

Challenges and Opportunities in Multifunctional Nanocomposite Structures for Aerospace Applications

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Abstract

One important application of nanocomposites is their use in engineered structural composites. Among the wide variety of structural applications, fiber-reinforced composites for aerospace structures have some of the most demanding physical, chemical, electrical, thermal, and mechanical property requirements. Nanocomposites offer tremendous potential to improve the properties of advanced engineered composites with modest additional weight and easy integration into current processing schemes. Significant progress has been made in fulfilling this vision. In particular, nanocomposites have been applied at numerous locations within hierarchical composites to improve specific properties and optimize the multifunctional properties of the overall structure. Within this article, we review the status of nanocomposite incorporation into aerospace composite structures and the need for continued development.

Introduction

Current advanced engineered materials systems, such as organic-matrix composites, have a myriad of applications including aerospace structures, sporting goods, high-performance automobiles, and boats. Composite aerospace structures often have extreme property demands that make the adoption of higher-performance materials systems, such as nanocomposites, inviting. However, there is also a strong need to balance the multiple demands of performance, weight, processability, risk, and/or life-cycle cost in selecting new structural materials. In this article, we discuss the current and potential impact of nanotechnology

on composites, with a particular focus on their relevance to aerospace applications.

As air travel continues to grow, lightweight, multifunctional, and easily manufactured structural materials such as polymer matrix composites (PMCs) are being increasingly used. PMCs combat increased fuel and maintenance costs, which account for roughly 50% and 20%, respectively, of the operation costs, beyond ownership, of a commercial airplane.¹ Considering that the recent cost of launching a heavy lift system into low Earth orbit² is \$6000–\$20,000/kg and approximately \$36,000/kg for geosynchronous orbit,³

PMCs are also being increasingly used for space structural applications.

PMCs are generally preferred over metals for moderate-temperature applications (<300°C), based on their weight savings, fatigue resistance, corrosion suppression, and significantly decreased part count (especially fasteners). Future aerospace systems and current developmental systems seek to further enhance both the mechanical and multifunctional properties of PMCs by incorporating nanoparticles.

Property Improvement of Composite Structures with Nanoparticles

A particular challenge for traditional composites is the integration, control, and exploitation of nanoparticle-enabled properties within a hierarchical structured composite made with commercially viable processing methods. Although industrial efforts continue to pursue low-cost processing methods for composite fabrication, the current large capital investment of composite processing equipment (automated fiber coating and positioning systems, equipment for infusing uncured resin into fiber preforms, high-temperature and high-pressure vessels for void-free composite curing, etc.) makes it initially preferable to use traditional composite processing schemes for integrating nanocomposites. Thus, nanoparticles can be incorporated in a number of different ways within the traditional composite material forms, including within a fiber, as a thin coating on a fiber, in place of a bundle of fibers (i.e., a fiber tow), as an inner layer, as a veil, as a coating, or as a part of the polymer resin system. Where the nanoparticles should be placed will depend on the property being sought and the ability to exploit the suite of properties imparted. An illustration of the potential multiscale incorporation is shown in Figure 1. A summary of approaches and possible applications of nanocomposites to aerospace structural composites is given in Table I.

In comparison, many of the current non-nanocomposite approaches to property improvement incorporate larger-scale conducting materials (foils, grids, coatings, etc.) that can often have increased weight, leading to manufacturing issues, or that complicate repairs because of phase discontinuities and their larger sizes. Nanocomposites provide an opportunity to lessen these traditional tradeoffs because properties are improved with small additions of nanoparticles, without significant changes in the manufacturing process and without the incorporation of an additional bulky phase that often requires formal connections. Overall, such a system

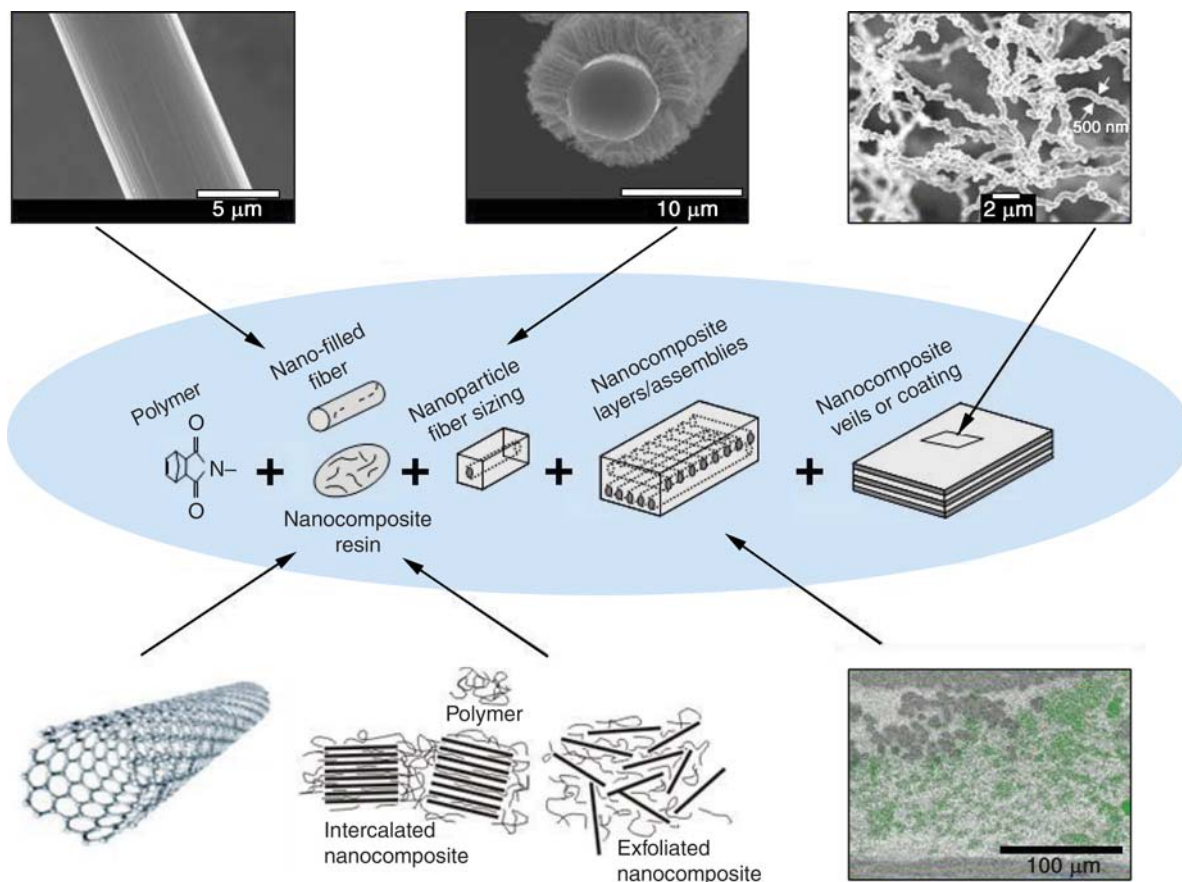


Figure 1. The potential hierarchical integration of nanoparticles within a multiscale composite.

is expected to eliminate redundancy, improve fabrication efficiency, reduce weight and volume, and decrease operating or repair costs. The following sections give some specific examples of improvements currently being made.

Physical/Chemical Properties

The ability of a solid material to maintain dimensional and chemical stability in adverse environments is important for both air and space structures. For example, some large, space-based optical structures require that the deviation in optical path length not exceed a few picometers as the satellite is cycling in and out of extreme thermal environments. Ideally, the structural material would be chemically inert to the radiation environment and resistant to dimensional or chemical changes as a function of temperature until the end of the service life of the material.

One of the most promising nanoscale fillers for enhancing the physical and chemical integrity of a polymer system without adding significant weight is layered silicates. Loadings of only a few percent exfoliated

silicate nanoparticles in the appropriate polymer can result in significant enhancement of several physical properties, including resistance to atomic oxygen in low Earth orbit,⁴ gas barrier properties for cryogenic tanks,⁵ heat distortion temperatures, resistance to solvent swelling, and flammability resistance.⁶ For example, previous work demonstrated the reduction of oxygen permeability from a value near 100 cc mil/m² day atm for the pristine polymer to values of 1 to 0.1 cc mil/m² day atm for film nanocomposites.⁷ Figure 2 shows the decrease in helium permeability of a composite-overwrapped tank using layered silicates within the resin. There was also an additional 45%–55% decrease in structural weight with the elimination of the inner liner.⁵

Current reusable launch concepts that would use such tanks are envisioned to thermally cycle hundreds of times and require the tank to experience thermal extremes of about –240°C at the inner cryogenic fluid wall and up to ~343°C at the outer wall. Such thermal extremes will require management of the internal stresses that can

lead to microcracking. A major contributor to the overall stresses is the stress induced by the coefficient of thermal expansion (CTE) mismatch between the carbon fiber and the thermosetting resin. Preferential swelling of the polymer by diffusing species (moisture, condensate, etc.) can also contribute to internal stresses. Fortunately, in addition to decreasing permeability, organically modified layered silicates decrease the CTE and the moisture expansion coefficient. For example, decreases in the CTE of 20%–50% for some epoxies^{8,9} and about 20% for some polyimides¹⁰ have been observed at modest layered silicate loadings. Decreases in moisture expansion values of 40%–80% for epoxy¹¹ and ~30%–40% for polyimides¹⁰ have also been observed. Impeding the transport of oxidative species also appears promising, as indicated by the substantial increase in atomic oxygen resistance with a few percent of layered silicate dispersed in an epoxy matrix.⁹ Other nanoparticles, such as functionalized carbon nanotubes (CNTs) and graphite flakes, have also been investigated^{12–14} and

Table I: Summary of Approaches and Possible Applications of Nanocomposites in Aerospace Structural Composites.

Property	Common Nanocomposite Approach	Potential Application
Physical/Chemical		
Permeability	Inclusion of impermeable, high-aspect-ratio silicate or graphite flake in resin	Cryogenic tanks, durability to diffusion species
Outgassing	Inclusion of impermeable, high-aspect-ratio silicate or graphite flake in resin	Optical benches, interferometers, antenna truss structures
Oxidation resistance	Incorporate high-temperature, oxidation-resistant fillers (silicate, CNTs, POSS, etc.) that form passivating layers or slow oxidative erosion in resin or as coating	Thermal protection systems, atomic oxygen resistance, space structures
Electrical		
Electrostatic dissipation (ESD)	Incorporate high-aspect-ratio conductive particles such as CNTs, graphite flake, metals, as percolated networks in resin between conductive fibers	Charge-dissipating adhesives, coatings, and gap fillers
Electromagnetic interference (EMI)	Create films of highly percolated networks of conductive nanofillers (nickel nanostrand veil, SWNT buckypaper, etc.) that can both absorb and dissipate broadband frequencies	Bus compartment enclosures, electronic enclosures
Lightning strike	Incorporate conductive nanofillers (nickel nanostrands, CNTs, etc.) as highly percolated coatings, appliqués, resins, or veils that can carry large currents and have controlled failure modes	Composite aircraft exteriors
Thermal		
Thermal conductivity	Incorporate highly thermally conductive particles (CNTs, metals, etc.) into resin and optimize structure for heat transfer along continuous path to heat sink	Thermally conductive adhesives, gaskets, radiators, doublers, electronics boards, solid-state laser heat removal
Thermal protection systems	Use thermally conductive and insulating nanofillers within resin to assist larger structural components to direct heat away from protected systems or enhance mechanical properties at high temperature	Aircraft brakes, re-entry vehicles, missiles
Coefficient of thermal expansion	Incorporate nanofillers with low expansion coefficients and good matrix bonding such as functionalized CNTs, CNFs, silicate, into resin or as fiber sizing to reduce CTE mismatch with fiber by composite effect and restriction of polymer motion	Adhesives, space apertures with improved thermal cycling durability
Mechanical		
Toughness	Incorporate nanofillers, such as CNTs, layered silicate, and silica, into resin to increase energy dissipation on failure through deformation, pull-out, crack bridging, etc., at needed plies	Membrane structures, damage-tolerant structures
Modulus	Incorporate high-modulus nanoparticles like continuous CNT yarns/sheets as reinforcement or grow reinforcements between plies to increase out-of-plane modulus	Stable, precision structures
Compression strength	Incorporate high-strength nanoparticles such as functionalized CNTs into the resin	Propulsion tanks, fittings
Interfacial shear stress	Grow high-strength nanoparticles such as CNTs from fiber to tailor the interfacial properties as a smart sizing	High-temperature composites, vehicle health monitoring
Interlaminar shear strength	Incorporate nano-filled resins with increased toughness at mid-ply via coating or pre-pregging	Tubular structures

Notes: CNT is carbon nanotube; POSS is polyhedral oligomeric silsesquioxane, SWNT is single-wall carbon nanotube, CNF is carbon nanofiber, CTE is coefficient of thermal expansion.

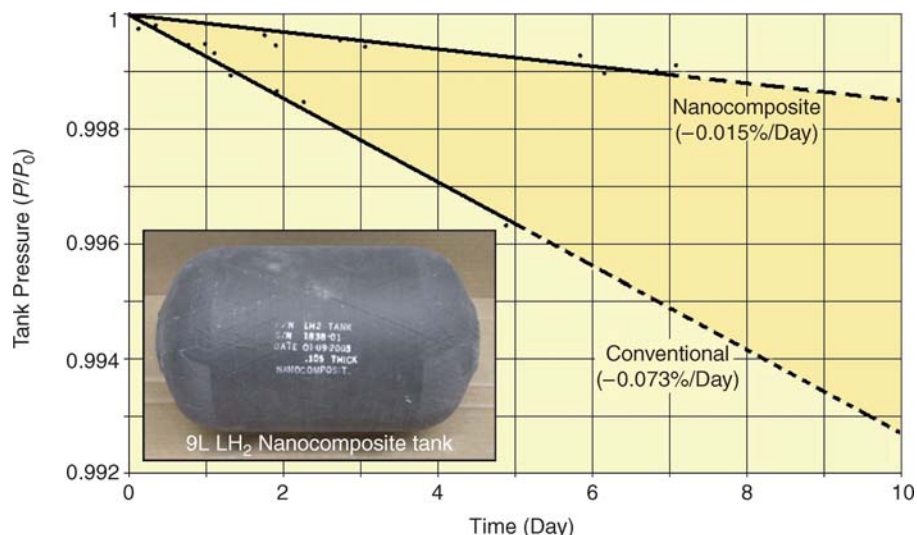


Figure 2. Comparison of leak rates for a nanocomposite-overwrapped tank using layered silicates within the resin. Nanoclays show reduced permeability to helium for tank applications (helium is used for leak detection). P_0 is the initial pressure of helium in the tank. Inset shows a photograph of a liquid-hydrogen tank.

may be able to impart multifunctional properties such as electrical and thermal conductivity.

Mechanical Properties

Mechanical improvements in traditional composite materials through the use of nanocomposites can be targeted toward improvement of resin-dominated properties or, eventually, toward fiber-dominated properties. Resin-dominated properties include interlaminar shear strength (ILSS), compression strength, and fatigue properties. Fiber-dominated properties include modulus and ultimate tensile strengths. The theoretically predicted high modulus and strength of nanoparticles such as single-wall carbon nanotubes (SWNTs) are of interest. For resin-dominated properties such as ILSS and toughness, a detailed understanding of the fracture mechanics within the nanocomposite morphology is needed to fully exploit the ultimate properties of nanocomposites. Characterization of the deformation and failure mechanisms in a manner similar to that used for traditional composites (pull-out, bridging, interfacial cracking, matrix cracking, etc.) are needed to more fully understand and exploit improvements made with nanocomposites. Although more work is needed, a 20% increase in ILSS for only 0.3 wt% functionalized double-wall carbon nanotubes has been reported in the literature for glass-fiber epoxy composite,¹⁵ and a 180% increase for a similar epoxy/glass

fabric composite with carbon nanofibers has been reported by a commercial material provider.¹⁶

A key benefit of nanocomposites for fiber-reinforced composites is the ability to selectively tailor the deformation mechanism at different locations within the composite. Thus, one might only need to use the nano-enhancement within selected plies. A recently reported extension of this concept is to grow carbon nanotubes directly on the fiber ply to create a mechanically and multifunctionally enhanced composite.¹⁷ With these fiber-like, out-of-ply nano-reinforcements, the final composite begins to more closely resemble a hierarchical three-dimensional (3D) reinforced fabric rather than a composite laminate with nano-enhanced resin. This highlights the great flexibility of using nanoparticles within a composite material. Table II, which compares some of the properties of carbon nanotubes against more traditional aerospace materials, illustrates the basis of this potential. Although nanocomposite properties are discussed in more detail elsewhere,¹⁸ these properties raise the intriguing possibility of applying the nanotubes as super-strong reinforcing fibers with strength and stiffness orders of magnitude higher than any other known material.

Although major advances have been made on the fabrication of carbon nanotube sheets^{19–27} and yarns,^{28–33} no one has yet assembled carbon nanotubes into yarns and sheets that retain the spectacular properties

of the individual SWNTs. Individual single-wall nanotube properties include a tenfold higher strength than existing sheets and yarns, a higher thermal conductivity than diamond, a thousandfold larger current-carrying capability than copper, and many other fascinating and useful properties for active devices. Even though some of the produced CNT yarns are nearly as tough as the Kevlar fibers used for antiballistic vests, efforts to increase the strength, yarn toughness, and production capability continue. Correspondingly, the actual performance of nanotube/polymer composites has also been below the theoretically predicted performance.

Thermal Properties

Thermal management of aerospace structures is important for many applications including space platforms, re-entry vehicles, propulsion systems, electronics, and high-energy (e.g., laser) systems. For example, heat generated by spacecraft components often presents difficult thermal design problems because of the high and localized heat flux, the need for large total power dissipation, and the wide temperature changes over time. The increasing need to fly larger, higher-performance payloads with higher-density microprocessors for longer periods of time has escalated power dissipation and heat flux at the silicon level. Future military communication satellites will have higher-power-density microelectronics packaging design concepts that will increase the data processing throughput by five to ten times, resulting in a possible tenfold increase in the thermal density.³⁴

Next-generation aerospace structures could potentially use more thermally conductive materials to spread out and judiciously direct heat flow in satellites, thermal protection systems, near-propulsion structures, electronic boxes, chip packaging, directed energy systems, radiators, and their accompanying thermal interfaces. CNTs offer some of the strongest promise, since the measured thermal conductivity of individual multiwall nanotubes (MWNTs) (3000 W/m K) is higher than diamond³⁵ and have predicted values even higher.³⁶ The theoretical thermal conductivity of SWNTs is 6000 W/m K,³⁷ which, when combined with exceptional tensile strength, could form the basis for a multitude of future high-performance materials.

Experimentally, unoptimized MWNT sheets have been measured to give a room-temperature thermal conductivity of about 150 W/m K. This is close to the thermal conductivity reported for magnetically oriented single-wall nanotube sheets,³⁸ but substantially higher than the <3 W/m K

Table II: Properties of Carbon Nanotubes Compared with Traditional Aerospace Materials.

Material	Specific Gravity (g/cm ³)	Yield Strength (GPa)	Elastic Modulus (GPa)	Thermal Conductivity (W/m K)	Electrical Resistivity (μΩ cm)	Normalized Strength-to-Mass Ratio
Carbon nanotube (SWNT theory)	1.4	65	1000	~6000	30–100	225
Measured SWNT yarns and sheets	1.4	1.8	80	150	150	7
Conventional carbon fiber, M55J	2.2	4	550	70	800	9
IM7 carbon composites	1.6	2.1	152	30	2000	7
Titanium	4.5	0.9	103	12	127	1
Aluminum	2.7	0.5	69	180	4.3	1

Note: SWNT is single-wall carbon nanotube.

reported for highly loaded (up to 20 wt%) vapor-grown carbon nanofibers (VGNFs) in epoxy.³⁹ Inefficient phonon transport between nanotubes is considered the major limitation to approaching the thermal conductivity of the individual nanotubes.⁴⁰ Because the phonon dispersion occurs at discontinuities such as tube ends, a simple argument would suggest that increasing nanotube length from 0.3 to 3 mm will increase nanotube yarn thermal conductivity tenfold, or from 150 to 1500 W/m K. However, creating nanotube junctions in which tubes efficiently exchange thermal energy to other nanotubes or carbon fibers would also significantly increase the thermal conductivity of composite resins. One of the first aerospace applications using this type of nanofiller could be thermally conductive adhesives and reinforced interface gaskets.

Electrical Properties

Many aerospace applications require electrically conducting, polymer-based composites for static discharge, electrical bonding, interference shielding, primary and secondary power, and current return through the structure. However, present carbon-reinforced polymer composites alone cannot provide robust solutions to satisfy these requirements because of the presence of insulating resin regions including the surface. Traditionally, secondary conductive materials such as foils, wires/straps, and coatings would be incorporated into the structure with additional

processing steps. However, integrated composite structures that use percolated networks of conductive particles with high aspect ratios appear to be a preferred method for obtaining low-resistivity composites at low volume fractions and with little additional weight. For example, materials such as carbon nanofibers,^{39,41} single-wall nanotube buckypaper (a collapsed film of CNTs),⁴² nickel nanostrands,⁴³ or graphite flakes¹⁴ have potential application in near-term electrostatic dissipation (ESD) and electromagnetic shielding systems, as discussed in detail next.

Control of Electrostatic Discharge

Composite structures, including graphite/epoxy and Kevlar, are known to locally charge to 4000 or 6000 V, respectively, when exposed to electron fluxes, despite the presence of a conductive path through carbon fibers.⁴⁴ To avoid discharging to a proximate ground and harming electronics or personnel, electrical shielding is required over the entire exposed surface. Materials that have resistivity values above 1×10^{13} ohm/square can develop a static charge that will not dissipate even when bonded. The measurement of ohm/square refers to the resistance (in ohms) of a surface film multiplied by the surface width and divided by the length. If one considers a square of equal length and width, the resistivity can be expressed as ohms per unitless square. A resistivity of 1×10^7 ohm/square is sufficient to dissipate charge for an electrically bonded structure and is

generally the range at which the carbon filaments are adequately connected to the proximate ground. By adding high-aspect-ratio conductive nanoparticles to the resin-rich regions of a composite, the electrical connection with the proximate ground and the conducting carbon fibers can be assured at modest additional weight. For example, coatings of VGNFs and hybrid VGNF/graphene platelet nanocomposites on conventional composite substrates can reduce the surface resistivity from $>10^{12}$ ohm/square to 10^3 – 10^4 ohm/square to successfully satisfy the electrostatic discharge requirements for spacecraft applications.⁴⁵

Conducting Adhesives

Good electrical bonding of a joint is needed to assist in controlling and dissipating the buildup of electrostatic charges. Typically, the requirement is less than 1000 Ω for bonds between composite materials and the structure. For bonding across joints in composite materials, an electrically conductive adhesive is filled with high amounts (up to 60% by volume) of powdered silver, nickel, or carbon black. However, this makes the adhesive bond weaker, and hence, a structural adhesive is needed in addition to the electrically conductive adhesive. Recent industry and government research efforts aim to develop a multifunctional, carbon, nanofiber-filled adhesive with high electrical conductivity that meets the requirements for lap shear strength and viscosity.⁴⁶

Lightning Strike Protection

Another related application involving much larger currents (up to 200 kA) is lightning strike protection. With 40 aircraft accidents and 290 fatalities attributed to lightning strike incidents between 1963 and 1989,⁴⁷ this unpredictable act of nature can lead to loss of pilot control as well as burning, erosion, and distortion of the structure. As more structures use composite materials, strategies that use bulky films and meshes are being employed for protection. The key challenge is to either fully dissipate the energy or direct it into an easily repairable failure mode without compromising the structure or the flight.^{48,49} New approaches that attempt to exploit lighter-weight conductive nanofilled composites are actively being explored by several researchers.⁴³

Enclosures for Electromagnetic Shielding

Traditional enclosures of electronics for air and space structures have usually been made of aluminum and other electrically

conductive metals that provide electrostatic discharge protection, electromagnetic shielding, fault current return, an antenna ground plane, and intrinsic lightning protection. In recent years, composite materials have been used because of their light weight, high strength, and ease of fabrication. But extra steps must again be taken to achieve the desired electromagnetic properties. In this particular application, the electrical properties of the structure must meet the >60 dB shielding effectiveness level to shield against electrical interference. One traditional solution is to use a ~75- μ m-thick aluminum foil co-cured with the graphite fiber composite. However, this is not the best solution because of cost, questionable adhesion, and limitation in the ability to repair or rework areas despite the favorable shielding efficiency.

An alternative approach is to use a light-weight veil of nickel nanostrands to achieve the desired level of shielding with good adhesion and the ability to repair. A composite with alternating layers of fibers oriented 0° and 90° relative to each other and with two top layers of nickel nanostrand veils showed shielding levels of >60 dB over the useful frequency range, as shown in Figure 3.⁴³ Hence, only a few tens of micrometers of a nanostrand composite film created a highly effective electromagnetic interference shield across a wide bandwidth. Although 60 dB is a respectable shielding level, it is anticipated that thicker or more concentrated nanostrands may provide even better broadband shielding with minimal weight increase.

Conclusion

In this article, we have provided a general overview of the near-term promise for nanotechnology within aerospace polymer-matrix structural composites. Whereas these composites are often considered light weight and integrated alternatives to traditional metals, they also have tradeoffs in dimensional stability, temperature capability, electrical conductivity, and thermal transport.

Nanocomposites are addressing many of the near-term needs of composite structures by providing mechanical and multifunctional improvements with modest additional weight. In the far term, one can envision integrated structures in which more advanced functions are embedded into the structure to actively manage mechanical, thermal, electrical, or optical loads, as well as actively select, sense, convert, store, and transmit the various energies within an intelligent structure.

Acknowledgments

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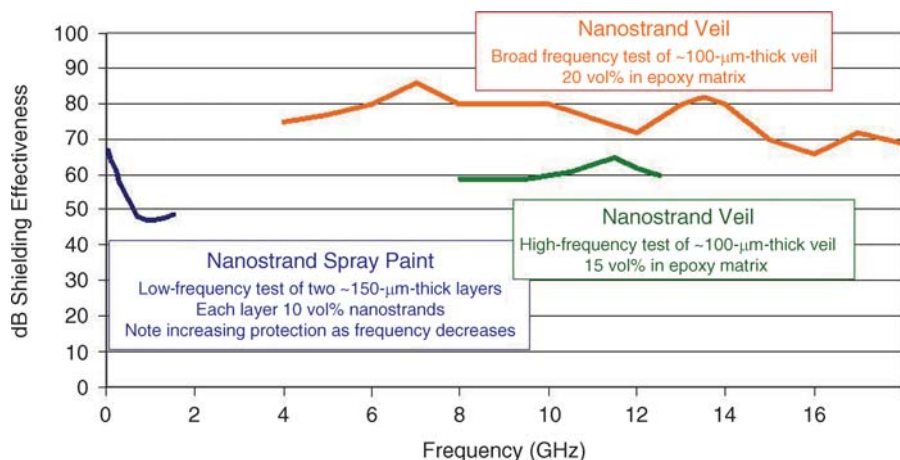


Figure 3. Summary of shielding effectiveness test results for composites with nickel nanostrand coating and epoxy-infused nickel nanostrand veil of two different thicknesses.

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