Composites with Negative Refractive Index, Thermal, Self-healing and Self-sensing Functionality

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ABSTRACT

Here, we outline recent achievements in creating structural composite materials with controlled electromagnetic, self-healing, thermal management, and self-sensing properties, i.e., a truly multifunctional material system. The electromagnetic response is tailored by incorporating within the material small amounts of suitably configured, periodically distributed, electric conductors to produce distributed electric inductance and capacitance. The self-healing is achieved via Diels-Alder reaction in a newly developed polymer that can covalently and exothermally rebond upon the application of rather low external temperatures and pressures. The embedded conductive wires are used as resistive elements to heat the material, as communication links between embedded sensors to detect internal damage, and as electrical conductors to tune the electromagnetic properties of the material system. The structurally-integrated embedded microelectronic sensors render the composite information-based, so that it can monitor and report on the local structural environment, on request or in real-time as necessary. In this paper we give an overview of the various components of our multifunctional concept, and present results on compression testing of the healable polymer at low and high strain rates.

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INTRODUCTION

We seek to develop structural composite materials with additional integrated functions. Such properties include controlled electromagnetic, self-healing, thermal management, and self-sensing properties that interact to create an innovative multifunctional material system. The electromagnetic properties of these materials may be controlled by design of embedded periodic scattering elements that alter the response of these materials to EM radiation, such that the index of refraction may become negative.[1] These arrays act as inductive and capacitive structures with a plasma-like response to control the electric permittivity and/or the magnetic permeability. Integration of metallic elements into traditional fiber-reinforced polymer composites has introduced further opportunities for multifunctionality, most notably self-healing and thermal transport functionalities. To serve as the polymer matrix in our composite, we are utilizing a highly cross-linked polymer with the ability to heal internal cracking through thermo-reversible covalent bonds.[2] Application of moderate heat allows fractured bonds to reform and thus repair the damaged interface. Metallic elements, such as continuous conductors as used for our EM functionality, may be heated resistively to induce this healing mechanism. Furthermore, microelectronic sensors integrated into the composite serve to detect internal damage and alert that repair is needed.

INTEGRATED ELECTROMAGNETIC FUNCTIONALITY

The electromagnetic response of structural composites can be tailored by incorporating within the material small amounts of suitably configured, periodically distributed electric conductors to create distributed inductive and capacitive elements. Over wave lengths that are at least several times greater than the size of a typical electrically-conducting unit cell, the overall electromagnetic (EM) properties, i.e., electric permittivity and magnetic permeability, of the resulting composite can then be tuned to desirable values, resulting in composites with, for example, dielectric constant of 1 (i.e., transparent to that wave length), or even with a negative index of refraction. The design can incorporate arrays of straight wire or coil conductors to control the dielectric permittivity and folded doubled resonators (FDRs) or other suitable versions of FDR, to control the magnetic permeability.

To tune the dielectric permittivity of the composite, we have identified two wire architectures, based on initial work by Pendry et al.[3] and Smith et al.[4], namely thin straight wire arrays and coiled wire arrays, that are suitable for direct integration into fiber-reinforced composites.[5] Straight wire arrays, such as those shown in Figure 1, are designed such that the radius of the wires is very small compared to the lattice spacing, so that the wavelength of the electromagnetic excitation frequency is large compared to the lattice size. By increasing the length of wire per volume of material, the same degree of inductance may be achieved with thicker wire in a coil geometry as with thin straight wire. As examples, we have introduced arrays of thin, straight wire and alternatively coiled wire arrays into various types of composite materials. Composite panels were made by hand-layup of pre-impregnated woven fabric (prepreg) around arrays of embedded straight copper wire of diameter 50-100 μm. In the case of the coiled wire arrays copper wire with radius 254 μm was co-braided with Kevlar reinforcing fibers to form the coil elements. Greater detail of the construction techniques are given elsewhere.[6] Representative dispersion relations of the dielectric constant in the microwave regime for these panels are given in Figure 1, which compare both numerical predictions with the experimental results. This graph shows the characteristic trend of changing the dielectric constant from negative to positive values as a result of the plasmon media.

To control the magnetic permeability of a composite, we must introduce conductive elements that mimic the behavior of Pendry's original split-ring resonators (SRR).[7, 8] The unit cell of the SRR consists of a ring of conductive material (typically copper) with a gap in its circumference, which is positioned concentrically within a slightly larger ring with an opposing gap. In this geometry, the magnetic field of the incident electromagnetic radiation must be orthogonal to the center of these rings so that electric current flows circumferentially along conductive rings. Capacitance is developed between the rings and between the splits in the rings. When periodic arrays of these elements are combined with periodic arrays of the thin wire and coil wire arrays, the material may exhibit a band over which the index of refraction is negative.[9] Integrating such arrays into structural composites is challenging due to the required orientation of the split ring arrays in relation to the incident EM radiation. However at UCSD we have now developed a technique of manufacturing composites with these arrays by modifying the design of the SRR to create a Folded Doubled Resonator (FDR). These FDRs and wire arrays may be fabricated into a composite using multilayer lithographically produced circuit elements; a three-dimensional physical (as opposed to electromagnetic) structure is introduced that achieves negative index in the propagation direction normal to the composite surface. The method of fabrication is amenable to mass production and can be readily scaled to higher frequencies. Experimental details of this novel technique are the subject of a future publication.

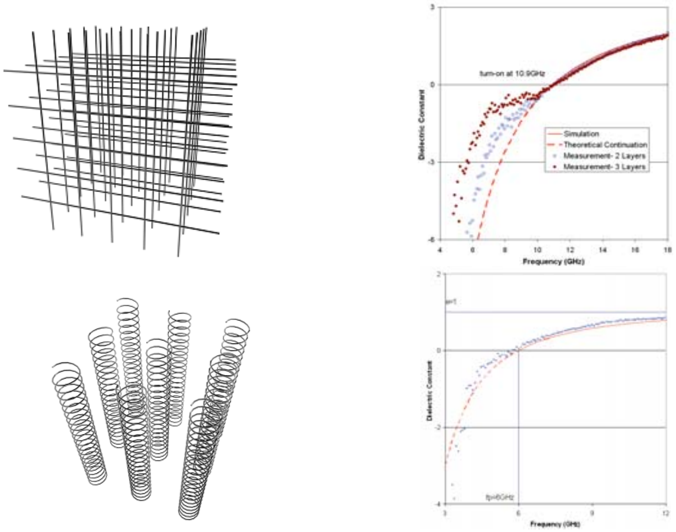

Figure 1. [Top Left] Schematic of thin, straight wire array. [Top Right] Numerical prediction and experimental results of thin wire (50μm) array embedded in Cyanate Ester / Quartz Fiber composite panel. [Lower Left] Schematic of thick wire coil array. [Lower Right] Numerical prediction and experimental results of thick wire (254μm) coil array embedded in Kevlar® braids.

INTEGRATED SELF-HEALING FUNCTIONALITY

Chen et al. have recently developed a novel polymer with the unique ability to heal internal damage by means of thermo-reversible covalent bonds.[2] As a result, cracking that may occur inside the material can be healed through the application of mild heat to repair the interface and restore the material to near its original strength. The ability of this polymer to repair broken bonds is a result of Diels-Alder adducts in the backbone of the polymer. The material is formed by the polymerization of furan monomer with maleimide monomer via a Diels-Alder reaction, which yields a cross-linked polymer with an ultra-high molecular weight. This polymer is referred to as 3M4F polymer, indicating 3 maleimide and 4 furan groups per polymer unit. The healing mechanism results from the reversibility of the DA reaction, which is thermally activated. The weakest bond in the polymer structure is the polymerization /cross-linking bond of the DA adduct. While strong in comparison to other types of chemical bonds, this is the first bond to break when the material is loaded to. However, because this bond is reversible, this is also the bond that reforms when the material is heated above the transition temperature. We have observed the healing mechanism in samples of 3M4F polymer, as reported elsewhere.[6] After heating cracked samples to a temperature above 80°C for at least six hours under compression normal to the crack face, the crack had disappeared. Visually the material had been restored to it original state, indicating healing.

When this polymer is used as the matrix of our multifunctional composite, the electromagnetic wire medium may further serve as the means of applying heat to induce this healing mechanism. Initial simulation and testing has been conducted to verify the heating capabilities of our integrated thin wire arrays. Using the same wire diameter and array dimensions, we have applied direct current to resistively heat a composite sample. The testing was designed to achieve a uniform 80°C temperature throughout the sample, since we have demonstrated healing in the 3M4F polymer at this temperature. A square array with lattice spacing 3.175 mm was constructed with 100μm diameter copper wire and embedded in a representative glass-fiber/epoxy matrix composite. Various heating conditions were simulated and tested and it was demonstrated that the target temperature could be achieved in a matter of 20 minutes with a power density of 0.073 W/cm^2.[10]

We have also tested the mechanical properties of the 3M4F polymer. Compression tests at high and low strain rate were conducted to compare the 3M4F polymer to other structural thermoset and thermoplastic polymers. Comparison polymers included vinyl ester (Dow Derakane 411-350 with 1.5% MEKP), epoxy (Devcon DGEBA resin), PEEK (polyetheretherketone) thermoplastic and nylon 6,6. All polymers were machined into cylindrical samples of diameter 0.35” and length 0.225”. Low strain rate tests were performed on a MTS universal testing machine at a strain rate of 10-3 per second. High strain rate tests at 2,000 per second were performed using the split Hopkinson bar technique,[11] shown schematically in Figure 2. All of the tests were performed at room temperature, and the ends of the samples in contact with the testing equipment were lightly lubricated with lithium grease.

The sample stress strain curves for compression testing at high and low strain rates are given in Figure 3. Each of the polymers tested showed strain rate sensitivity, where the strength and ultimate strain increased with the strain rate. At the high strain rate of 2,000 per second the 3M4F polymer proved to be the strongest and stiffest material. Furthermore, the 3M4F polymer showed the greatest increase in strength at the higher strain rate, where the ultimate strength increased by over two and a half times the value at low strain rate. At high and low strain rate the 3M4F polymer performed similarly to epoxy in terms of modulus, yield strain and the overall failure behavior. However its ultimate strength was slightly higher than that of epoxy. At low strain, PEEK thermoplastic was clearly the toughest material, but at the high strain rate the 3M4F polymer proved toughest.

INTEGRATED SENSORS

To sense damage within this composite, we are also developing a compact network sensor array to be integrated into the material. We are developing methods to integrate these sensors into the actual reinforcement phase of the composite by braiding and other processing techniques to mitigate the structural flaws that may arise from the presence of the sensors. A related paper presented at this same conference, entitled "Development of Embedded Sensing Technology for Structural Composite Materials" provides further detail on this aspect of our design. We visualize a multi-component, multifunctional braid that integrates our electromagnetic, healing and other functionalities into a single unit. These structurally-integrated embedded sensors render the composite information-based, so that it can monitor and report on the local structural environment, on request or in real-time as necessary and signal that a healing operation is required.

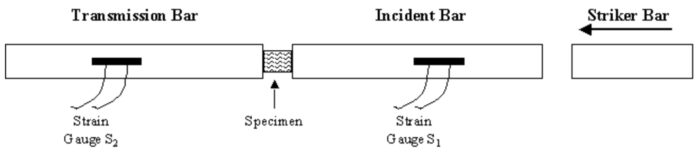

Figure 2. Schematic of classical compression split Hopkinson bar technique for high strain rate testing.

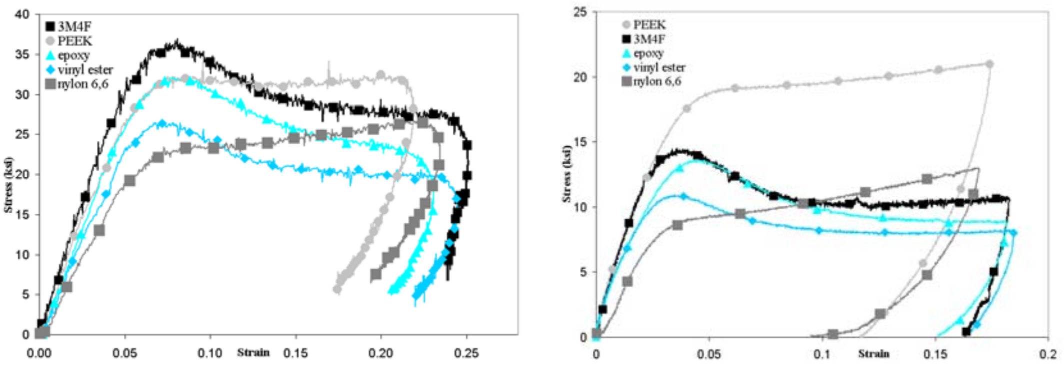

Figure 3. Compression test results for 3M4F polymer and other structural polymers: [left] at 2,000 sec-1 and [right] at 0.001 sec-1 strain rate.

SUMMARY

We have presented the concept of a self-healing structural composite with integrated electromagnetic and sensing functionalities. The composite's EM properties result from tuning the electric permittivity and magnetic permeability to yield a materials with a dielectric constant of unity or with a negative index of refraction. These conductive elements may further serve as heating elements to induce a healing mechanism in a highly cross-linked polymer matrix. Sensors also integrated in this material will detect damage and signal that repair is necessary. Each of these components is being developed independently so that in future they may be combined together to form the integrated material.

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