Self-healing structural composites with electromagnetic functionality

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ABSTRACT

We have incorporated arrays of conductive electromagnetic scattering elements such as straight copper wires and copper coils into fiber-reinforced polymer composites, resulting in materials with required structural and further electromagnetic functionality. The scattering elements provide controlled electromagnetic response for tasks such as filtering and may be used to tune the overall index of refraction of the composite. Integration of these metallic elements into traditional fiber-reinforced polymer composites has introduced other opportunities for multifunctionality, in terms of self-healing, thermal transport and perhaps sensing applications. Such functionalities are the result of fiber/wire integration through textile braiding and weaving, combined with a new polymer matrix that has the ability to heal internal cracking through thermo-reversible *covalent* bonds. Multifunctional composites of this kind enhance the role of structural materials from mere load-bearing systems to lightweight structures of good thermo-mechanical attributes that also have electromagnetic and other functionalities.

Keywords: artificial dielectric; electromagnetic scattering; multifunctional composite; self-healing

1. INTRODUCTION

Multifunctional materials, in the context of our research, integrate other functions into materials that foremost have outstanding structural integrity. Our primary goal is to develop structural composite materials with controlled electromagnetic properties. Those properties include electromagnetic enhancements in the form of a tunable index of refraction, RF absorption, and when considering Negative Index Materials, a negative index of refraction.[1] Such properties are the result of embedding periodic metal scattering elements into the material to create an *effective medium* response over desired RF frequency ranges. These arrays act as inductive structures with a plasma-like response to control the electric permittivity. As a result the dielectric constant may be tuned to negative or positive values. Artificial dielectrics with similar electromagnetic response have been studied in the past,[2,3] to which we refer as *artificial plasmon media*. Typically such designs had little or no structural integrity. In contrast, we seek to create hybrid materials systems through the development of analytical, computational and experimental models for the design of *structural composites* with these electromagnetic properties.

Integration of metallic elements into traditional fiber-reinforced polymer composites has introduced other opportunities for multifunctionality, most notably self-healing and thermal transport functionalities. Recent interest in self-healing materials has emerged from initial concepts proposed by Dry and Sottos[4,5] and later modified and developed by White et al.[6] These material systems rely on an encapsulated healing agent embedded in a polymer; as a crack propagates through the material, the healing agent is released and subsequently polymerizes to fill the crack. Such a material is therefore able to sense damage and initiate repair, referred to as autonomic healing. Alternatively, a new cross-linked polymer has been developed with the ability to heal internal cracking through thermo-reversible covalent bonds.[7] Application of moderate heat allows fractured bonds to reform and thus repair the damaged interface. Since the repair mechanism is not automatically activated it may not be considered an autonomic healing material. However it does constitute a self-healing material, particularly when the healing agent (heat source) is integrated into the material, for example in the form as conductive metal wires. Such a material system is presented here with further built-in mechanisms to enhance the healing process.

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2. PLASMON MEDIA AND ELECTROMAGNETIC FUNCTIONALITY

Introduction of thin straight conductive wires into any dielectric medium creates plasmonic effects that modify the overall electromagnetic material properties of the medium as a homogenized material. In principle, a plasma is defined as a medium in which freely moving charges are abundant. The dielectric constant κ of a dilute plasma can be written as:

$$k = 1 - \left(\frac{f_p}{f} \right)^2 \qquad \textbf{(1)}$$

where f_p is the plasma frequency and f is the electromagnetic excitation frequency. This parameter must be evaluated empirically for any configuration, but analytical and numerical results can be easily used for design purposes. Pendry et al. [8] provide the following analytical formula for thin wire media:

$$f_p = \frac{c_0}{d} \sqrt{\frac{1}{2p\left(\ln\left(\frac{d}{r}\right) - \frac{1}{2}(1 + \ln p)\right)}} \qquad \textbf{(2)}$$

where c_0 denotes the speed of light in vacuum, d is the lattice spacing, and r is the radius of the wires. It is important to note that this formula is valid when r is very small compared to d. Accordingly, Pendry dropped the second term in the denominator of the radical since it was assumed $ln(d/r) >> 1$. However for engineering applications it is necessary to retain both terms, since r must be on the order of tens of micron and spaced on the order of millimeters for the medium to behave as plasma at microwave frequencies. Doing so ensures that the wavelength becomes at least an order of magnitude larger than the lattice spacing. Processing such thin wire into host materials such as fiber composites can pose challenges in the manufacturing, though an alternative to this problem is explained later in the paper.

Numerical calculations further show the validity of the analytical arguments. Frequency domain calculations were executed using the HFSS electromagnetic finite element calculation package, available from ANSOFT Corporation, which can predict the dispersion relation of a periodic medium. Initially a cubic unit cell must be created that, when repeated in three directions, spans the entire medium. If an electromagnetic wave is propagating in the x direction, the faces of the unit cell parallel to this direction will have the same field values. Therefore the field solutions are periodic in y and z directions, in addition to the geometry and the material properties. The fields on the other two faces normal to the direction of propagation however are not exactly equal, but have a phase shift φ relative to each other. The shift can be written in terms of the wavelength as:

$$j = \frac{2pd}{l} \qquad \textbf{(3)}$$

where d represents the size of the unit cell in the direction of propagation and l is the wavelength. The unit cell is created in the software and appropriate material properties are assigned. The boundary conditions are set to be periodic on the faces normal to the y and z directions and periodic with phase advance parameter j on the faces normal to the x direction. The resonance frequency of such a configuration is the frequency of the propagating wave through the periodic medium with wavelength l. For example, the resonant frequency when $j = 0°$ is the smallest possible frequency of a propagating electromagnetic wave, referred to as the turn-on frequency of the medium. Below the turn-on the medium exhibits a stop band behavior. The index of refraction of such a medium will be frequency dependent and can be written as:

$$n = \frac{j c_0}{2pfd}. \qquad \textbf{(4)}$$

It should be mentioned here that based on analytical and experimental results, one expects very low magnetic activity from the thin wire medium. Therefore one can approximate the effective real part of the dielectric constant of the medium as:

$$e = n^2. \quad \textbf{(5)}$$

In the straight wire structures the wire diameter is a sensitive parameter. The inductance of the conductors is inversely proportional to the diameter. Simultaneously, the plasma frequency is inversely proportional to the inductance. When the size of the unit cell is held constant while the turn-on frequency is increased, the wavelength decreases and the electromagnetic response moves outside the effective medium regime. When the ratio of this wavelength to the cell size approaches unity, the medium can no longer be approximated as a homogeneous material. At $l/d = 2$, a standing wave exists rather than a propagating wave, which is related to a phase advance $j = 180°$. To allow the use of thicker wires in the medium, the length of the wires must be increased per unit volume in order to achieve an equivalent amount of inductance. This may be accomplished by introducing a loop into the wire, referred to as a loop-wire design, or by introducing a series of loops, such as a coil design. Samples made through this technique have been reported and analyzed previously.[9,10]

The loop-wire and coil structures have an inherent chiral behavior if all of the coils constituting the medium have the same sense, right-handed or left-handed. A chiral medium results when its permittivity tensor is not diagonal when written in terms of the linearly polarized components. For coil configurations, an incident wave polarized such that the electrical field lies parallel to the axis of the coil also produces current along the coil. The circular component of this current creates a magnetic field parallel to the axis of the coil. However, the magnetic field accompanying the incident wave is normal to the axis. Therefore the magnetic field does not retain its polarization as it travels through the medium, which causes the electrical field vector to rotate as well. For such media, the main independent wave components are not linearly polarized, but have circular or elliptic polarization. If the complex permittivity tensor is written in these bases it will be diagonal. However, if transformed to usual Cartesian components, it will include complex off-diagonal components. It is worth mentioning that for lossless materials, the off-diagonal elements are purely imaginary.

Though chirality may be useful in some cases, our current designs are based on linearly polarized waves. To eliminate chiral effects we have investigated two geometric arrangements. By alternating the sense of the coils in one or both directions of the array, the rotating field vector of an individual coil is effectively eliminated by the counter behavior of its surrounding neighbor coils. Numerical simulations show the validity of this argument, illustrated in Figure 1. A similar method of eliminating chirality may be achieved by introducing double coils, where coils of the opposite sense, with slightly different diameters, are arranged concentrically. Examples of this arrangement have been studied numerically, also shown in Figure 1, and its effectiveness has been demonstrated.

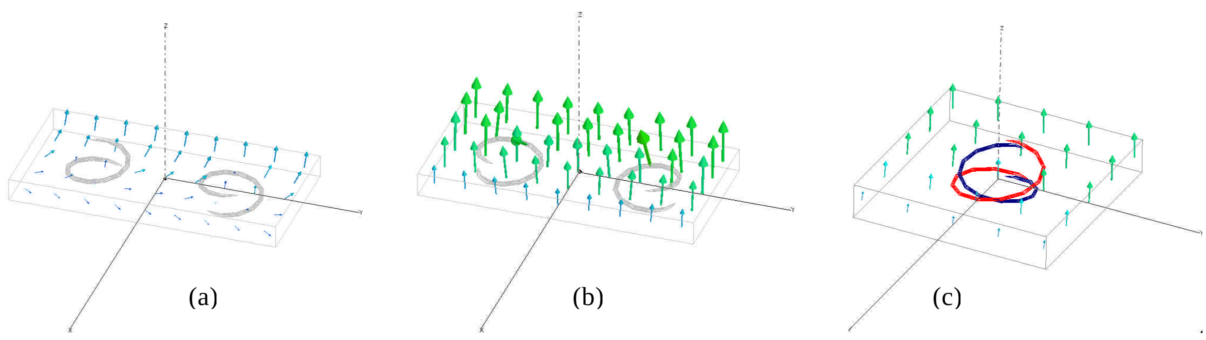

Figure 1. HFSS simulations of chiral and non-chiral media with 90° phase advance across the unit cell. (a) Unit cell containing two right-handed coils reveals chiral behavior exhibited by rotating field vector. (b) Unit cell containing one left-handed coil adjacent to one right-handed coil. (c) Unit cell containing one left-handed coil inside one right-handed coil. Field vectors remain parallel across unit cells that contain both left-handed and right-handed coils, indicating non-chiral behavior.

3. INTEGRATION INTO STRUCTURAL COMPOSITES

To integrate such electromagnetic designs into materials, one needs a periodic material that can accommodate the explicit three-dimensional arrangement of the electromagnetic elements. Fiber-reinforced polymer composites facilitate such arrangements due to the natural periodicity of their laminate construction. The arrangement of fibers within each layer provides flexibility in orientation, spacing, and geometry of the electromagnetic elements. Each layer may contain elements with orientation in only one direction, as in a unidirectional laminate, or the elements may be woven such that each layer has bidirectional elements. Variation of the spacing of these elements in the thickness (z) dimension of the material is controlled by the sequence in which laminae are stacked to form the laminate.

Thin Wire Composites

To validate the theoretical claims made here, a diverse set of experiments were carried out that further support results presented in this conference last year.[10] New experiments focusing on extraction of the effective material properties were conducted in an anechoic chamber developed by A. Starr and his colleagues in the Physics Department of UCSD. Composite panels were made by hand-layup of pre-impregnated woven fabric (prepreg). The samples varied in the type of host material, wire diameter, and number of electromagnetic layers. Host materials included E-glass fibers impregnated with epoxy resin, Spectra® (Honeywell UHMW polyethylene) fibers impregnated with vinyl ester resin, and quartz fibers impregnated with cyanate ester resin, chosen for their mechanical attributes and favorable dielectric characteristics. The dielectric constant of Epoxy/E-glass was 4.44 in microwave frequency with a loss tangent of 0.01, and that of vinyl ester/Spectra was 2.45 with a loss tangent of 0.002. Cyanate ester/quartz provided the best overall electromagnetic characteristics with a dielectric constant of 3.01 and a loss tangent of 0.001, where a low dielectric constant and loss tangent are preferred for optimal microwave transmission. The fiber volume fraction for each material was about 60%. In making each panel, copper wire of 0.003" (75µm) or 0.002" (50µm) diameter was strung across a frame to form the desired pattern and was subsequently encased in layers of prepreg. Panels were processed at elevated temperature and pressure to cure the resin and form the solid composite. A list of representative panels is given in Table 1, where each layer denotes one set of wires strung at 90° to another set of wires, separated by a layer of prepreg. Samples containing more than one layer of wires had 0.125" of composite material separating such layers.

The turn-on frequencies were numerically calculated using ANSOFT-HFSS and inserted in the theoretical relations to estimate the negative values of the dielectric constant at the stop frequency and lower than the turn-on frequency, since these values cannot be calculated through frequency domain simulations. The measurement setup comprised of an anechoic chamber and an Agilent vector network analyzer (model number 8722ES). The standard S-parameters of the chamber with and without the panel were measured and an adaptive macro was then used to extract the material properties. The experimental results and the numerical calculations, along with the theoretical continuation to the negative dielectric values, are shown in Figure 3 for all the samples.

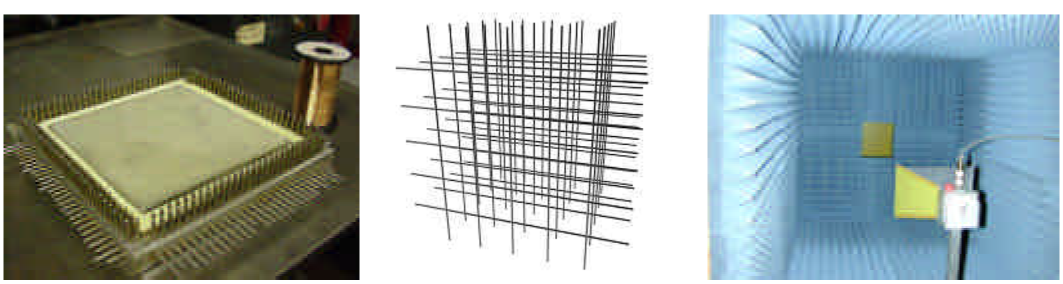

Figure 2. [Left] Layup tool used for fabrication of the fiber reinforced composites. Prepreg layers are stacked in this device and encase wires strung around peripheral rods with the prescribed spacing. [Center] Schematic of thin wire array; wires are arranged horizontally and vertically in the plane and repeat through the thickness of the panel. [Right] The incident side of the anechoic chamber used for microwave transmission measurements through the panel. Walls are covered with microwave absorber material to eliminate reflection and approximate free space wave propagation.

Composite Material	Dimensions (inches)	Wire Diameter (inches)	Wire Spacing (inches)	Number Wire Layers
EG	6x6x0.125	0.003	0.125	1
EG	6x6x0.250	0.003	0.125	2
EG	6x6x0.375	0.003	0.125	3
EG	6x6x0.125	0.002	0.125	1
EG	6x6x0.250	0.002	0.125	2
EG	6x6x0.375	0.002	0.125	3
CEQ	6x6x0.250	0.002	0.125	2
CEQ	6x6x0.375	0.002	0.125	3
VES	6x6x0.250	0.002	0.125	2
VES	6x6x0.375	0.002	0.125	3

Table 1. Description of representative fiber reinforced composite panels. EG, CEQ, and VES represent Epoxy/E-glass, Cyanate Ester/Quartz, and Vinyl Ester/Spectra materials, respectively.

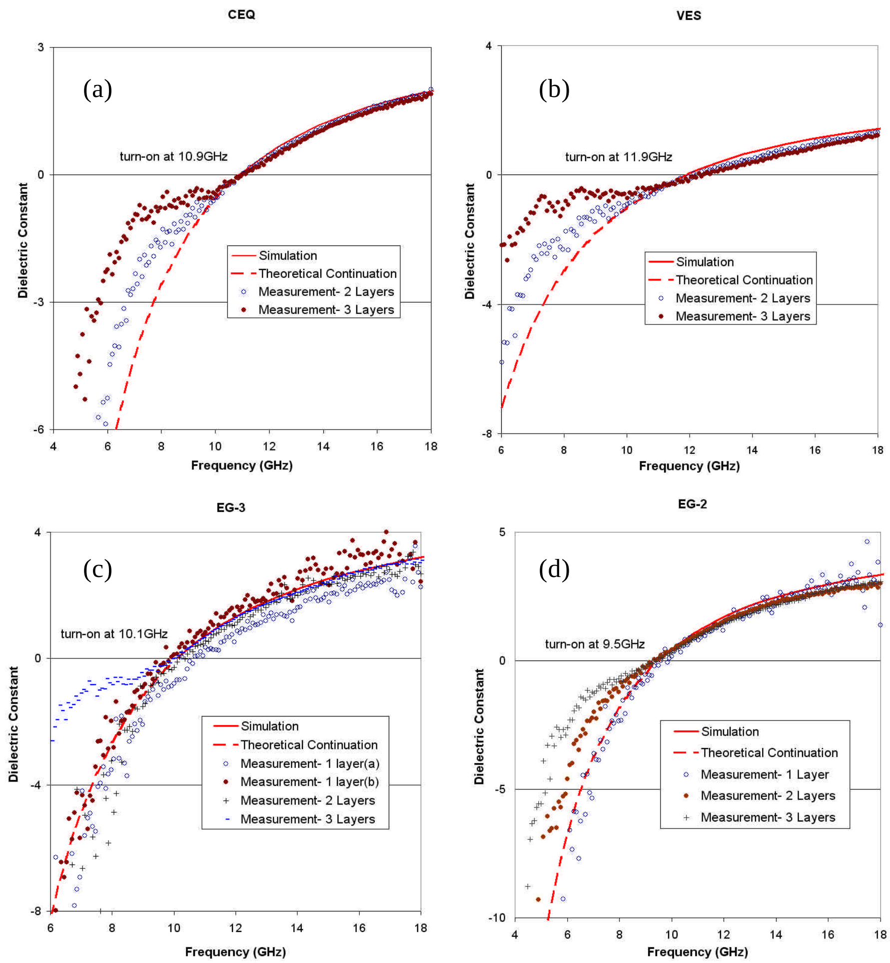

Figure 3. Numerical and experimental characterization of the samples listed in Table 1. Data for panels made of the same host composite material and wire diameter are displayed in one chart since their numerical simulations are identical. "Turn-on" indicates the transition between the stop-band and pass-band, or the frequency above which the material transmits electromagnetic radiation. (a) 0.002" diameter wires embedded in Cyanate Ester/Quartz composite. (b) 0.002" diameter wires embedded in Vinyl Ester/Spectra composite. (c) 0.003" diameter wires embedded in Epoxy/E-glass composite (two single layer samples were manufactured and measured for this case). (d) 0.002" diameter wires embedded in Epoxy/E-glass composite.

Thick Wire Composites

Since using thicker wire with coil geometry improves processing of these electromagnetic designs, we have identified textile braiding as an ideal method to integrate the conductive wires with the reinforcing fibers of the structural composite. Braiding allows fine control of the pitch and diameter of the wire coil such that the electromagnetic properties may be tuned for desired performance. Additionally, the sense of the coil, as left-handed or right-handed, may be differentiated in the braiding process to address issues of chirality. Braiding the wires with the reinforcing fibers results in an electromagnetic element with uniform geometry that maintains its shape under considerable handling and other processing conditions. The braid itself is a tough structure that protects elements woven into the outer sheath, as well as other elements in the core.

We have tested the viability of braiding wires and fibers to create the coil elements with tunable electromagnetic properties. As an example, we have braided coil elements with para-aramid (DuPont Kevlar® 49) reinforcing fiber and polyamide (DuPont nylon 6,6) thermoplastic fiber. The outer braid consists of a single 30 gauge (0.254 mm diameter) copper wire with seven tows of 1000 denier Kevlar fiber. The wire and fibers are braided in a 2-dimensional tubular braider around a core consisting of one tow of 8520 denier Kevlar fiber to create a two-under, two-over braid architecture. The braided elements had the following specifications: a pitch of 1 turn per 0.14” along the axis and a braid diameter of 0.061”. The braided elements were spaced at a distance of 0.39” in two directions such that there were two layers of unidirectional coils. Furthermore, coils of left-handed sense were placed alongside coils of right-handed sense to eliminate chiral effects. The geometry of the test arrangement is pictured below in Figure 4. The plasma frequency of this sample was numerically predicted at f_p = 6GHz. Since the Kevlar fills a small fraction of the total volume, the rest being air, the dielectric constant is expected to approach 1 for higher frequencies. One may see in Figure 4 that the experimental results showed excellent agreement with our simulations.

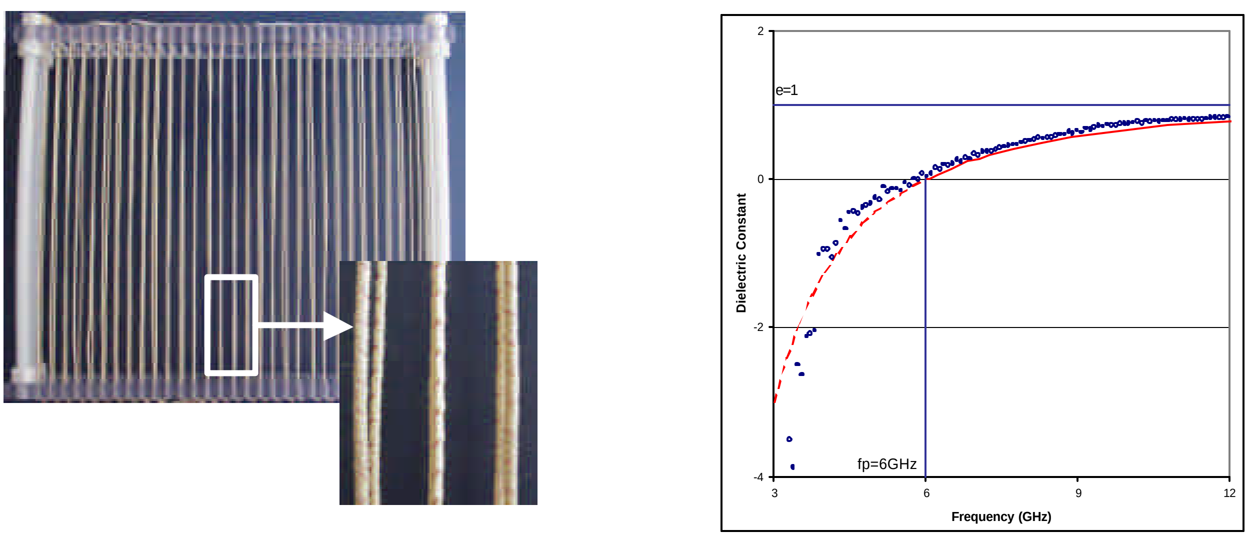

Figure 4. [Left] Test frame containing Kevlar braided with copper wire. Braids are arranged such that adjacent braid elements contain wire coils with opposite sense (inset). [Right] Simulated (dashed line) and experimental (circles) characterization of the braided elements.

4. SELF-HEALING FUNCTIONALITY

To serve as the matrix for our braided fiber composite were are incorporating a novel polymer developed by Xiangxu et al. at UCLA.[7] This polymer has the unique ability to heal internal damage by means of its thermo-reversible covalent bonds. 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 back to its original strength. Combined with our electromagnetic wire medium, this composite has tremendous potential for further multifunctionality.

The ability of this material to repair broken bonds is a result of the presence of a Diels-Alder (DA) adduct in the backbone of the polymer. The material is formed by the reaction of a furan monomer with a maleimide monomer, as shown in Figure 5. Polymerization occurs by the joining of maleimide groups to furan groups via a Diels-Alder reaction. This polymer is referred to as 3M4F polymer, indicating 3 maleimide and 4 furan groups per polymer unit. The healing mechanism is a result of the DA reaction, since most are thermally reversible. 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 failure or when heated above its transition temperature. However, because this bond is reversible, it will also reform when the material cools back below the transition temperature.

The classification of this polymer is in between that of a thermoplastic and a thermoset. It is most like a thermoset, in that it is a highly cross-linked, rigid polymer. Its mechanical properties are similar to epoxies and other thermoset resins commonly used in fiber composites. The majority of the bonds within the structure interact through covalent bonding. However, since some of these bonds are thermally reversible, the material has partial thermoplastic character in that it can be heated to its transition temperature, whereby there is a significant decrease in the modulus of the material due to breaking of the DA adduct. Upon cooling the adduct reforms and the modulus returns to its original value. This process may be carried out repeatedly with little change in mechanical properties, much like traditional thermoplastic polymers. It is important to make the distinction, however, between healing events observed in thermoplastic polymers,[11-13] and healing observed in this material. Crack healing and welding of thermoplastics is a result of diffusion of chains across the interface to bridge the crack face and rejoin the material. The strength across that interface is largely the result of secondary bonding, such as hydrogen bonding, and an entanglement network formed between chains across the interface. The strength of the interface varies greatly depending upon the depth of penetration and number of the chains that bridge the cracked interface. No primary bonds, such as covalent bonds are created or reformed in this process. In the 3M4F material however, healing of the crack interface is a result of reforming broken covalent bonds.

Xiangxu et al. conducted quantitative testing of the crack healing process at UCLA. Compact tension samples were notched with a razor blade and loaded in a direction perpendicular to the pre-crack. Complete crack propagation occurred across the sample such that two halves were created. The halves were matched together as close as possible and heated at 120°C to 150°C for two hours under clamping pressure. A slight interface remained in the healed specimen, indicating imperfect matching of the sample halves. To test the healing efficiency the samples were then reloaded and the fracture load was measured. Depending on heating conditions, the healing efficiency was measured between 41% and 50%. Furthermore, multiple healing at or near the same interface was also observed. While respectable healing efficiency was achieved, higher efficiency is expected with improved re-matching of the halves at the fractured interface.

In addition, we have observed the healing mechanism in samples of 3M4F polymer. Our aim was to arrest crack growth prior to complete fracture of the sample. In this way we could improve the ability to match the severed interfaces back to their original location prior to heating. Due to the inherent high mechanical strength of this material a controlled cracking procedure was devised. Samples were machined to 0.25” x 0.15” x 0.20” dimensions with a 0.08” diameter hole penetrating through the middle. Two notches were cut into the hole to initiate the crack on opposing sides of the hole. The samples were cooled in liquid nitrogen and immediately loaded in compression in the direction of the machined notch. The applied load caused cracks to grow from the notches in a controlled manner in the direction of the applied load. Cracked samples were then placed in a spring device that applied compression normal to the crack faces so as put the crack faces in contact. Heat was then applied at various levels and durations. For samples treated for at least 6 hours above 80°C, under a nitrogen atmosphere with about 8 kPa of compression normal to the interface, the crack was observed to disappear, indicating healing. In these cases, no visible scar remained, apart from the initial starter notch. These tests were only qualitative in nature. Quantitative tests of the healing efficiency are being developed. However, it appeared that the crack had been completely repaired and visually the material had been restored to its original state. Figure 5 shows representative photographs before and after the healing event.

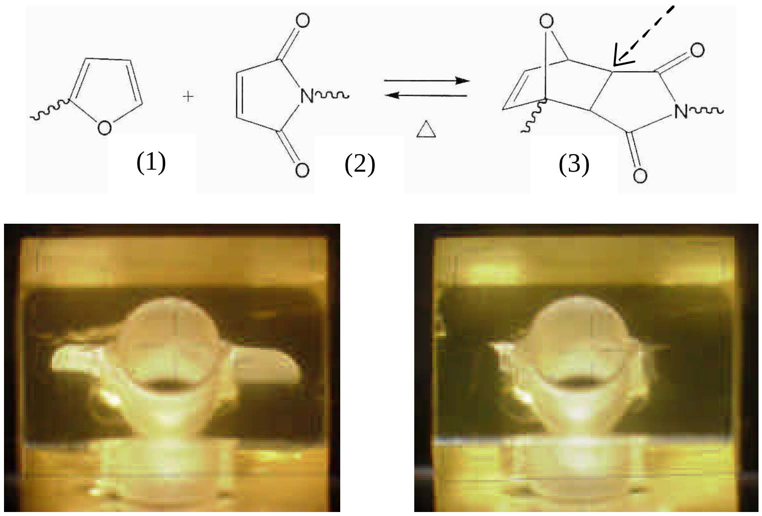

Figure 5. [Top] Chemical reaction of furan monomer (1) with maleimide monomer (2) to form 3M4F polymer (3). Dotted arrow indicates thermally reversible DA adduct (figure adapted from Xiangxu et al.[7]) [Bottom] Optical photographs taken at 20X magnification of representative 3M4F sample. Diagonal view of sample with pre-drilled hole and starter notches is shown. [Left] 3M4F polymer sample after controlled cracking. Note cracks have propagated from the starter notches to the left and right of the sample. [Right] Same sample after healing for 6 hours under nitrogen and about 8kPa of compression normal to the crack face. Crack faces have disappeared leaving only starter notches and pre-drilled hole visible.

5. INTERACTIVE FUNCTIONALITY

Combining the braided electromagnetic elements with the 3M4F polymer leads to a material with many novel functionalities. Together the components work in synergy to enhance one another. On its own, the 3M4F material is an outstanding engineering polymer. With the addition of reinforcing fibers the material competes with other high performance engineering composites in terms of mechanical strength. The electromagnetic properties of the polymer are well suited for communications devices, and furthermore the presence of the braided wire elements allows for tuning of the dielectric constant of the bulk material. Moreover, the wires enhance the self-repairing properties of the polymer. Acting as both electrical and thermal conductors, the wires provide channels through which heat is transported to heal cracks within the material. They may be heated resistively if connected to an external current source, or they may act as inductive heaters if external magnetic fields are applied. Since the wires are distributed periodically throughout the composite, heat is also uniformly distributed. Furthermore, the reinforcing fibers may also contribute to the healing mechanism. If a fiber with a negative coefficient of thermal expansion is chosen to reinforce the core of the braid or fill in the weave of the laminate, then it will provide compression to close the crack faces as the material is being heated. For instance, both Kevlar® and Zylon® (Toyobo PBO) fibers have negative axial CTEs, on the order of –2 to –6 ppm/°C. Upon heating, a cracked polymer matrix (with a positive CTE) will expand as the reinforcing fibers contract, thus putting the matrix into compression and closing the crack faces. A schematic of this concept is provided in Figure 6.

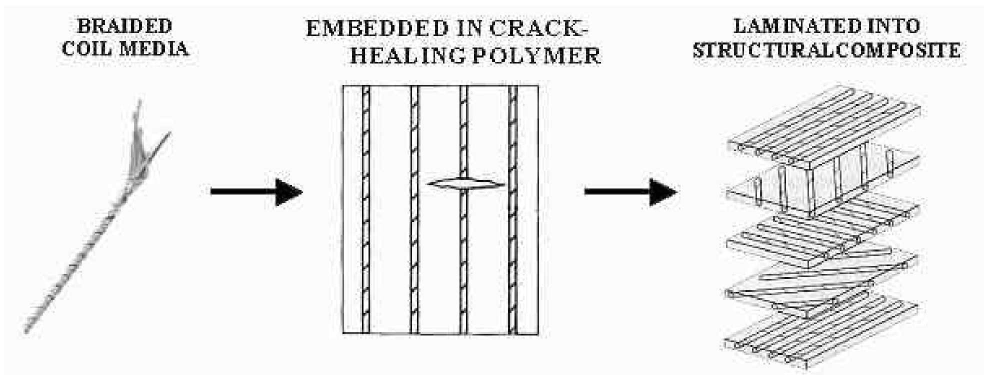

Figure 6. Schematic of self-healing multifunctional concept. [Left] Braided coil media consist of wires for electromagnetic and heating functionality, and reinforcing fibers for strength and compression functionality. [Center] Braids are woven into fabric and embedded in 3M4F polymer matrix. [Right] Woven layers are laminated into structural composite with integrated electromagnetic and self-healing functions. Internal damage, in the form of polymer matrix cracking, may be repaired when heat is applied through the wires. Crack faces will close as matrix expands and fibers contract, while thermally induced healing mechanism of polymer repairs the damage.

6. CONCLUSIONS

We have presented the concept of a self-healing structural composite with integrated electromagnetic functionalities. Such functionalities include the ability to tune the dielectric constant and filter RF radiation, among others. Our future efforts in the area of electromagnetic functionality include development of composites with controlled magnetic behavior in addition to tunable electric properties. Moreover, by combining negative electric permittivity and negative magnetic permeability, we are planning to introduce negative index composites. The self-healing concept is achieved through contributions from all components, including the thermo-reversible covalent bonds of the 3M4F polymer, the thermal transport of the wires, and the compression provided by the reinforcing fibers. Further work is under consideration to incorporate sensing ability into the core of the braid to detect and repair damage autonomously.

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