Composites get smart

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Intrinsically smart structural composites are multifunctional structural materials which can perform functions such as sensing strain, stress, damage or temperature; thermoelectric energy generation; EMI shielding; electric current rectification; and vibration reduction. These capabilities are rendered by the use of materials science concepts to enhance functionality without compromising structural properties. They are not achieved by the embedding of devices in the structure. Intrinsically smart structural composites have been attained in cement-matrix composites containing short electrically conducting fibers and in polymer-matrix composites with continuous carbon fibers. Cement-matrix composites are important for infrastructure, while polymer-matrix composites are useful for lightweight structures.

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Smart structures are important because of their relevance to hazard mitigation, structural vibration control, structural health monitoring, transportation engineering, thermal control, and energy saving. Research on smart structures has emphasized the incorporation of various devices in a structure for providing sensing, energy dissipation, actuation, control or other functions. Work on smart composites has focused on the incorporation of a functional material or device in a matrix material for enhancing the smartness or durability, while that on smart materials has studied materials (e.g. piezoelectric) used for making relevant devices. However, relatively little attention has been given to the development of structural materials (e.g. concrete and composites) that are inherently able to provide some of the smart functions, so that the need for embedded or attached devices is reduced or eliminated, thereby lowering cost, enhancing durability, increasing the smart volume, and minimizing mechanical property degradation (which usually occurs in the case of embedded devices).

Smart structures have the ability to sense certain stimuli and respond in an appropriate fashion, somewhat like a human being. Sensing is the most fundamental aspect of a smart structure. A structural composite which is itself a sensor is said to be self-sensing. It is multifunctional.

This article focuses on structural composites for smart structures. It addresses cement-matrix and polymer-matrix composites. The smart functions covered include strain/stress sensing (for structural vibration control, traffic monitoring and weighing), damage sensing (both mechanical and thermal damage in relation to structural health monitoring and hazard mitigation), temperature sensing (for thermal control, hazard mitigation and structural performance control), and thermoelectricity (for thermal control, electrical energy generation, and energy saving). These functional abilities of structural composites have been shown in the laboratory and applications in the field are forthcoming.

1. Cement-matrix composites

Cement-matrix composites include concrete (containing coarse and fine aggregates), mortar (containing fine but no coarse aggregate), and cement paste (containing no aggregate, neither coarse nor fine). Other fillers, called admixtures, can be added to the mix to improve the properties of the composite. Admixtures are discontinuous, so that they can be included in the mix. They can be particles, such as silica fume (a fine particulate) or latex (a polymer in the form of a dispersion). Short fibers, such as polymer, steel glass or carbon fibers, and liquids, such as methylcellulose aqueous solution, water reducing agents or defoamers, can be used. Admixtures for rendering the composite smart while maintaining or even improving the structural properties are the focus of the following sections.

1.1 Radio wave reflectivity

The electrical conductivity of carbon fibers means that the addition of short fibers to cement significantly increases the ability of the composite to reflect radio waves, thus allowing electromagnetic interference (EMI) shielding and lateral guidance in automatic highways. However, thanks to the skin effect (the phenomenon by which electromagnetic radiation at a high frequency, such as 1 GHz, penetrates only the near surface region of a conductor) discontinuous carbon filaments of 0.1 µm diameter, made from carbonaceous gases by catalytic growth, are much more effective for radio wave reflection than conventional pitch-based carbon fibers[1-3] of diameter 15 µm. However, the 0.1 µm diameter filaments are less effective than the 15 µm diameter fibers as a reinforcement.

Cement-matrix composites are more effective than corresponding polymer-matrix composites for radio wave reflection, because of the slight conductivity of the cement matrix compared with the insulating nature of the polymer matrix. The conductivity of the cement matrix allows some electrical connectivity of the filler units, even when the filler concentration is below the percolation threshold[3].

1.2 Strain sensing

Cement reinforced with short carbon fibers is capable of sensing its own strain thanks to the effect of strain on the volume electrical resistivity[4-21] (piezoresistivity) and the electric polarization[22] (direct piezoelectricity).

Uniaxial tension of carbon fiber reinforced cement in the elastic regime causes reversible increases in the volume electrical resistivity in both longitudinal and transverse directions, such that the gage factor (fractional change in resistance per unit strain) is comparable in magnitude in the two directions[15]. In contrast, uniaxial compression causes reversible decreases in the resistivity in both directions[16]. Without fibers, the resistivity changes are much smaller and less reversible. The resistivity increase is attributed to defect generation or aggravation under tension and defect healing under compression. The fractional change in resistance per unit strain (i.e. the gage factor) is up to 700.

The transverse resistivity increases upon uniaxial tension, even though the Poisson Effect causes the transverse strain to be negative. This means that the effect of the transverse resistivity increase overshadows the effect of the transverse shrinkage. The resistivity increase is a consequence of the uniaxial tension. In contrast, under uniaxial compression, the resistance in the stress direction decreases. Hence, the effects of uniaxial tension on the transverse resistivity and of uniaxial compression on the longitudinal resistivity are different; the gage factors are negative and positive for these cases respectively.

The similarity of the resistivity change in longitudinal and transverse directions under uniaxial tension suggests similarity for other directions as well. This means that the resistance can be measured in any direction in order to sense the occurrence of tensile loading. Although the gage factor is comparable in both longitudinal and transverse directions, the fractional change in resistance under uniaxial tension is much higher in the longitudinal direction than the transverse direction. Thus, the use of the longitudinal resistance for practical self-sensing is preferred. Similar piezoresistive behavior has been observed in carbon fiber cement in the form of a coating[17].

The direct piezoelectric effect was observed in cement pastes by voltage measurement[23] and by observing the electric polarization during repeated compressive loading[22]. The piezoelectric effect is attributed mainly to the movement of ions in the cement.

1.3 Damage sensing

Both mechanical damage and thermal damage are of concern to the integrity of cement-based materials. The self-sensing of damage in cement-based materials has been demonstrated with high sensitivity to even minor damage. Work on damage sensing mainly relates to mechanical rather than thermal damage, although damage from freeze-thaw cycling is well-known in cement-based materials, as well as fire damage caused by the heat.

Cement-based materials are capable of sensing major and minor mechanical damage – even damage during elastic deformation – because of the electrical resistivity increase that accompanies damage[24,25]. The use of short carbon fibers as an admixture enhances the sensitivity[24]. Both damage within the cement-based material and at an interface (e.g. between cement-based materials and steel rebar, or between old and new cement-based materials) can be sensed. Damage within a cement-based material is indicated by an increase in the volume electrical resistivity of the material, i.e. the material itself is the sensor[24]. Damage of an interface is indicated by an increase in the contact electrical resistivity of the interface[26,27], i.e. the interface itself acts as the sensor. That both strain and damage can be sensed simultaneously through resistance measurement means that the strain/stress condition (during dynamic loading) under which damage occurs can be obtained, thus facilitating damage origin identification. Damage is indicated by a resistance increase, which is larger and less reversible when the stress amplitude is higher. The resistance change can be a sudden increase during loading or a gradual shift of the baseline resistance.

Thermal damage can be sensed by electrical resistance measurement too, as shown during temperature cycling[28]. Even minor thermal cycling damage results in an irreversible increase in the electrical resistivity. In contrast, temperature increase causes a reversible decrease in the electrical resistivity. Thus, thermal damage and temperature can be sensed simultaneously and distinctly through resistivity measurements, thereby allowing study of the mechanism of thermal damage.

1.4 Thermistors

A thermistor is a thermoelectric device consisting of a material (typically a semiconductor, but in this case a cement-based material) whose electrical resistivity changes (typically decreases) with a rise in temperature.

The carbon fiber cement-based material described previously for strain sensing is a thermistor, because its resistivity decreasing reversibly with increasing temperature[29]; the sensitivity, as indicated by the activation energy (0.4 eV), is comparable to that of semiconductor thermistors. (The effect of temperature will need to be compensated when using the cement-based material as a strain or damage sensor.) Without fibers, the thermistor sensitivity is much lower[29,30]. The temperature dependence of the electrical resistivity, as embodied in the thermistor effect, gives fundamental information on the mechanism of conduction, particularly the activation energy for conduction.

1.5 Thermoelectric devices

The Seebeck effect[31-35] is a thermoelectric effect which is the basis for thermocouples and for thermoelectric energy generation. This effect involves charge carriers moving from a hot to a cold point within a material, thereby resulting in a voltage difference between the two. Hole carriers tend to make the absolute thermoelectric power more positive, while electron carriers tend to make the absolute thermoelectric power more negative.

The Seebeck effect in carbon fiber reinforced cement paste involves electrons and/or ions from the cement matrix[31] and holes from the fibers[31-33], such that the two contributions are equal at the percolation threshold, a fiber content between 0.5% and 1.0% by mass of cement[31]. The absolute thermoelectric power is -2 µV/°C for plain cement paste (without admixture)[31]. The hole contribution increases monotonically with increasing fiber content below and above the percolation threshold, as indicated by the absolute thermoelectric power becoming more positive[31]. By using carbon fibers that have been intercalated with an acceptor (bromine)[35], the hole contribution is enhanced and the absolute thermoelectric power reaches +17 µV/°C.

The free electrons in a metal mean that a cement containing metal fibers, such as steel, is even more negative in its thermoelectric power (as negative as -68 µV/°C) than cement without fiber[34]. The attainment of a very positive thermoelectric power is also attractive, since a material with a negative thermoelectric power and a material with a positive thermoelectric power are two very dissimilar materials, and together can form a thermocouple junction[36]. (The greater the dissimilarity, the more sensitive is the thermocouple.) The thermoelectric power magnitude of 68 μV/°C is lower than those of state-of-the-art thermoelectric materials (e.g. 220 μV/°C for ZnSb). However, state-of-the-art thermoelectric materials are typically semiconductors, which are expensive and poor in mechanical properties.

1.6 Diodes: the p-n junction

A p-n junction between a p-type conductor (a conductor with holes as the majority carrier) and an n-type conductor (a conductor with electrons as the majority carrier) is ideally rectifying, i.e. the current-voltage (I-V) characteristic is such that the current is large when the applied voltage is positive on the p-side relative to the n-side and is small when the applied voltage is positive on the n-side relative to the p-side. The p-n junction is central to electrical circuitry, essential as it is to diodes and transistors.

Akin to the p-n junction is the n-n$^+$ junction, formed between a weakly n-type conductor and a strongly n-type (n$^+$) conductor.

In conventional electronics, a p-n junction is obtained by allowing a p-type semiconductor to contact an n-type semiconductor, with each type obtained by doping with appropriate impurities which serve as electron donors (for n-type semiconductors) or electron acceptors (for p-type semiconductors).

Cement, however, is inherently n-type, although only slightly[31]. Upon addition of a sufficient amount of short carbon fibers to cement, a composite which is p-type is obtained[31-33]. Addition of short steel fibers to cement, however, creates a composite which is strongly n-type[34]. In other words, carbon fibers contribute to conduction by holes; steel fibers contribute to conduction by electrons.

Electric current rectification and thermocouples have been attained in cement-based junctions (preferably a p-n junction, as an n-n$^+$ junction gives poorer performance), fabricated by separate pouring and co-curing of electrically dissimilar cement mixes side by side[36]. Fig. 1 shows the current-voltage characteristic of a cement-based p-n junction.

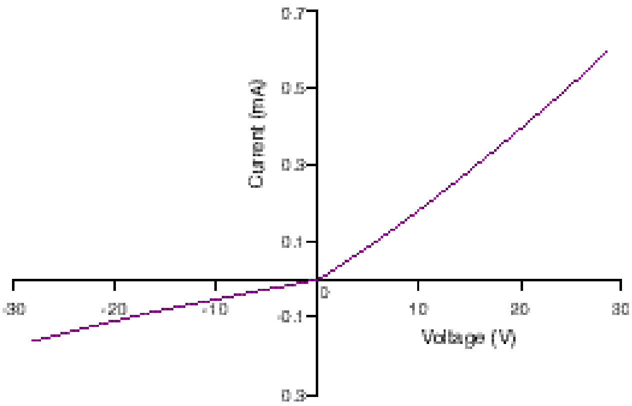

Fig. 1 Current-voltage characteristic of a cement-based p-n junction.

2. Polymer-matrix composites

Polymer-matrix composites for structural applications typically contain continuous carbon, polymer, or glass fibers, as continuous fibers tend to be more effective than short fibers as a reinforcement.

Polymer-matrix composites with continuous carbon fibers are used for aerospace, automobile and civil structures. (In contrast, continuous fibers are too expensive for reinforcing concrete.) The fact that carbon fibers are electrically conducting, whereas polymer and glass fibers are not, means that carbon fiber composites are predominant among polymer-matrix composites that are intrinsically smart.

2.1 Strain sensing

Smart structures which can monitor their own strain are valuable for structural vibration control. Self-monitoring of strain (reversible) has been achieved in carbon fiber epoxy-matrix composites without the use of embedded or attached sensors[37-41], as the electrical resistance of the composite in the through-thickness or longitudinal direction changes reversibly with longitudinal strain (gage factor up to 40) because of alterations in the degree of fiber alignment. Tension in the fiber direction of the composite increases the degree of fiber alignment, thereby increasing the chance of fibers in adjacent laminae to touch one another. As a consequence, the through-thickness resistance increases while the longitudinal resistance decreases.

The strain sensitivity (gage factor) is defined as the reversible part of $\Delta R/R_o$ divided by the longitudinal strain amplitude. It is negative (from -18 to -12) for the longitudinal $\Delta R/R_o$ and positive (from 17 to 24) for the through-thickness $\Delta R/R_o$. The magnitudes are comparable for the longitudinal and through-thickness strain sensitivities. As a result, whether the longitudinal R or the through-thickness R is preferred for strain sensing just depends on the convenience of electrical contact application for the geometry of the particular smart structure.

A dimensional change without any resistivity change would cause the longitudinal R to increase during tensile loading and decrease during compressive loading. In contrast, the longitudinal R decreases upon tensile loading and increases upon compressive loading. In particular, the magnitude of $\Delta R/R_o$ under tension is between seven and eleven times that of $\Delta R/R_o$ calculated by assuming that $\Delta R/R_o$ is only caused by dimensional change and not any resistivity change. Hence the contribution of $\Delta R/R_o$ from the dimensional change is negligible compared to that from the resistivity change.

The irreversible behavior, though small compared to the reversible behavior, is such that R (longitudinal or though-thickness) under tension is irreversibly decreased after the first cycle. This behavior is attributed to the irreversible disturbance of the fiber arrangement at the end of the first cycle, such that the fiber arrangement becomes less neat. A less neat fiber arrangement means more chance for the adjacent fiber layers to touch one another.

2.2 Damage sensing

Self-monitoring of damage (whether due to stress or temperature, under static or dynamic conditions) has been achieved in continuous carbon fiber polymer-matrix composites, as the electrical resistance of the composite changes with damage[42-56].

Minor damage in the form of slight matrix damage and/or disturbance to the fiber arrangement is indicated by the longitudinal and through-thickness resistance decreasing irreversibly, caused by the increase in the number of contacts between fibers. More significant damage in the form of delamination or interlaminar interface degradation is demonstrated by the through-thickness resistance (or more exactly the contact resistivity of the interlaminar interface) increasing with the decrease in the number of contacts between fibers of different laminae. Irreversible increase of the longitudinal resistance highlights major damage in the form of fiber breakage. During mechanical fatigue, delamination was observed to begin at 30% of the fatigue life, whereas fiber breakage was observed to begin at 50%[43]. During thermal cycling, however, an increase in the contact resistivity of the interface shows up damage at the interlaminar interface[57,58].

2.3 Temperature sensing

Continuous carbon fiber epoxy-matrix composites provide temperature sensing by acting as thermistors[59,60] and thermocouples[61]. The thermistor function stems from the reversible decrease of the contact electrical resistivity at the interface between fiber layers (laminae) with temperature. From the (negative) slope of the Arrhenius plot, which is quite linear, the activation energy can be calculated. This is the energy for an electron jumping from one lamina to another. Electronic excitation across this energy enables conduction in the through-thickness direction. The electron jump primarily occurs at points where there is direct contact between fibers of adjacent laminae. This direct contact is possible because of the flow of the epoxy resin during composite fabrication and due to the slight waviness of the fibers[42].

The thermocouple function originates from the use of n-type and p-type carbon fibers (obtained by intercalation) in different laminae. The thermocouple sensitivity and linearity are as good as or better than those of commercial thermocouples. By using two laminae that are crossply, a two-dimensional array of thermistors or thermocouple junctions can be obtained, allowing temperature distribution sensing.

By using junctions comprising strongly n-type and strongly p-type partners, a thermocouple sensitivity as high as +82 μV/°C was attained. Semiconductors are known to exhibit much higher values of the Seebeck coefficient than metals, but the need to have thermocouples in the form of long wires makes metals the material of choice for thermocouples. Intercalated carbon fibers exhibit much higher values of the Seebeck coefficient than metals. Yet, unlike semiconductors, their fiber and fiber composite forms make them convenient for practical use as thermocouples.

The thermocouple sensitivity of carbon fiber epoxy-matrix composite junctions is independent of the extent of curing and is the same for unidirectional and crossply junctions. This is consistent with the fact that the thermocouple effect hinges on the difference in the bulk properties of the two partners, and is not an interfacial phenomenon. This behavior means that the interlaminar interfaces in a fibrous composite serve as thermocouple junctions in the same way, irrespective of the lay-up configuration of the dissimilar fibers in the laminate. As a structural composite typically has fibers in multiple directions, this behavior facilitates the use of a structural composite as a thermocouple array.

It is important to note that the thermocouple junctions do not require any bonding agent other than the epoxy, which serves as the matrix of the composite but not as an electrical contact medium (since it is not conducting). In spite of the presence of the epoxy matrix in the junction area, direct contact occurs between a fraction of the fibers in adjacent laminae, thus resulting in a conduction path in the direction perpendicular to the junction.

Conclusion

Intrinsically smart structural composites for strain, damage, and temperature sensing, thermal control, thermoelectric energy generation, EMI shielding, electric current rectification, and vibration reduction are attractive for smart structures. They include cement-matrix and polymer-matrix composites, particularly cement-matrix composites containing short carbon fibers and polymer-matrix composites containing continuous carbon fibers. The electrical conductivity of the fibers enables the DC electrical resistivity of the composites to change in response to strain, damage or temperature, thereby allowing sensing. MT

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