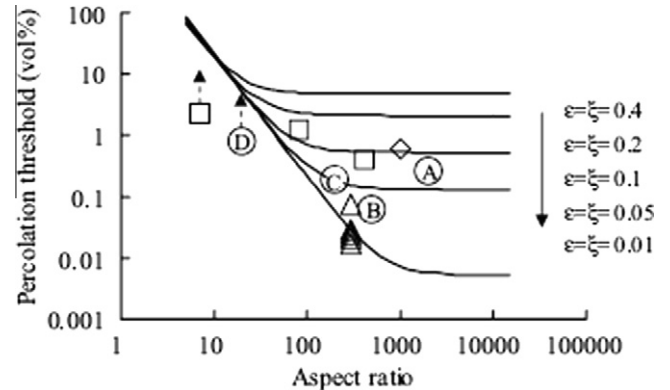


Fig. 11. Effect of CNT aspect ratio on percolation threshold for CNT nanocomposites with varying dispersion states. Copyright Wiley-VCH verlag GmbH & Co. KGaA. Reproduced from [51] with permission.

the CNTs are straight. The importance of waviness was confirmed by Li et al. [53], who used Monte Carlo simulations to show that the electrical conductivity of composites with wavy nanotubes is less than that of composites with straight nanotubes.

Although the thermal conductivity of CNT/polymer nanocomposites increases with the increasing CNT concentration, the increase is gradual and there is no sharp insulator–conductor transition or percolation threshold as in electrical conductivity [54]. According to Shenogina et al. [54], the difference lies in the

conductivity ratio k_f/k_m . For thermal transport, even for very conductive, high aspect ratio CNTs, k_f/k_m is only about 10^4 , but for electrical transport, k_f/k_m can be as much as 10^{12} – 10^{16} . As a result, electrical transport is dominated by the percolating CNT network, whereas thermal transport is strongly influenced by the polymer matrix. Although there is a lack of a percolation threshold for thermal conductivity in CNT/polymer composites, small amounts of CNTs still lead to disproportionate increases in composite thermal conductivity. For example, Biercuk et al. [55] found that 1 wt.% SWNTs in epoxy resulted in a 125% increase in thermal conductivity at room temperature, Bonnet et al. [56] measured a 55% increase in thermal conductivity for a 7 wt.% SWNT/PMMA composite, and Kim et al. [57] reported a 57% increase in thermal conductivity by adding 7 wt.% MWNTs in phenolic resin. However, since higher filler loadings are required to create significant improvements in thermal conductivity of polymers, this may lead to processing issues. For example, Ganguli et al. [58] were able to achieve a 28-fold increase in thermal conductivity of epoxy by adding 20 wt.% chemically functionalized and exfoliated graphite flakes, but graphite loading levels greater than 4 wt.% were found to increase the viscosity of the mixture beyond the desirable processing window for the vacuum-assisted-resin-transfer molding (VARTM) process. In some applications, only small amounts of CNTs are needed to produce acceptable thermal conductivity. For example, Sihn et al. [59] found that the through-thickness thermal conductivity of epoxy adhesive joints can be increased by several orders of magnitude when aligned MWNT “nanograss” is incorporated in the epoxy adhesive (Fig. 12).

3.2. Sensing and actuation

Sensing and actuation are two closely related non-structural functions, and in many cases, the same material or device can be used for both functions, as well as for other functions like energy harvesting/storage and structural health monitoring. Several recent review articles have already covered much of the recent research related to sensors and actuators that can be used in multifunctional structures. For example, Li et al. [6] and Gibson et al. [7] have reviewed recent research related to sensors and actuators based on carbon nanotubes and their composites. A review article by Ratna and Karger-Kocsis [18] covers recent research on shape memory polymers which have potential applications as sensors and/or actuators. Piezoelectric materials such as lead zirconate titanate (PZT), polyvinylidene fluoride (PVDF) and aluminum nitride (AlN) can be embedded in structures for sensing and actuation, as they naturally possess the required electromechanical coupling. The effectiveness with which a piezoelectric material converts applied mechanical energy to electrical energy (i.e., for sensing or energy harvesting) is characterized by the piezoelectric coupling coefficient [60]

$$k_s = \sqrt{\frac{U_e}{W_m}} \quad (2)$$

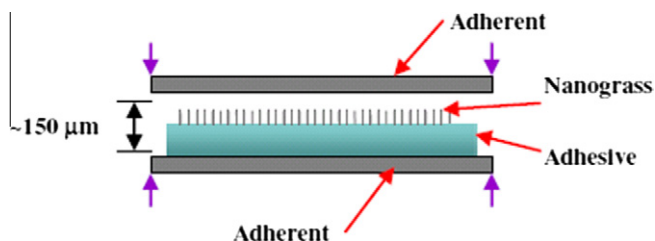


Fig. 12. Nanograss-enhanced polymer adhesive joint for improved through-thickness thermal conductivity. Reprinted from [59] with permission from Elsevier.

and the corresponding piezoelectric coupling coefficient for conversion of electrical energy to mechanical energy (i.e., for actuation) is

$$k_x = \sqrt{\frac{W_m}{U_e}} \quad (3)$$

The most widely used forms of piezoelectric materials are wafers [61] and thin films [62], and numerous publications have dealt with them over many years. Piezoelectric microelectromechanical systems (MEMS) for sensing and actuation have been the subject of extensive research, and the state-of-the-art in this area has been very recently reviewed by Tadigadapa and Mateti [63]. So in order to avoid duplication, we focus here on other important recent developments in structurally integrated sensing and actuation in load-bearing multifunctional composite structures.

Although not as common as piezoelectric wafers or thin films, piezoelectric fibers have been investigated as possible active components of multifunctional fiber-reinforced composites. The earliest reports of piezoelectric fiber composites (PFC) were apparently published by Hagood and Bent [64] and Bent et al. [65], who embedded micron sized piezoelectric fibers in an epoxy matrix to which PZT powder had been added to reduce the fiber/matrix dielectric mismatch. The PFC laminate was built up from PFC laminae embedded between conventional graphite/epoxy laminae and interlaminar electrodes which applied the electric field required for actuation. Good agreement was obtained between measured electrically-induced deformations and those predicted by a modified Classical Lamination Theory which included actuator-induced stress terms [65]. More recently developed hollow piezoelectric fibers [66,67] offer the advantage of lower operating voltage and a broader choice of possible matrix materials compared with solid cross-section piezoelectric fibers. Brei and Cannon [67] investigated the hollow piezoelectric fiber concept in Fig. 13, with emphasis on the effects of three key design parameters (matrix/fiber Young's modulus ratio, aspect ratio of the individual fibers, and overall active composite volume fraction) on the performance, manufacturing and reliability of the active composites. In Fig. 13, in the actuation mode, radial poling of the piezoelectric fiber results in longitudinal deformation of the fiber, while in the sensing mode, longitudinal deformation results in radial electrical output. Still more recently, Lin and Sodano [68,69] developed piezoelectric structural fibers consisting of conductive structural fibers such as

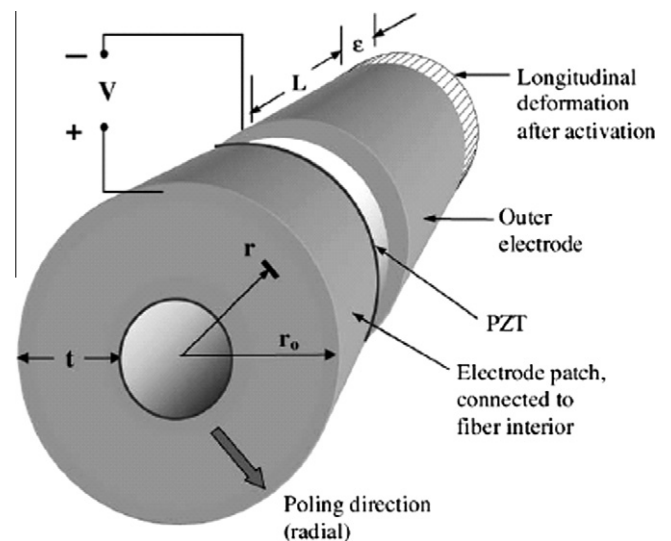


Fig. 13. Hollow piezoelectric fiber with radial poling and longitudinal actuation of the fiber. Reprinted from [67] with permission from Elsevier.

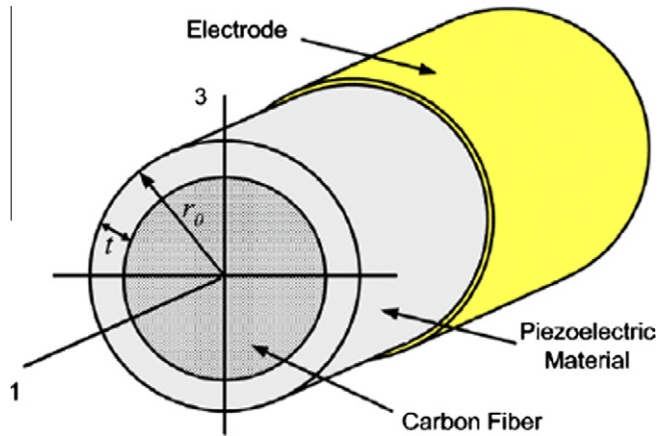


Fig. 14. Multifunctional piezoelectric structural fiber. Reprinted from [68] with permission from Elsevier.

carbon coated with a piezoelectric interphase layer and an outer electrode layer (Fig. 14). As with the hollow piezoelectric fiber in Fig. 13, radial poling results in longitudinal actuation of the fiber and so forth. Finite element models of piezoelectric structural fiber/polymer matrix composites such as the one in Fig. 15 showed that the electromechanical coupling coefficients available from such composites can be as high as 65–70% of the corresponding coupling coefficient for the fiber itself, and that piezoelectric structural fiber composites are suitable for vibration control, damping, energy harvesting or structural health monitoring.

The capability of simultaneous control of stiffness and damping is a significant advantage of a new class of materials known as magnetorheological elastomers (MRE), which consist of conventional elastomers filled with micron-sized magnetizable particles such as iron. As reported by Fuchs et al. [70], an applied magnetic field of variable strength was used to continuously and rapidly control stiffness and damping of a polybutadiene elastomer filled with 3–7 μm diameter carbonyl iron particles. In this case, the optimum concentration of the iron particles for greatest improvement of damping and stiffness was found to be 60 wt.%, and other important variables which govern the stiffness and damping of MREs are the alignment of the magnetic particles and the temperature.

As indicated earlier, several recent review articles have dealt with the general area of structural health monitoring [11–14]. Here we will focus specifically on the use of embedded piezoelectric sensor/actuator networks for damage detection in composite structures due to its importance in the development of multifunctional structures. Lin and Chang [71] described the fabrication and initial validation testing of the Stanford-Multi-Actuator-Receiver-Transduction (SMART) Layer[®] concept (Fig. 16). This concept involves the use of printed circuit technology to produce a thin flexible, dielectric film with an array of networked piezoceramic actuators/sensors, which is embedded within a conventional composite laminate. It was shown that a conventional autoclave process and cure cycle can be used to fabricate carbon/epoxy composite laminates containing the SMART Layer[®], that the layer does not significantly degrade the mechanical behavior of the composite, and that by measuring the phase delay between the transmitted and received stress wave during the cure process, the state of cure can be monitored. Subsequent research [72] showed that such layers can be integrated into composite structures fabricated by RTM and filament winding processes, and that the concept can be applied to either active or passive sensing to monitor the health of the structure throughout its lifetime. Still more recently, Wu et al. [73] demonstrated the feasibility of an improved actuator/sensor network for damage detection in composite laminates based on the use of PZT actuators and fiber Bragg grating (FBG) fiber optic sensors instead of using PZTs for both actuating and sensing. The advantage of this approach lies in the decoupling of the signal transmission mechanisms and elimination of the signal crosstalk between actuator and sensor signals in the PZT actuator/sensor network. Other approaches to active sensor networks for damage detection in composite structures have been reported by Su et al. [74,75]. Reports on the use of artificial neural networks to analyze the data from the piezoelectric sensor networks and classify and locate the damage in composite structures have been published by Watkins et al. [76], Haywood et al. [77], and Yu et al. [78]. Similar systems have been adapted for control of smart laminated structures by Srivastava et al. [79].

Layer-by-layer (LbL) assembly, which involves sequential deposition of dissimilar thin films at the nanoscale, has made it possible to develop sensors that are capable of detecting multiple phenomena. For example, Loh et al. [80] used the LbL method to fabricate a carbon nanotube-polyelectrolyte multilayer composite material

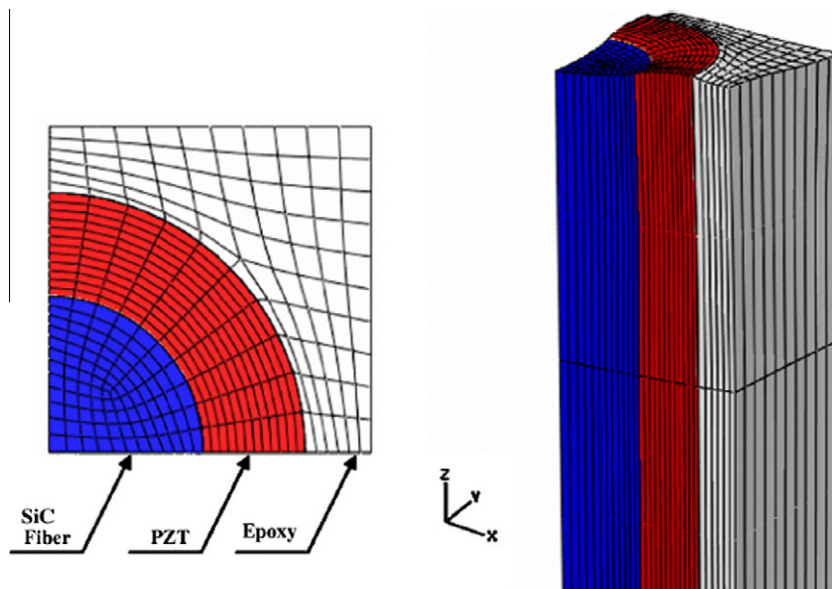


Fig. 15. Finite element model of piezoelectric structural fiber embedded in a polymer matrix. Reprinted from [68] with permission from Elsevier.

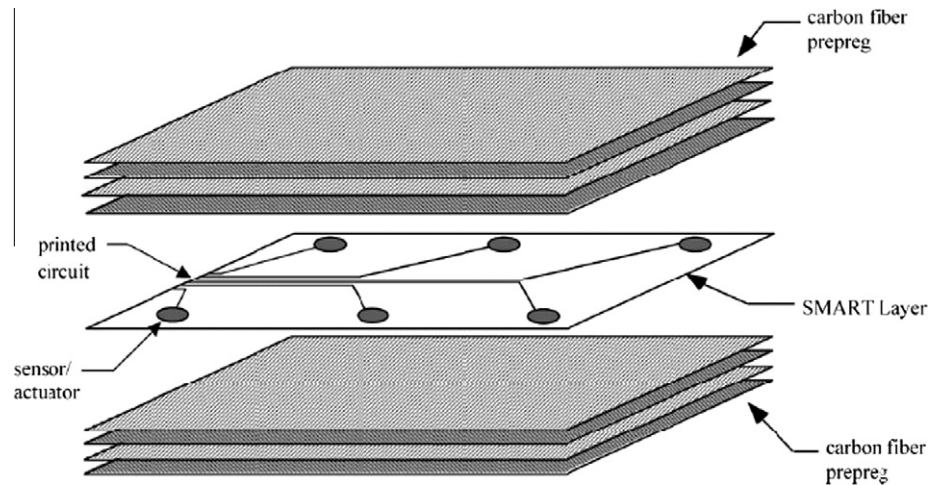


Fig. 16. Stanford-Multi-Actuator-Receiver-Transduction (SMART) layer concept of integrated sensor/actuator network in a composite laminate. Reprinted from [71] with permission from Elsevier.

for monitoring strain and corrosion. In this case, the concentration of carbon nanotubes determines the sensitivity to strain and the type of polyelectrolyte determines the sensitivity to pH. Deposition of such a LbL sensor on a miniature planar coil antenna results in a passive wireless sensor which does not require a battery power supply [81]. The LbL method can also be used to fabricate high strength multifunctional composites for biological implants, anti-corrosion coatings, and thermal/electrical interface materials [82,83]. Shape memory polymers also have great potential for use in sensors and actuators. This is particularly true for electroactive shape memory polymer composites containing conductive fillers [18].

3.3. Energy harvesting/storage

The basic idea behind energy harvesting/storage as related to multifunctional structures is to parasitically extract energy from the motion and/or deformation of a host structure and convert it to electrical energy which can be stored and used for other purposes. One popular application is to power small electronic devices such as wireless sensors for structural health monitoring. Several review articles have already been published on this subject [14–17], and since the discussion of sensors and actuators in the previous section is also highly relevant to energy harvesting, the emphasis in this section will be on recent developments in energy storage in load-bearing multifunctional structures.

The most common mode of energy harvesting involves the use of piezoelectric materials to convert mechanical deformations from vibrating structures such as beams and plates to electrical energy. It appears that Sodano et al. [84] were the first to report that the power output from a randomly vibrating piezoelectric material is capable of recharging a discharged nickel metal hydride battery. They also reported on the use of the piezoelectric output to charge a capacitor, but concluded that the capacitor discharge occurred too quickly for practical energy storage and that batteries provided more flexibility in use of the stored energy.

In a multifunctional structure, the battery should become part of the load-bearing structure. Pereira et al. [85,86] embedded thin film lithium energy cells within carbon/epoxy laminates to form energy storage structural composites. The lithium energy cells did not significantly change the strength and stiffness of the carbon/epoxy laminate, and the energy cells charged and discharged normally when the composite was mechanically loaded to as high as 50% of its ultimate tensile strength. Further integration was achieved by Kim et al. [87], who used a copper nano-inkjet-printed circuit on a polymer film to interconnect a thin-film solar module and a thin-film lithium-ion battery. The resulting film was embedded and co-cured within carbon/epoxy prepreg layers to fabricate an energy harvesting/storage laminate. The multifunctional laminate was then subjected to mechanical loading. As shown in Fig. 17, when the ink-jet-printed electrodes are thicker than 4 μm , they did not exhibit any significant resistance change up to the maxi-

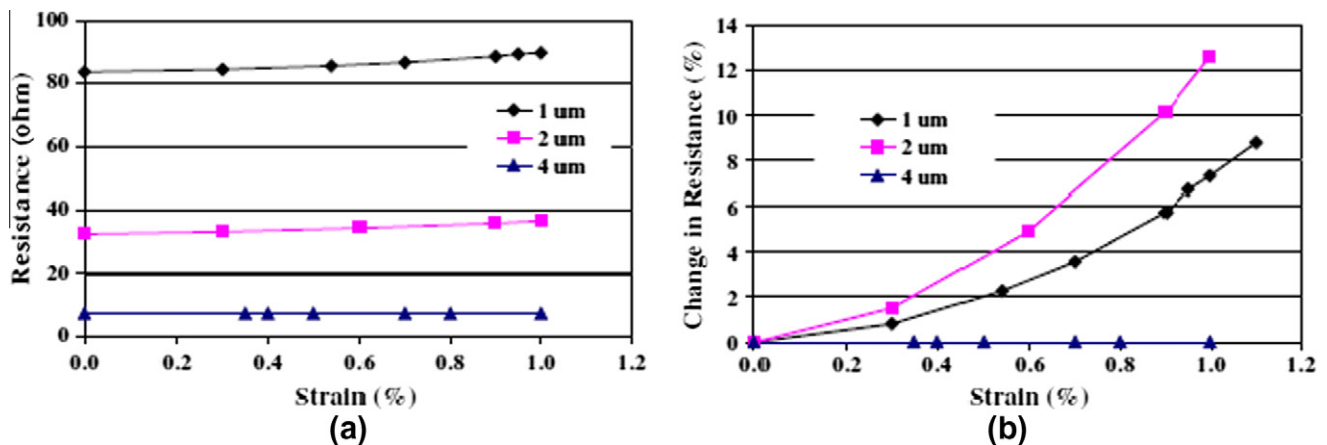


Fig. 17. Resistance of inkjet-printed 160 μm -wide electrode under static loading for several electrode thicknesses: (a) resistance and (b) percentage of resistance change. Reprinted from [87] with permission from Elsevier.

imum strain of 1%. Liu et al. [88] developed a new load/bearing structural battery in which the polymer cathode in a conventional polymer lithium-ion battery (Fig. 18) was replaced by a higher molecular weight, carbon nanofiber-reinforced polymer (Fig. 19), the organic liquid electrolyte was replaced with a solid-state polymer electrolyte and the separator region was reinforced with non-conducting fibers. Although this design represents a starting point, the tensile modulus of the battery was only about 3 GPa, and the energy density was low compared with that of a conventional lithium-ion battery, so further work is needed to develop a usable structural battery. Snyder et al. [89] investigated different polymer electrolyte formulations for multifunctional structural batteries ranging from highly conductive and structurally weak to poorly conductive and highly structural. As shown in Fig. 20, it was found that the electrical conductivity and the elastic modulus of the different formulations are inversely related, which makes it difficult to optimize both properties. In a separate paper, Snyder et al. [90] investigated the properties of commercial carbon fabric materials, carbon nanotube papers and nanofoam papers for possible use as anodes in multifunctional lithium-ion batteries. IM-7 and T300 PAN-based carbon fabrics yielded the best balance between electrochemical and tensile strength performance, whereas the pitch-based fabrics exhibited poor multifunctional performance. The nanofoam papers had the best electrochemical performance but the mechanical properties were poor.

Although structural integrated batteries are more practical for slower discharge over a longer period of time, structurally inte-

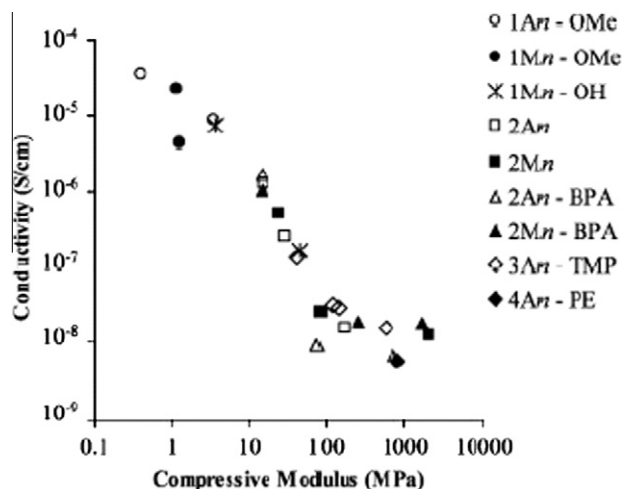


Fig. 20. Experimental data showing inverse relationship between electrical conductivity and compressive modulus for several polymer electrolytes for use in structural batteries. Reprinted from [89] with permission. Copyright 2007 American Chemical Society.

grated capacitors can provide energy storage for quick discharge at high energy levels. O'Brien et al. [91] compared stiffness and energy density of various structural capacitors. As shown in Fig. 21, conventional capacitors have high energy density but poor stiffness,

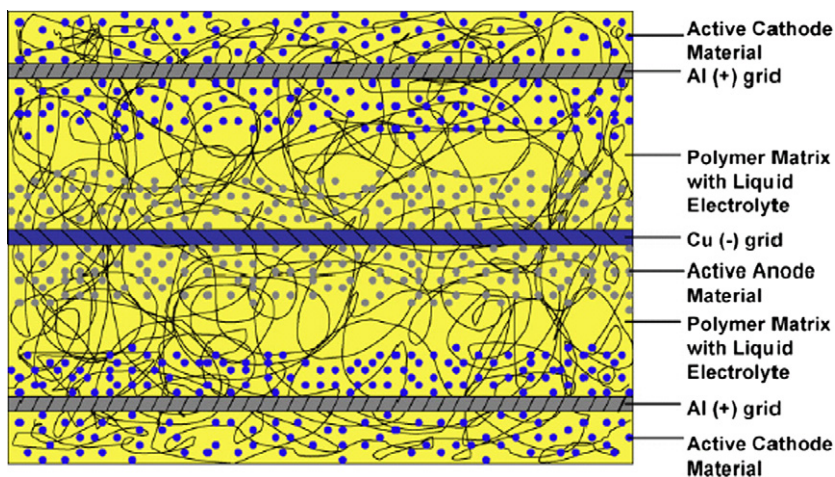


Fig. 18. Construction of conventional non-structural polymer lithium-ion battery. Reprinted from [88] with permission from Elsevier.

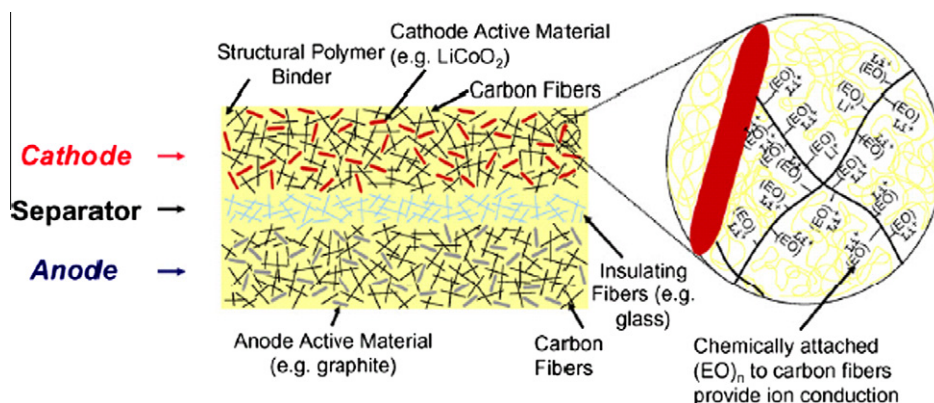


Fig. 19. Construction of new structural battery. Reprinted from [88] with permission from Elsevier.

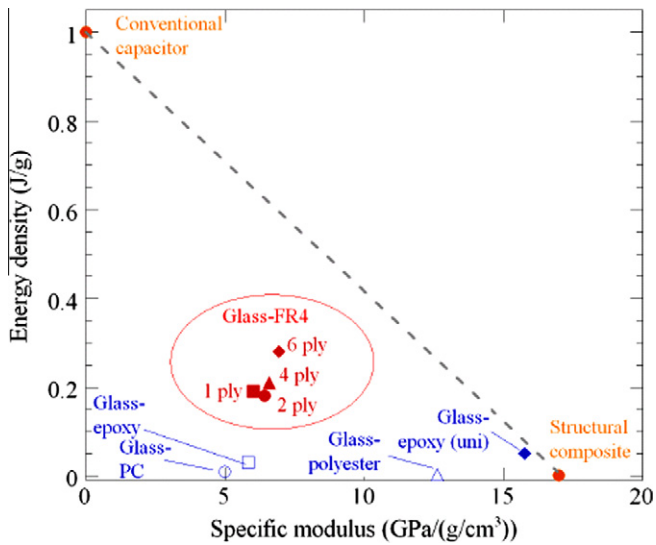


Fig. 21. Energy density and specific modulus of multifunctional structural capacitors. Dashed line represents design goal for true multifunctionality. Reprinted from [91] by permission of the Society for the Advancement of Material and Process Engineering (SAMPLE).

whereas structural composites have good stiffness but poor energy density. None of the materials evaluated met the design goal of multifunctional efficiency for system level weight savings shown by the dashed line in Fig. 21. In a continuation of this work, Baechle et al. [92] addressed design issues for improving multifunctional efficiency and scaling issues related to manufacturing. Luo and Chung [93] developed a high capacitance structural capacitor consisting of a carbon/epoxy laminate with a paper interlayer to reduce through-the-thickness conductivity, but the capacitor was not mechanically tested. Lin and Sodano [94] demonstrated that their previously developed SiC/BaTiO₃ piezoelectric structural fiber [69] could be used as a structural capacitor by taking advantage of the dielectric nature of the BaTiO₃ coating on the SiC fiber (i.e., the BaTiO₃ coating was employed as a cylindrical capacitor). Fibers with an aspect ratio of 0.23 were found to be the best for energy storage.

3.4. Self-healing capability

A truly autonomous multifunctional structure will be capable of healing itself when damaged, as a biological system would, and recent research has demonstrated the feasibility of such materials, particularly polymeric materials. A comprehensive review of publications in the area of self-healing polymeric materials has recently appeared [13], so only a few representative publications will be discussed here. White et al. [95] developed self-healing polymers and polymer composites based on the use of a microencapsulated healing agent and a catalyst for polymerizing the healing agent. As shown in Fig. 22, when damage causes cracks in the polymer, the cracks break open the microcapsules, causing the healing agent to leak into the crack by capillary action. The healing agent then reacts with the catalyst, causing polymerization that bonds the crack faces together. Mode I fracture toughness tests of virgin epoxy and self-healed epoxy specimens using the tapered double cantilever beam (TDCB) test in Fig. 23a showed that fracture load and corresponding fracture toughness for the self-healed specimens reached up to 75% of the corresponding values for the virgin uncracked specimens. The crack healing efficiency for the fracture toughness test is defined as

$$\eta = \frac{K_{Ic_{healed}}}{K_{Ic_{virgin}}} = \frac{P_{c_{healed}}}{P_{c_{virgin}}} \quad (4)$$

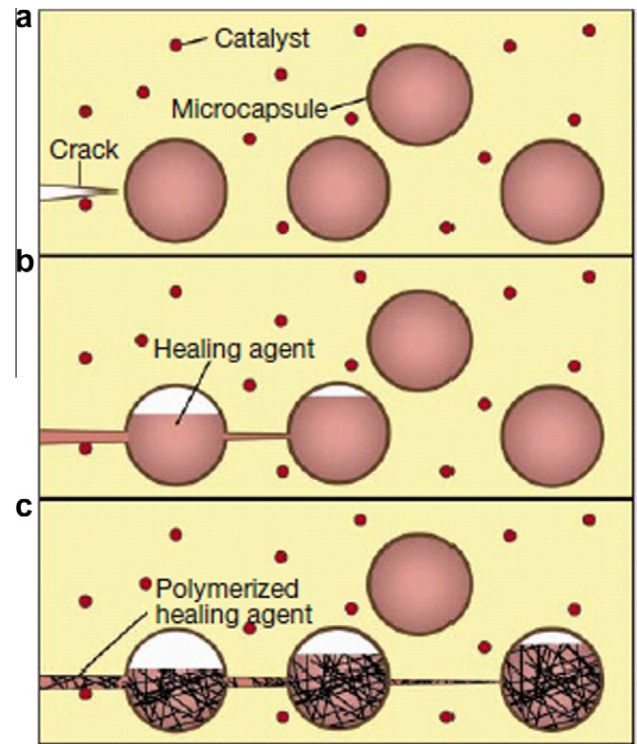


Fig. 22. Illustration of self-healing of cracks in polymers by the use of a microencapsulated healing agent and a catalyst for polymerizing the healing agent. Reprinted from [96] with kind permission from Springer Science+Business Media.

Further research on optimization of the microcapsule concentration and choice of catalyst led to crack healing efficiencies of over 90% ($\eta = 0.9$) in self-healed specimens and maximum healing efficiency was achieved within 10 h of the fracture event [96]. Still more recently, Caruso et al. [97] obtained complete recovery of virgin fracture toughness ($\eta = 1$) by replacing the original solvent healing agent in the microcapsules with epoxy-solvent microcapsules containing a mixture of epoxy monomer and solvent. As shown in Fig. 23b, the resulting load-displacement curves indicate full recovery of virgin fracture toughness. Related research by the same group has considered self-healing polymers under fatigue loading [98–100] and low-velocity impact loading [101], as well as the development of self-healing polymer coatings to provide effective corrosion protection for steel substrates [102], and the use of three-dimensional microvascular networks in the substrate beneath an epoxy coating to enable continuous delivery of healing agents for self-healing of repeated crack damage in the coating [103].

Other recent developments in self-healing polymer composites include the use of different methods of healing agent microencapsulation such as nanoporous silica capsules [104] and nanoporous glass fibers [105]. The use of self-healing polymers as the matrix material in carbon fiber-reinforced composites has also been considered by Williams et al. [106]. Yin et al. [107] found that the self-healing ability of woven glass fabric/epoxy composites containing healant microcapsules degraded with storage time. The likely cause is believed to be time-dependent diffusion of the epoxy monomer from the microcapsules following contraction of the microcapsules during the cure process. This degradation was found to be a self-limiting process as the leaked epoxy gradually cured and blocked the diffusion sites on the microcapsules, but it was concluded that further research is needed to improve the microcapsule designs and materials.

Most of the research on self-healing materials has been based on experimental work, and only a few publications have dealt with

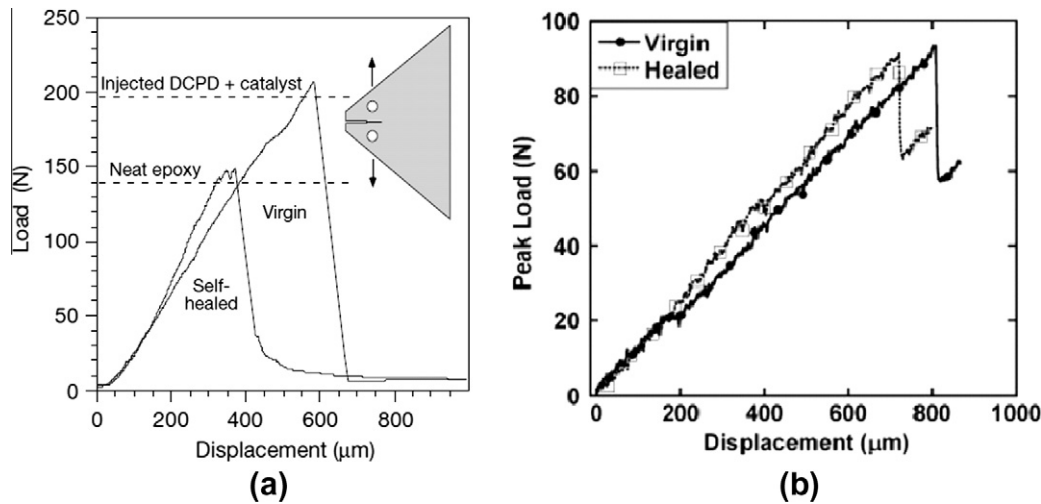


Fig. 23. Load–displacement curves for Mode I fracture toughness tests of virgin and self-healed specimens (a) microcapsules contain solvent healing agent only. Reprinted from [95] by permission from Macmillan Publishers Ltd, and (b) microcapsules contain a mixture of epoxy monomer and solvent Copyright Wiley-VCH verlag GmbH & Co. KGaA. Reproduced from [97] with permission.

analytical modeling of the self-healing process. Balazs [108] has briefly reviewed computational models for self-healing materials, while pointing out that the area is still in its infancy and that solutions will require the development of multidisciplinary methods involving models for fluid dynamics, structural mechanics, chemical reactivity, and phase transitions. Barbero et al. [109] have applied the principles of continuum damage mechanics to the case of self-healing composites, while Maiti et al. [110] and Geubelle and Maiti [111] employed an artificial crack closure approach involving cohesive modeling and a contact algorithm. Park et al. [112] used a conventional cure kinetics model and electrical resistance heating of the polymer matrix above the glass transition temperature to achieve self-healing of a carbon fiber/mendomer composite.

3.5. Electromagnetic interference (EMI) shielding

Electromagnetic interference (EMI) occurs when an undesirable disturbance due to electromagnetic conduction or radiation from an external source interferes with the operation of an electrical circuit. The usual solution to EMI is to protect the circuit with an EMI shielding material or structure, and the shielding effectiveness, SE, is defined in decibels (dB) as

$$SE = 20 \log \frac{E_t}{E_i} = 20 \log \frac{H_t}{H_i} \quad (5)$$

Electrically conducting metallic materials have excellent SE, but due to reduced weight and other desirable properties, non-metallic materials such as polymers and polymer composites are increasingly used to replace metals. SE is particularly important for multifunctional materials and structures which are typically based on polymer composites, and where both electrical and mechanical functions are typically involved. In order to achieve acceptable SE, the polymer must be either an intrinsically conducting polymer (ICP) or be filled with a conducting material such as carbon fibers or nanotubes or be coated with a conductive coating. Several recent review articles have discussed various aspects of EMI shielding, especially for polymers. Chung [113] reviewed publications on materials for EMI, Geetha et al. [114] surveyed recent research on methods and materials for EMI, while Wang and Jing [115] reviewed articles dealing with ICPs for EMI.

While ICPs such as polyaniline (PANI) and polypyrrole (PPY) are very effective for EMI shielding, their mechanical effectiveness

when used as matrix materials in multifunctional fiber composite structures is not clear. However, blends of ICPs such as PANI with established structural polymers like epoxy resins may be a more practical approach. Jia et al. [116] studied electrical conductivity of PANI/epoxy composites having different PANI morphologies. As shown in Fig. 24, the composites containing PANI wires had a lower percolation threshold than the composites containing PANI particles or PANI fibers. This is because the PANI wires have the highest aspect ratio and are able to more easily form continuous conductive networks within the non-conducting epoxy. As indicated in Section 3.1, the use of other high aspect ratio electrically conducting nanofillers in polymers is also an effective means of creating electrically conducting polymer composites, which in turn should be suitable for EMI shielding. For example, Huang et al. [117] and Al-Saleh and Sundararaj [118] have investigated the EMI shielding characteristics of carbon nanotube/polymer composites, while the EMI shielding properties of carbon nanofiber/polymer composites have been studied by Yang et al. [119]. A review of recent articles on conductivity and EMI shielding characteristics of vapor grown carbon nanofiber/polymer composites has been published by Al-Saleh and Sundararaj [120].

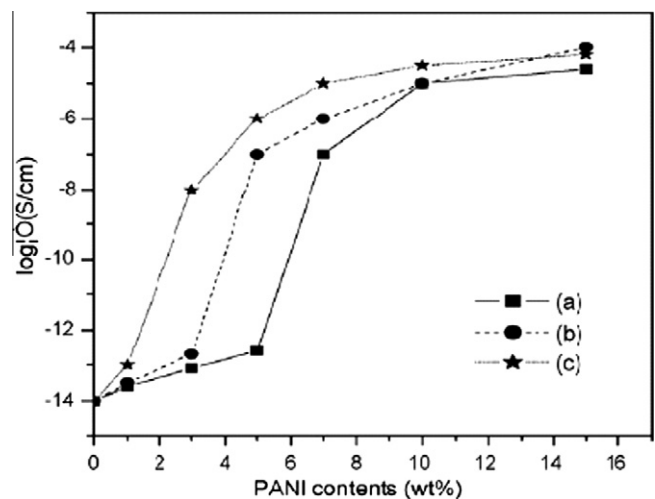


Fig. 24. Electrical conductivity for PANI/epoxy composites at different PANI contents and different PANI morphologies (a) PANI particles, (b) PANI fibers, and (c) PANI wires. Reprinted from [116] with permission from Elsevier.

3.6. Recyclability and biodegradability

As societal concerns about environmental impact, sustainability and renewable energy sources have increased in recent years, recyclability and biodegradability have taken on correspondingly important roles as non-structural functions of advanced materials. This is particularly true for polymers, polymer composites and nanocomposites. These are very active research areas, and a number of relevant review articles have already been published about these subjects, so the objective here will be limited to providing brief overviews of representative review articles.

Henshaw et al. [121], Pickering [122], Ramakrishna et al. [123], Vaidya and Chawla [124], and DeRosa et al. [125] have reviewed publications dealing with various recycling issues for polymer composite materials. Due to faster and simpler processing cycles for thermoplastic polymers, recycling of thermoplastic composites by processes such as injection or compression molding as “new” composites is easier than for thermoset matrix composites. More likely recycling scenarios for thermoset matrix composites are to either mechanically recycle them by grinding them into small particles and using them as fillers in “new” composites, or to thermally recycle them by using intense heat to break down the composite into reusable components. Possible loss of mechanical properties during recycling is a significant issue, and methods of improving properties of mechanically recycled thermoplastics have been described by Tall et al. [126]. Recycling of composites containing nanoparticles, nanofibers or nanotubes and other nanowaste requires special consideration due to potential toxicity, carcinogenicity, and other health-related concerns, as discussed in the review article by Bystrzejewski-Piotrowska et al. [127].

If a composite is to be biodegradable, natural fibers and polymer matrix materials made from renewable resources are obviously of great interest. Research on natural fibers such as jute, ramie, flax and sisal and their composites has been reviewed by Nabi Saheb and Jog [128], Bogoeva-Gaceva et al. [129], Mishra et al. [130], Yan et al. [131], Eichhorn et al. [132], and Cheung et al. [133]. Typically, the strength and modulus values for natural fibers are well below those of conventional structural fibers such as glass, but due to their low densities, the specific moduli of natural fibers are as good or better than that of glass. Publications dealing with the development of polymers from renewable resources have been surveyed by Yu et al. [134], and Raquez et al. [135], while test methods for characterizing biodegradability of polymeric materials have been reviewed by Gu and Gu [136]. Natural protein-based materials have received considerable attention for biomedical applications, as indicated by Kumar et al. [137]. Biodegradable bio-based “green” nanocomposites consisting of matrix materials such as cellulosic plastics, corn-derived plastics, or plastics made from bacterial sources reinforced by nanoclay particles have been the subject of extensive recent research, as reviewed by Pandey et al. [138], and Ray and Bousmina. [139]. One drawback to “green” composites is that their mechanical properties are typically more sensitive to hygrothermal conditions than those of conventional composites. For example, absorbed moisture has been found to significantly degrade the mechanical properties of hemp fiber composites [140], and flax fiber composites are strongly affected by elevated temperatures [141]. However, special chemical treatments for natural fibers can reduce their sensitivity to hygrothermal conditions [142].

Most of the publications listed so far involve experimental work, and there is a need for development of more analytical models to complement the experiments. Analytical models are needed not only to help in interpreting the experimental results, but in optimizing the multifunctional material or system for specific applications. Obviously, there are other issues such as hygrothermal response and sound absorption that may become functional

requirements in the design of multifunctional composites, and this makes optimization of such systems an even greater challenge.

4. Recent applications of multifunctional materials and structures

Much of the research on multifunctional materials and structures has been driven by current and potential aerospace applications. For example, motivated primarily by potential aircraft applications and by technological advances in composite materials, sensing, actuation and controls, the ability of a multifunctional structure to reconfigure, or morph itself as its operating environment and/or its mission profile changes has been a subject of great research interest in recent years. One major goal of such research is to develop multifunctional aircraft wings which can change shape in different phases of flight as a bird wing does. A major application of these technologies is for morphing aircraft skins, and a comprehensive review of publications on morphing skins has been published recently by Thill et al. [143]. Since the publication of this review article, several relevant applications-oriented publications have appeared. For example, Wildschek et al. [144] reported on the development of an all-composite, all-electric morphing trailing edge for flight control on a blended wing body airliner, Hartl et al. [145,146] described the use of a shape memory alloy for active jet engine chevron applications, and Mudupu et al. [147] discussed the design and validation of a fuzzy logic controller and a piezoelectric composite actuator for a smart projectile fin.

Structurally integrated batteries for energy storage are another recent application of multifunctional structure design. The effectiveness of a multifunctional system is best defined by using a metric that characterizes the particular system, such as flight endurance time for an aircraft vehicle. For example, as reported by Thomas and Qidwai [148,149] structurally integrated batteries can extend the flight endurance time of an electrically-propelled unmanned air vehicle (UAV). The flight endurance time of the UAV is given by [148,149]

$$t_E = \left(\frac{E_B \eta_B}{(W_S + W_B + W_{PR} + W_{PL})^{3/2}} \right) \left[\frac{\rho S C_L^3}{2 C_D^2} \right]^{1/2} \eta_p \quad (6)$$

This equation shows that integrating the battery with the structure or one of the other subsystems can lead to an increased flight endurance time, t_E . Further analysis of this equation for change in t_E with changes in battery and structure weight shows that decreasing the weight is 1.5 times more effective in increasing t_E than is increasing the battery energy [148]. By integrating a polymer lithium-ion battery in the carbon/epoxy composite wing skin structure of the DARPA Wasp micro air vehicle (MAV), a record-setting flight endurance time for the vehicle was achieved [149]. A photo of this vehicle is shown in Fig. 25.

Another example of multifunctional structure technology that is driven by aerospace applications is the integration of an electronic communications antenna into the load-bearing composite structure of an aircraft. The conformal load bearing antenna structure (CLAS) development effort sponsored by the US Air Force's Smart Skin Structure Technology Demonstration (S³TD) program intends to develop the technology to embed a broad band RF antenna into the composite skin of a fighter aircraft [150–153]. More recent research related to the CLAS has involved the design and fabrication of a microstrip antenna which is integrated in a three dimensional orthogonal woven composite structure [154], impact testing of these structures [155], and wireless detection of damage in composite structures by making use of the composite structure itself as an antenna/sensor system [156].

Composite sandwich structures present some interesting possibilities for multifunctional applications. For example, Wirtz et al.



Fig. 25. First generation DARPA Wasp micro air vehicle with polymer lithium-ion battery (silver quadrilaterals) integrated in composite wing skin structure. Reprinted from [149] with kind permission from Springer Science+Business Media.

[157] have described the thermal and mechanical behavior of a multifunctional thermal energy storage sandwich structure for use in the temperature control system of an electronics module. The multifunctional structure has a thermal interface connected to a hollow aluminum plate which has a series of small compartments that are filled with phase change material. Heat storage is via the latent heat of the phase change material. The thermal energy storage and mechanical behavior of the structure are characterized and it is determined that the structure has an excellent performance-to-weight ratio. Queheillalt et al. [158] developed a multifunctional heat pipe sandwich structure which integrates the thermal management capabilities of a heat pipe with structural load support. Ozaki et al. [159] reported on multifunctional sandwich panels for space satellites, in which electronic modules are embedded between the face sheets of carbon fiber composite/honeycomb core sandwich panel. The mechanical, electrical and thermal characteristics of the panel were evaluated, and significant reductions in weight, cost and production time were achieved. The use of a carbon foam core and carbon fiber composite face sheets to enhance both through-the-thickness and in-plane thermal conductivities of sandwich panels for lightweight spacecraft thermal radiators has been described by Silverman [160]. In the automotive industry, there is great interest in multifunctional structures in which static, dynamic and acoustic behaviors are optimized. Rather than taking the traditional approach of treating the design, manufacture and assembly of the automobile body structure, acoustic treatments and interior trim separately, Cameron et al. [161] have used finite element models to study a multifunctional approach in which an integrated, multi-layered sandwich is used to replace a traditional roof panel with its separate components. Vaidya et al. [162] developed a multifunctional sandwich structure in which the woven E-glass face sheets are connected with vertical woven E-glass piles and the foam core. This construction enhances the impact resistance and sound/vibration damping and accommodates wires or sensors. Sandwich structures often consist of composite face sheets and foam cores, and there is increased activity in the use of nanoparticles to enhance both the manufacturing process and the mechanical properties of foams. The manufacturing process for foams is enhanced because the nanoparticles serve as nucleation sites for bubbles during the foaming process, leading to increased density and reduced cell size. Mechanical properties of the foams are also enhanced due to the reinforcement effect of the nanoparticles. Lee et al. [163]

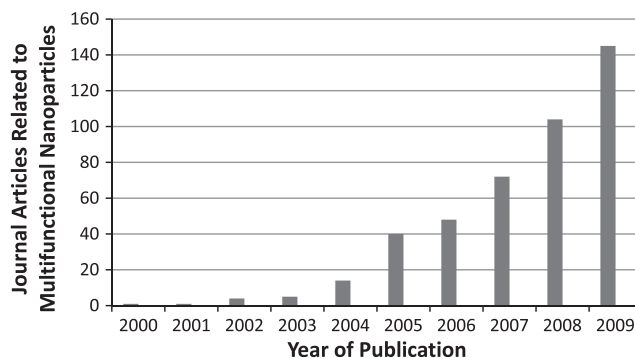


Fig. 26. Recent English language refereed journal articles related to multifunctional nanoparticles. Data collected from Engineering Village® web-based information service.

have reviewed the literature in the area of polymer nanocomposite foams.

Among the most challenging and promising applications of multifunctional materials and structures are those in the biomedical field, and much of the recent activity in this area has been driven by advances in nanomaterials and nanostructures. For example, multifunctional nanoparticles have great potential for drug/antibody delivery in combination with diagnostics and therapeutics. Since 2000 there has been a surge in the number of journal articles related to multifunctional nanoparticles, as shown clearly in Fig. 26. Suh et al. [164] have reviewed the developments in multifunctional nanoparticle systems (MFNPS) for biomedical applications, and Fig. 27 illustrates one possible configuration of such a MFNPS. The matrix of the MFNPS could be a metal oxide network which hosts sub-domain inclusions such as fluorescent optical probes, magnetically susceptible particles for magnetic resonance imaging, and pores or functionalities which can host small bioactive molecules such as drugs or antibodies. Inclusions can be either organic, inorganic or hybrid organic/inorganic [164]. A bionanoengineering design process for multilayered MFNPS is described by Haglund et al. [165], and such a multilayered particle is illustrated in Fig. 28. MFNPS offer great hope for early detection of cancer and delivery of therapeutic drugs for cancer treatment. Publications related to the development of MFNPS for cancer imaging and therapy have been reviewed by Park et al. [166]. MFNPS which have a combination of magnetic and fluorescent properties are of great interest for in vitro imaging techniques such as MRI, as well as for therapy and for external magnetic manipulation in building biomedical nanodevices. Corr et al. [167] have reviewed recent publications in multifunctional magnetic-fluorescent nanocomposites for biomedical applications. The surface area-to-volume ratio, A/V , for a spherical particle is inversely proportional to its radius, so A/V for a nanometer-sized particle will be 1000 times greater than A/V for a micron-sized particle. The large A/V ratios and resulting large pore volumes for porous hollow nanostructures make them particularly attractive for multifunctional delivery of drugs and biomolecules. Recent publications on the synthesis and applications of hollow micro/nanostructures have been reviewed by Lou et al. [168], while biomedical applications of hollow nanostructures have been reviewed by An and Hyeon [169].

A number of biomedical applications for multifunctional materials require substantial flexibility in order to accommodate large deformations. For example, artificial muscles must be flexible and strong enough to be capable of sensing and actuation over large ranges of deformation. Biomedical applications include peristaltic pumps, robot arms, artificial hands and grippers. One such class of materials that has been the subject of considerable research are the ionic polymer-metal composites (IPMC), which

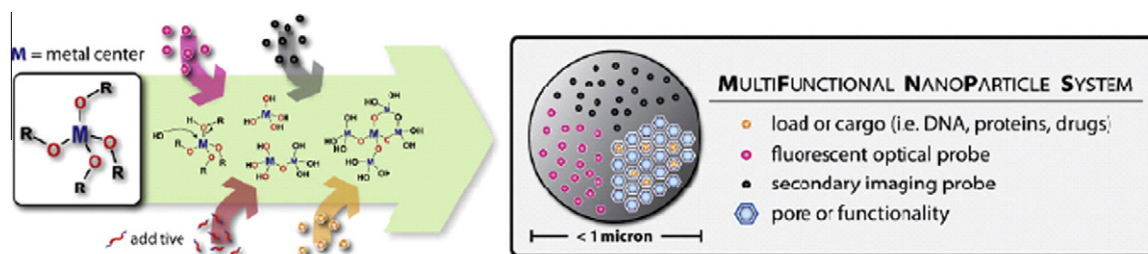


Fig. 27. Illustration of multifunctional nanoparticle system (MFNPS) for biomedical applications. Reprinted from [164] with permission from Elsevier.

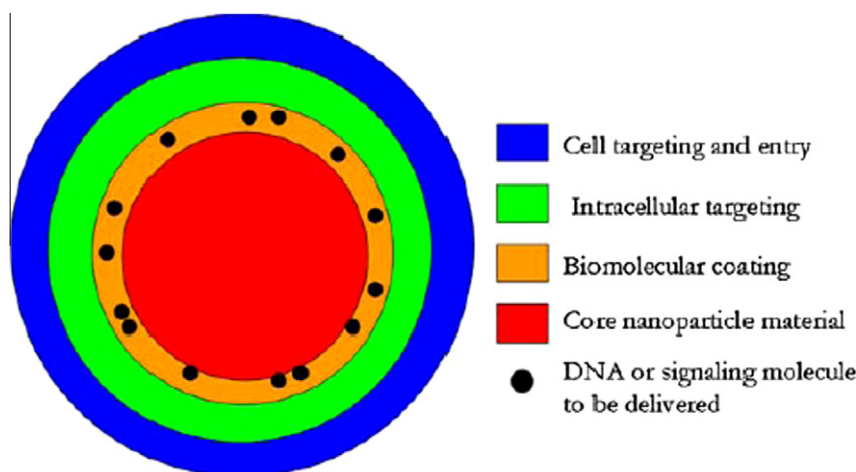


Fig. 28. Illustration of multilayered MFNPS. Reprinted from [165] with kind permission from Springer Science+Business Media.

are excited by an electric field. Shahinpoor and Kim have published a series of four review articles dealing with the fundamentals [170], manufacturing techniques [171], modeling and simulation [172], and industrial and biomedical applications [173] of IPMCs. Electroactive polymers with high dielectric constants can also generate large deformations under an electric field, as reviewed by Bar-Cohen. [174]. As another example, energy harvesting from normal motions and deformations of the human body requires that the energy conversion device be very flexible. Qi et al. [175] have developed a flexible energy conversion device based on printing of piezoelectric PZT ribbons with micrometer-scale widths and nanometer scale thicknesses on rubber substrates. The use of carbon nanotubes in flexible electronic yarns and fabrics for use in wearable biomonitoring and telemedicine sensors has been reported by Shim et al. [176]. An energy harvesting backpack for use by soldiers was developed by Granstrom et al. [177] who replaced the nylon shoulder straps on a standard backpack with flexible PVDF piezoelectric straps. During normal walking motions, the relative motions between the soldier's body and the backpack generate deformations in the PZT straps, which then convert these deformations to electrical energy for use in powering small portable electronic devices carried by the soldier.

Multifunctionality in impact resistant materials for military transport vehicles, helicopters and fighter aircraft is becoming increasingly important, and one example is optically transparent, impact-resistant nanocomposite materials for windows in such vehicles. The extremely small size and small concentration of nanoreinforcements makes it possible to improve impact energy absorption while maintaining good transparency. Such materials have been investigated by Rai and Singh [178], who fabricated and tested sandwich panels consisting of PMMA sheets with thin layers of nano-enhanced polymer adhesive sandwiched between them. The polymer adhesive layers were enhanced with 2 wt.% of 35 nm sized alumina powder. Drop weight impact tests were used

to determine impact energy and optical transparency was measured using a spectrophotometer. Significant improvement in impact energy was achieved with the nano-enhanced adhesive layers, while transparency was somewhat reduced but acceptable. Related investigations of impact resistant, optically transparent composites have been reported by Liu et al. [179], Rojanapitayakorn et al. [180], Song et al. [181], and Huang et al. [182].

5. Concluding remarks

This article attempts a reasonably comprehensive review of representative journal publications covering developments in mechanics of multifunctional composite materials and structures. Most of the articles have appeared since 2000, and many involve polymer composites, nanomaterials and nanostructures. Functions of interest include structural properties like strength, stiffness, fracture toughness, and damping, and non-structural functions like electrical and/or thermal conductivity, sensing and actuation, energy harvesting/storage, self-healing capability, electromagnetic interference (EMI) shielding, recyclability and biodegradability. Much of the future research on multifunctional materials and structures will be driven by not only structural applications like aircraft, but by needs in other areas like biomedical. There is a need for more analytical modeling work in most of the areas covered in this review, since most of the published results to date tend to be experimental in nature. Analytical models are needed not only to help in interpreting the experimental results, but in optimizing the multifunctional material or system for specific applications.

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