Polymers in electronics, EMI - neutron shielding, self sensing applications

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ABSTRACT

Water, Food and Shelter "were" the basic needs of human being ….. is it right or we are wrong?
Electronics have become a integral part of the human daily activities, right from dawn to dusk and polymers have been most crucial players in all technologies let it be a agricultural technology, pharmaceutical technology, packaging technology, automobiles technology, textile technology also electrical and electronics industries, here in this article we have focused on the use of polymeric material in electronics and electrical industries to manufacture various types of gadgets and accessories required for working of an electrical appliances. In the current article we will discuss on materials for thermal conduction and electromagnetic induction shielding, polymer matrix composites for microelectronics, carbon fiber based self sensing composites will be discussed. Let us start with a short introduction.　　　© 2015 Trade Science Inc. - INDIA

Engineering materials constitute the foundation of technology, whether the technology pertains to structural, electronic, thermal, electrochemical, environmental, biomedical, or other applications. The history of human civilization evolved from the Stone Age to the Bronze Age, the Iron Age, the Steel Age, and to the Space Age (contemporaneous with the Electronic Age). Each age is marked by the advent of certain materials. The Iron Age brought tools and utensils. The Steel Age brought rails and the Industrial Revolution. The Space Age brought structural materials (e.g., composite materials) that are both strong and lightweight. The Electronic Age brought semiconductors. Modern materials include metals, polymers, ceramics, semiconductors, and composite materials. Metals, polymers, ceramics, semiconductors, and composite materials constitute the main classes of materials. Metals (including alloys) consist of atoms and are characterized by metallic bonding (i.e., the valence electrons of each atom are delocalized and shared among all the atoms). Most of the elements in the Periodic Table are metals. Examples of alloys are Cu-Zn (brass), Fe-C (steel), and Sn-Pb (solder). Alloys are classified according to the majority element present. The main classes of alloys are iron-based alloys for structures; copper-based alloys for piping, utensils, thermal conduction, electrical conduction, etc.; and aluminum based alloys for lightweight structures and metal-matrix composites. Alloys are almost always in the polycrystalline form.

Ceramics are inorganic compounds such as Al_2O_3 (for spark plugs and for substrates for microelectronics), SiO_2 (for electrical insulation in microelectronics), Fe_3O_4 (ferrite for magnetic memories used in computers), silicates (clay, cement, glass, etc.),

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and SiC (an abrasive). The main classes of ceramics are oxides, carbides, nitrides, and silicates. Ceramics are typically partly crystalline and partly amorphous. They consist of ions (often atoms as well) and are characterized by ionic bonding and often covalent bonding.

Polymers in the form of thermoplastics (nylon, polyethylene, polyvinyl chloride, rubber, etc.) consist of molecules that have covalent bonding within each molecule and vander Waals' forces between them. Polymers in the form of thermosets (e.g., epoxy, phenolics, etc.) consist of a network of covalent bonds. Polymers are amorphous, except for a minority of thermoplastics. Due to the bonding, polymers are typically electrical and thermal insulators. However, conducting polymers can be obtained by doping, and conducting polymer-matrix composites can be obtained by the use of conducting fillers.

Semiconductors have the highest occupied energy band (the valence band, where the valence electrons reside energetically) full such that the energy gap between the top of the valence band and the bottom of the empty energy band (the conduction band) is small enough for some fraction of the valence electrons to be excited from the valence band to the conduction band by thermal, optical, or other forms of energy. Conventional semiconductors, such as silicon, germanium, and gallium arsenide (GaAs, a compound semiconductor), are covalent network solids. They are usually doped in order to enhance electrical conductivity. They are used in the form of single crystals without dislocations because grain boundaries and dislocations would degrade electrical behavior.

Composite materials are multiphase materials obtained by artificial combination of different materials to attain properties that the individual components cannot attain. An example is a lightweight structural composite obtained by embedding continuous carbon fibers in one or more orientations in a polymer matrix. The fibers provide the strength and stiffness while the polymer serves as the binder. Another example is concrete, a structural composite obtained by combining cement (the matrix, i.e., the binder, obtained by a reaction known as hydration, between cement and water), sand (fine aggregate),

gravel (coarse aggregate), and, optionally, other ingredients known as admixtures. Short fibers and silica fume (a fine SiO_2 particulate) are examples of admixtures. In general, composites are classified according to their matrix materials. The main classes of composites are polymer-matrix, cement matrix, metal-matrix, carbon-matrix, and ceramic-matrix.

Polymer-matrix and cement-matrix composites are the most common due to the low cost of fabrication. Polymer-matrix composites are used for lightweight structures (aircraft, sporting goods, wheelchairs, etc.) in addition to vibration damping, electronic enclosures, asphalt (composite with pitch, a polymer, as the matrix), and solder replacement. Cement-matrix composites in the form of concrete (with fine and coarse aggregates), steel-reinforced concrete, mortar (with fine aggregate, but no coarse aggregate), or cement paste (without any aggregate) are used for civil structures, prefabricated housing, architectural precasts, masonry, landfill cover, thermal insulation, and sound absorption. Carbon-matrix composites are important for lightweight structures (like the Space Shuttle) and components (such as aircraft brakes) that need to withstand high temperatures, but they are relatively expensive because of the high cost of fabrication. Carbon-matrix composites suffer from their tendency to be oxidized ($2C + O_2 \rightarrow 2CO$), thereby becoming vapor. Ceramic-matrix composites are superior to carbon-matrix composites in oxidation resistance, but they are not as well developed. Metal-matrix composites with aluminum as the matrix are used for lightweight structures and low-thermal-expansion electronic enclosures, but their applications are limited by the high cost of fabrication and by galvanic corrosion.

Not included in the five categories above is carbon, which can be in the common form of graphite, diamond, or fullerene (a recently discovered form). They are not ceramics because they are not compounds.

Graphite, a semimetal, consists of carbon atom layers stacked in the sequence such that the bonding is covalent due to sp_2 hybridization and metallic (two-dimensionally delocalized 2pz electrons) within a layer, and is vander Waals between the layers. This bonding makes graphite very anisotropic, so it is a

good lubricant due to the ease of the sliding of the layers with respect to one another. Graphite is also used for pencils because of this property. Moreover, graphite is an electrical and thermal conductor within the layers, but an insulator in the direction perpendicular to the layers. The electrical conductivity is valuable in its use for electrochemical electrodes. Graphite is chemically quite inert; however, due to anisotropy, it can undergo a reaction (known as intercalation) in which a foreign species called the intercalate is inserted between the carbon layers. Disordered carbon (called turbostratic carbon) also has a layered structure, but, unlike graphite, it does not have the stacking order and the layers are bent. Upon heating, disordered carbon becomes more ordered, as the ordered form (graphite) has the lowest energy. Graphitization refers to the ordering process that leads to graphite. Conventional carbon fibers are mostly disordered carbon such that the carbon layers are along the fiber axis. Flexible graphite is formed by compressing a collection of intercalated graphite flakes that have been exfoliated i.e. allowed to expand over 100 times along the direction perpendicular to the layers, typically through heating after intercalation. The exfoliated flakes are held together by mechanical interlocking because there is no binder. Flexible graphite is typically in the form of sheets, which are resilient in the direction perpendicular to the sheets. This resilience allows flexible graphite to be used as gaskets for fluid sealing. Diamond is a covalent network solid exhibiting the diamond crystal structure due to sp_3 hybridization (akin to silicon). It is used as an abrasive and as a thermal conductor. Its thermal conductivity is the highest among all materials; however, it is an electrical insulator. Due to its high material cost, diamond is typically used in the form of powder or thin-film coating. Diamond is to be distinguished from diamond-like carbon (DLC), which is amorphous carbon that is sp_3 hybridized. Diamond-like carbon is mechanically weaker than diamond, but it is less expensive. Fullerenes are molecules (C60) with covalent bonding within each molecule. Adjacent molecules are held by vander Waals' forces; however, fullerenes are not polymers. Carbon nanotubes are derivatives of the fullerenes, as they are essentially fullerenes with extra carbon atoms at the equator. The extra atoms cause the fullerenes to be longer. For example, ten extra atoms (one equatorial band of atoms) exist in the molecule C 70. Carbon nanotubes can be single-wall or multiwall, depending on the number of carbon layers.

Many types of radiation, such as neutrons, X-rays and γ rays cause ionization of the media with which they interact, through a complicated mechanism involving the emission of energetic secondary charged particles. The ionizing ability of these types of radiation is the reason for the importance of studying shields. A shield is a physical entity interposed between a source of ionizing radiation and an object to be protected, such that the radiation level at the position of the object will be reduced. The object to be protected is most often a human being, but it can be anything that is sensitive to ionizing radiation[9]. Shielding refers to the reflection and/or absorption of radiation by a material that acts as a shield against its penetration. The primary mechanism of shielding is reflection. For reflection of radiation, the shield must have mobile charge carriers (electrons or holes) that interact with the radiations. As a result, the shield tends to be electrically conducting, although a high conductivity is not required. A secondary mechanism of shielding is absorption. For significant absorption of radiation, the shield should have electric and/or magnetic dipoles that interact with the electromagnetic fields in radiation. The electric dipoles may be provided by materials having a high value of the dielectric constant. The magnetic dipoles may be provided by materials with a high value of magnetic permeability[1]. Lithium, Cadmium, Boron, Gadolinium are the fillers which are used for the absorption of neutrons, due to their peculiarity in mechanism for absorption of neutrons.

Cadmium (Cd) and Boron (B) are generally used for thermal-neutron shielding, absorption cross-sections of these elements for thermal neutrons are large, 2450 and 759 b, respectively in natural compositions[13]. Boron and Cadmium have tendency to absorb neutrons without forming long lived radio nuclides. Lithium-6 (^{6}Li) has a large absorption cross section of 940 b, thus, ^{6}Li is normally used for thermal-neutron shielding in medical and biological ap-

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plications. The natural abundance of ^{6}Li is small, 7.5%, so enriched ^{6}Li (to ≈96%) is usually used. Stable and manageable compounds, lithium fluoride (LiF) and lithium carbonate (Li_2CO_3), are often employed due to the chemical reactivity of metallic lithium. These compounds are powdery in normal atmosphere which makes it possible to use as filler in blends[13].

Radiation at high frequencies penetrates only the near surface region of an electrical conductor. This is known as the "skin effect." Due to the skin effect, a composite material having conductive filler with a small unit size is more effective than one having conductive filler with a large unit size. For effective use of the entire cross-section of a filler unit for shielding, the unit size of the filler should be comparable to or less than the skin depth. A filler of unit size 1 µm or less is typically preferred, though such a small unit size is not commonly available for most filler, and the dispersion of the filler is more difficult when the filler unit size decreases. Earlier, electrically conducting polymers were used, but they tend to be poor in processability and mechanical properties, later metal-coated polymer fibers or particles were used as fillers for shielding, but they suffer from the fact that the polymer interior of each fiber or particle did not contribute to shielding, thereafter coatings with neutron absorbing pigments were tried but the coating suffered from its poor wear resistance[1]. Polymer-matrix composites containing conductive fillers are attractive for shielding due to their processability. In addition, polymer-matrix composites are attractive due to their low density. The polymer matrix is electrically insulating and does not contribute to shielding, though the polymer matrix can affect the connectivity of the conductive filler, and connectivity enhances shielding effectiveness. An elastomer is resilient, but is not able to shield unless it is coated with a conductor (a metal coating called metallization) or is filled with conductive filler (typically metal particles). The coating suffers from its poor wear resistance. The use of conductive filler is problematic because of the resulting decrease in resilience, especially at the high filler volume fraction that is required for shielding effectiveness. Because the decrease in resilience be-

comes more severe as the filler concentration increases, filler that is effective even at a low volume fraction is desirable[1]. Hence researchers propose to use nanofillers based on Lithium as well as Boron in blends with rubbers and plastics i.e, thermoplastic elastomeric blends. A feasible material solution to meet requirements is polymer nanocomposites with neutron absorbing fillers. Owing to high specific surface characteristics, well dispersed nanoparticles can effectively enhance the comprehensive properties of nanocomposites. Firstly the much higher specific surface area can promote stress transfer from matrix to nanoparticles, nanoparticles improves the elastic modulus of polymers more than resulting in enhanced fracture toughness of composites.

Secondly the required loadings of nanoparticles in polymer matrices are usually much lower than those of micro particulate fillers. Therefore the intrinsic merits of polymers such as low weight, ductility and easy processing can be retained after addition of nanoparticles[14]. Rubber due to its excellent chemical resistance properties can be blended with Plastics to ease processing; some rubber like EPDM on contrary has a capacity to accept high filler as well as processing oil loading. On contrary Natural Rubber too has excellent mechanical properties and being non polar it can be blended with non polar plastics to get a blend with all set of properties required. Hence these blends have been selected as a matrix for incorporating lithium based nanofillers as well as boron based nanofillers for neutron shielding applications.

Additionally the blend of rubbers with plastics will give rise to a new class of materials which could be processed like thermoplastics and behave according to the properties of rubbers. Different amounts of boric acid (H_3BO_3) were mixed with a conductive natural rubber (loaded with 40 phr of HAF carbon black) to get thermal neutron radiation shielding composites. It was found that the total macroscopic cross section reaches 0.29 cm^{-1} at 30 phr of H_3BO_3. The dependence of thermal and electrical properties of such composites on the concentration of H_3BO_3 was also studied. Thermal oxidative aging was found to markedly affect the above proper-

ties[10]. Composites of conductive natural rubber (40 HAF/NR) were loaded with different concentrations of boron carbide (B_4C) and subjected to thermal neutron radiation shielding investigation. The highest value obtained for the linear absorption coefficient was ≈ 0.34 cm^{-1} for the composite containing 20 phr of B_4C. Moreover, the effects of B_4C on the thermal and electrical properties of these composites were also studied[11]. High-density polyethylene (HDPE) composites with modified boron nitride (mBN) fillers, functionalized with an organo silane, were fabricated through conventional melt-extrusion processing techniques. The properties and performances of these composites were compared with those of the composites containing pristine BN and boron carbide (B_4C) fillers. The silane functionalization of the BN fillers strongly improved the interfacial adhesion between the polymer matrix and the filler. As a result, the HDPE/mBN composites showed a better dispersion state of the filler particles, larger tensile modulus, greater effective thermal conductivity, and better neutron shielding property compared with the HDPE/BN and HDPE/B_4Ccomposites[14]. Composites of ethylene-propylene diene rubber and low density polyethylene were prepared with two different concentrations of boron carbide powder, namely, 47 and 57 wt%. The composites were investigated for their gamma and slow neutron radiation shielding properties. In addition, the temperature dependence of the electrical and thermal properties of the composites in the temperature range 30-150°C has been studied. The initial 1.5 cm thickness of the composite sample containing 57wt% boron carbide sharply reduced the initial direct slow neutron flux by about 85%. The total macroscopic cross-section of this sample is 0.215 cm^{-1}[9]. High functional epoxy nanocomposites with three different filler materials, i.e., B_4C, PbO, and $Al(OH)_3$, were fabricated using an effective fabrication method consisting of an ultrasonic dispersion of nanoparticles in low-viscosity hardener and a subsequent mixing of a hardener-nanoparticles colloid with epoxy resins. It was confirmed that this approach provided not only a uniform dispersion but also an excellent wetting with enhanced interfacial adhesion of nano-particulate fillers within the matrix. By incorporating those three fillers, a synergistic effect was verified in multiple properties such as mechanical strength properties, thermal degradation, flame retardancy, and radiation shielding performance[14].

The self-sensing of continuous carbon fiber polymer-matrix structural composites has been attained by electrical measurements. The sensing pertains to strain, damage, temperature, bond degradation, structural transitions, and the fabrication process. Polymer-matrix composites for structural applications typically contain continuous fibers such as carbon, polymer, and glass fibers; 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. Because carbon fibers are electrically conducting, whereas polymer and glass fibers are not, carbon fiber composites exhibit electrical properties that depend on parameters such as strain, damage, and temperature, thereby attaining the ability to sense themselves through electrical measurement. The self-sensing ability is valuable for smart structures, smart manufacturing, structural vibration control, and structural health monitoring. Self-sensing means the elimination of attached or embedded sensors, as the structural material itself is the sensor. The consequence is reduced cost, enhanced durability, larger sensing volume, and the absence of mechanical property degradation.

This review is focused on the use of DC electrical measurements for self-sensing in continuous carbon fiber polymer-matrix structural composites. The sensing is in terms of the strain, damage, temperature, bond degradation, structural transitions, and the composite fabrication process. Carbon fibers are electrically conducting, while the polymer matrix is electrically insulating (except for the rare situation in which the polymer is an electrically conducting one). The continuous fibers in a composite laminate are in the form of layers called laminae. Each lamina comprises many bundles (called tows) of fibers in a polymer matrix. Each tow consists of thousands of fibers. There may or may not be twists in a tow. Each fiber has a diameter ranging from 7 to 12 μm. The tows within a lamina are typically oriented in

the same direction, but tows in different laminae may or may not be in the same direction. A laminate with tows in all the laminae oriented in the same direction is said to unidirectional. A laminate with tows in adjacent laminae oriented at an angle of 90° is said to be cross-ply. In general, an angle of 45° and other angles may be involved for various laminae. This is desire for attaining the mechanical properties required for the laminate in various directions in the plane of the laminate. Within a lamina with tows in the same direction, electrical conductivity is highest in the fiber direction. In the transverse direction in the plane of the lamina, the conductivity is not zero, even though the polymer matrix is insulating. This is because there are contacts between fibers of adjacent tows. In other words, a fraction of the fibers of one tow touches a fraction of the fibers of an adjacent tow here and there along the length of the fibers. These contacts result from the fact that fibers are not perfectly straight or parallel (even though the lamina is said to be unidirectional), and that the flow of the polymer matrix (or resin) during composite fabrication can cause a fiber to be not completely covered by the polymer or resin (even though, prior to composite fabrication, each fiber may be completely covered by the polymer or resin, as in the case of a prepreg, i.e., a fiber sheet impregnated with the polymer or resin). Fiber waviness is known as marcelling. Transverse conductivity gives information on the number of fiber-fiber contacts in the plane of the lamina. For similar reasons, the contacts between fibers of adjacent laminae cause the conductivity in the through-thickness direction (direction perpendicular to the plane of the laminate) to be nonzero. Thus, the through-thickness conductivity gives information on the number of fiber-fiber contacts between adjacent laminae.

Matrix cracking between the tows of a lamina decreases the number of fiber-fiber contacts in the plane of the lamina, thus decreasing transverse conductivity. Similarly, matrix cracking between adjacent laminae (as in delamination) decreases the number of fiber-fiber contacts between adjacent laminae, thus decreasing through-thickness conductivity. This means that the transverse and through-thickness conductivities can indicate damage in the form of matrix cracking. Fiber damage (as distinct from fiber fracture) decreases the conductivity of a fiber, thereby decreasing longitudinal conductivity. However, due to the brittleness of carbon fibers, the decrease in conductivity because of fiber damage prior to fiber fracture is rather small. Fiber fracture causes a much larger decrease in the longitudinal conductivity of a lamina than does fiber damage. If there is only one fiber, a broken fiber results in an open circuit, i.e., zero conductivity. However, a lamina has a large number of fibers, and adjacent fibers can make contact here and there. Therefore, the portions of a broken fiber still contribute to the longitudinal conductivity of the lamina. As a result, the decrease in conductivity due to fiber fracture is less than what it would be if a broken fiber did not contribute to the conductivity. Nevertheless, the effect of fiber fracture on longitudinal conductivity is significant, so longitudinal conductivity can indicate damage in the form of fiber fracture. The through-thickness volume resistance of a laminate is the sum of the volume resistance of each of the laminae in the through-thickness direction, and the contact resistance of each of the interfaces between adjacent laminae (i.e., the interlaminar interface). For example, a laminate with eight laminae has eight volume resistances and seven contact resistances, all in the through-thickness direction. Thus, to study the interlaminar interface, it is better to measure the contact resistance between two laminae rather than the through-thickness volume resistance of the entire laminate. Measurement of the contact resistance between laminae can be made by allowing two laminae (strips) to contact at a junction, and using the two ends of each strip for making four electrical contacts. An end of the top strip and an end of the bottom strip serve as contacts for passing current. The other end of the top strip and the other end of the bottom strip serve as contacts for voltage measurement. The fibers in the two strips can be in the same direction or in different directions. This method is a form of the four-probe method of electrical resistance measurement. The configuration is illustrated in Figure 1 for cross-ply and unidirectional laminates. To make sure that the volume resistance within a lamina in the through-thickness direction does not contribute to the mea-
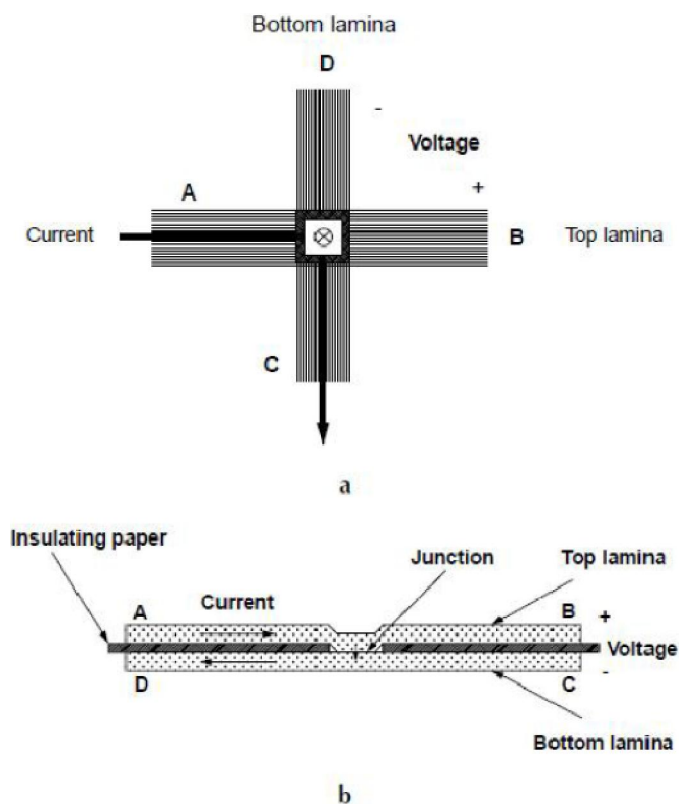
Figure 1 : Contact electrical resistivity between laminae a. cross ply, b. unidirectional

sured resistance, the fibers at each end of a lamina strip should be electrically shorted together by using silver paint or other conducting media. The measured resistance is the contact resistance of the junction. This resistance, multiplied by the area of the junction, gives the contact resistivity, which is independent of the area of the junction and just depends on the nature of the interlaminar interface. The unit of the contact resistivity is $\Omega.m^2$, whereas that of the volume resistivity is Ωm. The structure of the interlaminar interface is more prone to change than the structure within a lamina. For example, damage in the form of delamination is much more common than damage in the form of fiber fracture. Moreover, the structure of the interlaminar interface is affected by the interlaminar stress, which is particularly significant when the laminae are not unidirectional (as the anisotropy within each lamina enhances interlaminar stress). The structure of the interlaminar interface also depends on the extent of consolidation of the laminae during composite fabrication. The contact resistance provides a sensitive probe of the structure of the interlaminar interface.

The measurement of the volume resistivity in the through-thickness direction can be conducted by using the four-probe method, in which each of the two current contacts is in the form of a conductor loop on each of the two outer surfaces of the laminate in the plane of the laminate, and each of the two voltage contacts is in the form of a conductor dot within the loop. An alternate method is to have four of the laminae in the laminate be extra long to serve as electrical leads. The two outer leads are for current contacts; the two inner leads are for voltage contacts. The use of a thin metal wire inserted at an end into the interlaminar space during composite fabrication to serve as an electrical contact is not recommended because the quality of the electrical contact between the metal wire and carbon fibers is hard to control, and the wire is intrusive to the composite. The alternate method is less convenient than the method involving loops and dots, but it approaches more closely the ideal four-probe method.

Polymer-matrix composite materials for microelectronics are reviewed in terms of the science and applications. They include those with continuous and discontinuous fillers in the form of particles and fibers, as designed for high thermal conductiv-

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ity, low thermal expansion, low dielectric constant, high/low electrical conductivity, and electromagnetic interference shielding. Applications include heat sinks, housings, printed wiring boards, substrates, lids, die attach, encapsulation, interconnections, and thermal interface materials. Composite materials are usually designed for use as structural materials. With the rapid growth of the electronics industry, they are finding more and more electronic applications. Due to the vast difference in property requirements between structural and electronic composites, the design criteria are different. While structural composites emphasize high strength and high modulus, electronic composites emphasize high thermal conductivity, low thermal expansion, low dielectric constant, high/low electrical conductivity, and/or electromagnetic interference (EMI) shielding effectiveness, depending on the particular electronic application. Low density is desirable for both aerospace structures and aerospace electronics. Structural composites stress processability into large parts, such as panels, whereas electronic composites emphasize processability into small parts, such as stand-alone films and coatings. Because of the small size of the parts, material costs tend to be less of a concern for electronic composites than for structural composites. For example, electronic composites can use expensive fillers such as silver particles, which provide high electrical conductivity.

Polymer-matrix composites with continuous or discontinuous fillers are used for electronic packaging and thermal management. Composites with continuous fillers are used as substrates, heat sinks, and enclosures. Composites with discontinuous fillers are used for die attach, electrically/thermally conducting adhesives, encapsulations, thermal interface materials, and electrical interconnections. Composites with discontinuous fillers can be in a paste form during processing, thus allowing application by printing and injection molding. Composites with continuous fillers cannot undergo paste processing, but the continuous fillers provide lower thermal expansion and higher conductivity than discontinuous fillers. Composites can have thermoplastic or thermosetting matrices. Thermoplastic matrices have the advantage that a connection can be reworked by heat-

ing for the purpose of repair, whereas thermosetting matrices do not allow reworking. On the other hand, controlled-order thermosets are attractive for their thermal stability and dielectric properties. Polymers exhibiting low dielectric constant, low dissipation factor, low coefficient of thermal expansion, and compliance are preferred. Composites can be electrically conducting or electrically insulating; the electrical conductivity is provided by conductive filler. The composites can be both electrically and thermally conducting, as attained by the use of metal or graphite fillers. They can also be electrically insulating but thermally conducting, as conveyed by the use of diamond, aluminum nitride, boron nitride, or alumina fillers. An electrically conducting composite can be isotropically conducting or anisotropically conducting. A z-axis conductor is an example of an anisotropic conductor.

Polymer matrix with continuous fillers for micro electronics

Epoxy-matrix composites with continuous glass fibers and made by lamination are used for printed wiring boards because of the electrically insulating property of glass fibers, and the good adhesive behavior and established industrial usage of epoxy. Aramid (Kevlar™) fibers can be used instead of glass fibers to provide lower dielectric constant. Alumina (Al_2O_3) fibers can be used for increasing the thermal conductivity. By selecting the fiber orientation and loading in the composite, the dielectric constant can be decreased and the thermal conductivity increased. By impregnating the yarns or fabrics with a silica-based sol and subsequent firing, the thermal expansion can be reduced. Matrices other than epoxy can be used, such as polyimide and cyanate ester. For heat sinks and enclosures, conducting fibers are used since they enhance thermal conductivity and the ability to shield electromagnetic interference. EMI shielding is particularly important for enclosures. Carbon fibers are most commonly used for these applications due to their conductivity, low thermal expansion, and wide availability as a structural reinforcement. For high thermal conductivity, carbon fibers made from mesophase pitch or copper plated carbon fibers are preferred. For EMI

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shielding, both uncoated carbon fibers and metal-coated carbon fibers have been used. For avionic electronic enclosures, low density is essential for saving aircraft fuel. Aluminum is the traditional material for this application. Because of mechanical, electrical, environmental, manufacturing/producibility, and design-to-cost criteria, carbon fiber reinforced epoxy has been judged more attractive than aluminum, glass fiber reinforced epoxy, glass fiber reinforced epoxy with aluminum interlayer, beryllium, aluminum-beryllium, and SiC particle reinforced aluminum. A related application is thermal management of satellites, for which the thermal management materials need to be integrated from the satellite structure down to the electronic device packaging. Continuous carbon fibers are suitable for this application due to their high thermal conductivity, low density, high strength, and high modulus.

Polymer matrix with discontinuous fillers for micro electronics

Polymer-matrix composites with discontinuous fillers are widely used in electronics, despite their poor mechanical properties compared to composites with continuous fibers. This is because materials in electronics do not need to be mechanically strong and discontinuous fillers enable processing through the paste form that is particularly suitable for making films, whether standalone or on a substrate. Screen printing is a common method for patterning a film on a substrate. In the case of an electrically conducting paste, the pattern is an array of electrical interconnections and electrical contact pads on the substrate. As screen printing involves the paste going through a screen, screen printable pastes contain particles and no fiber, and the particles must be sufficiently small, typically less than 10 μm. The larger the particles, the poorer the patternability, i.e., the edge of a printed line is not sufficiently well defined. In applications not requiring patternability, such as thermal interface materials, short fibers are advantageous in that the connectivity of the short fibers is superior to that of particles at the same volume fraction. For a conducting composite, better connectivity of the filler units means higher conductivity for the composite. Instead of using short fibers, one may use elongated particles or flakes for the sake of the connectivity. In general, the higher the aspect ratio, the better the connectivity for the same volume fraction. The use of elongated particles or flakes can provide an aspect ratio larger than one, while retaining patternability. It is an attractive compromise.

In case of a conducting composite, the greater the volume fraction of the conducting filler, the higher the conductivity of the composite, since the polymer matrix is insulating. However, the greater the filler volume fraction, the higher the viscosity of the paste, and the poorer its processability. To attain a high filler volume fraction while maintaining processability, a polymer of low viscosity is preferred, and good wettability of the filler by the matrix, as provided by filler surface treatments and/or the use of surfactants, is desirable. The matrix used in making a polymer-matrix composite can be in the form of a liquid (a thermosetting resin) or a solid (a thermoplastic powder) during the mixing of the matrix and the filler. In the case of the matrix in the form of a powder, the distribution of the filler units in the resulting composite depends on the size of the matrix powder particles; the filler units line the interface between adjacent matrix particles and the filler volume fraction needed for percolation (i.e., the filler units touching one another to form a continuous path) decreases with increasing matrix particle size. The reaching of percolation is accompanied by a large increase in conductivity. However, a large matrix particle size is detrimental to processability, so a compromise is needed. In the case of the matrix in the form of a thermoplastic powder, the percolation attained may be degraded or destroyed after subsequent composite fabrication involving flow of the thermoplastic under heat and pressure. In this case, a thermoplastic that flows less is preferred for attaining high conductivity in the resulting composite.

A less common way to attain percolation in a given direction is to apply an electric or magnetic field to align the filler units along the direction. For this technique to be possible, the filler units must be polarizable electrically or magnetically. Such align-

ment is one of the techniques used to produce z-axis conductors. In percolation, the filler units touch one another to form continuous paths, but there is considerable contact resistance at the interfaces between them. To decrease this contact resistance, thereby increasing the conductivity of the composite, one can increase the size of the filler units so the amount of interface area is decreased, provided percolation is maintained. A less common but more effective way is to bond the filler units together at their junctions by using a solid (like solder) that melts and wets the surface of the filler during composite fabrication. The low melting- point solid can be in the form of particles added to the composite mix, or in the form of a coating on the filler units. In this way, a three-dimensionally interconnected conducting network is formed after composite fabrication.

An intimate interface between the filler and the matrix is important to the conductivity of a composite, even though the filler is conducting and the matrix may be perfectly insulating. This is because conduction may involve a path from a filler unit to an adjacent one through a thin film of the matrix by means of tunneling. In the case of the matrix being slightly conducting (but not as conducting as the filler), the conduction path involves both the filler and the matrix, and the filler-matrix interface is even more important. This interface may be improved by filler surface treatments prior to incorporating the filler in the composite, or by the use of a surfactant. The difference in thermal expansion coefficient between filler and matrix, and the fact that composite fabrication occurs at an elevated temperature, cause thermal stress during cooling of the fabricated composite. The thermal expansion coefficient of a polymer is relatively high, so the filler units are usually under compression after cooling. Compression helps to tighten the filler-matrix interface, though the compressive stress in the filler and the tensile stress in the matrix may degrade the performance and durability of the composite. In case of the matrix being conducting, but not as conducting as the filler, as for conducting polymer matrices, percolation is not essential for the composite to be conducting, though percolation would greatly enhance conductivity. Below the percolation threshold (the filler volume

fraction above which percolation occurs), the conductivity of the composite is enhanced by a uniform distribution of the filler units since the chance increases of having a conduction path that involves more filler and less matrix as filler distribution becomes more uniform. Uniformity is never perfect; it is described by the degree of dispersion of the filler. The degree of dispersion can be enhanced by rigorous agitation during mixing of the filler and matrix, or by the use of a dispersant. In the case of a matrix in the form of particles that are coarser than the filler units, the addition of fine particles to the mix also helps dispersion of the filler. Because the thermal expansion coefficient of a polymer is relatively high, the polymer matrix expands more than the filler during the heating of a polymer-matrix composite. This results in the proximity between adjacent filler units changing with temperature, decreasing the conductivity of the composite. This phenomenon is detrimental to the thermal stability of composites.

Corrosion and surface oxidation of the filler are the most common causes of degradation that decreases the conductivity of the composite. Thus, oxidation-resistant fillers are essential. Silver and gold are oxidation resistant, but copper is not. Due to the high cost of silver and gold, the coating of copper, nickel, or other lower cost metal fillers by gold or silver is common for improving oxidation resistance. The most common filler by far is silver particles.

A z-axis anisotropic electrical conductor film is electrically conducting in the direction perpendicular to the film, but is insulating in all other directions. This film is technologically valuable for use as an interconnection material in electronic packaging, as it electrically connects the electrical contact pads touching one side of the film with the corresponding contact pads touching the direct opposite side of the film. Even though the film is in one piece, it contains numerous z-axis conducting paths, so it can provide numerous interconnections. If each contact pad is large enough to span a few z-axis conducting paths, no alignment is needed between the contact pad array and the z-axis film, whether the conducting paths are ordered or random in their distribution.

In this situation, in order to attain a high density

of interconnections, the cross-section of each z-axis conducting path must be small. However, if each contact pad is only large enough to span one z-axis conducting path, alignment is needed between the contact pad array and the z-axis film, and this means the conducting paths in the z-axis film must be ordered in the same way as the contact pad array. An example of an application of a z-axis conductor film is in the interconnections between the leads from (or contact pads on) a surface-mount electronic device and the contact pads on the substrate beneath the device. In this application, one piece of z-axis film can replace a whole array of solder joints, so the processing cost can be reduced. Furthermore, the problem of thermal fatigue of the solder joints can be avoided by this replacement. Another example is in the vertical interconnections in three-dimensional electronic packaging.

A z-axis film is a polymer-matrix composite containing conducting units that form the z-axis conducting paths. The conducting units are usually particles, such as metal particles and metal-coated polymer particles. The particles can be clustered so that each cluster corresponds to one conducting path. Metal columns, metal particle columns (e.g., gold-plated nickel), and individual metal-coated polymer particles have been used to provide z-axis conducting paths. Particle columns were formed by magnetic alignment. Using particle columns, Researchers attained a conducting path width of 400 μm and a pitch (center-to-center distance between adjacent conducting paths) of 290 μm. Also using particle columns, also attained a conducting path width of ~ 10 μm and a pitch of ~ 100 μm. In general, a large conducting path width is desirable for decreasing the resistance per path, while a small pitch is desirable for high density interconnection.

In contrast to the use of metal wires, metal columns, or metal particle columns, scientist used one metal particle per conducting path. The concept of one particle per path had been demonstrated by using metal-coated polymer particles. However, due to the high resistivity of the metal coating compared to the bulk metal, the z-axis resistivity of the film was high (0.5 Ω.cm for a conducting path). By using metal particle in place of metal coated polymer par-

ticles, decreased the z-axis resistivity of a conducting path to 10^{-6} Ω.cm. Furthermore, did not rely on a polymer for providing resilience; resilience is provided by the metal particles, which protrude from both sides of the stand-alone film. As a result, the problem of stress relaxation of the polymer is eliminated. In addition, the protrusion of the metal particles eliminates the problem of open-circuiting the connection upon heating because of the higher thermal expansion of the polymer compared to the conductor. Most work on z-axis adhesive films used an adhesive with randomly dispersed conductive particles (8–12 μm diameter) suspended in it. The particles were phenolic spheres that had been coated with nickel. After bonding under heat (180–190°C) and pressure (1.9 MPa), a particle became oval in shape (4 μm thick). There was one particle per conducting path. The main drawback of this technology is the requirement of heat and pressure for curing the adhesive. Heat and pressure are not desirable in practical use of the z-axis adhesive. Researchers removed the need for heat and pressure through the choice of the polymer. A different kind of z-axis adhesive film used screening or stenciling to obtain a regular two-dimensional array of silver-filled epoxy conductive dots, but this technology suffers from the large pitch (1500 μm) of the dots and the consequent need for alignment between z-axis film and contact pad array. In the work, the pitch of the conducting paths in the z-axis adhesive film is as low as 64 μm. Capacitors require materials with a high dielectric constant. Such materials in the form of thick films allow capacitors to be integrated with the electronic packaging, allowing further miniaturization and performance and reliability improvements. These thick-film pastes involve ceramic particles with a high dielectric constant, such as barium titanate ($BaTiO_3$), and a polymer (e.g., epoxy). Inductors are needed for transformers, DC/DC converters, and other power supply applications. They require magnetic materials. Such materials in the form of thick films allow inductors and transformers to be integrated with the electronic packaging, allowing further miniaturization. These thick-film pastes involve magnetic particles (e.g., ferrite) and a polymer. The need for EMI shielding is increasing rapidly due to

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the interference of radio frequency radiation (such as that from cellular phones) with digital electronics, and society's increasing dependence on digital electronics. The associated electronic pollution is an interference problem. EMI shielding is achieved by using electrical conductors, such as metals and conductive-filled polymers.

EMI-shielding gaskets are resilient conductors. They are needed to electromagnetically seal an enclosure. The resilient conductors are most commonly elastomers (rubber) that are filled with a conductive filler, or elastomers that are coated with a metalized layer. Metallized elastomers suffer from poor durability because of the tendency of the metal layer to debond from the elastomer. Conductive-filled elastomers do not have this problem, but they require the use of a highly conductive filler, such as silver particles, in order to attain a high shielding effectiveness while maintaining resilience. The highly conductive filler is expensive, which makes the composite expensive. The use of a less conducting filler results in the need for a large volume fraction of the filler in order to attain a high shielding effectiveness; the consequence is diminished resilience or even loss of resilience. Moreover, these composites suffer from degradation of shielding effectiveness in the presence of moisture or solvents. In addition, the polymer matrix in the composites limits the temperature resistance, and the thermal expansion mismatch between filler and matrix limits the thermal cycling resistance. Due to the skin effect (electromagnetic radiation at a high frequency interacting with only the near surface region of an electrical conductor), a filler for a polymer matrix composite for EMI shielding needs to be small in unit size. Although connectivity between the filler units is not required for shielding, it helps. Therefore, a filler in the form of a metal fiber of very small diameter is desirable. For this purpose, nickel filaments of diameter 0.4 μm and length > 100 μm, with a carbon core of diameter 0.1 μm, were developed. Their exceptionally small diameters compared to those of existing metal fibers made them outstanding for use as fillers in polymers for EMI shielding. A shielding effectiveness of 87 dB at 1 GHz was attained in a polyethersulfone-matrix composite with only 7 vol.% nickel filaments. The low volume fraction allows resilience in a silicone-matrix composite for EMI gaskets.

CONCLUSION

Materials for thermal conduction include those exhibiting high thermal conductivity, as well as thermal interface materials. The former includes metals, diamond, carbon, graphite, ceramics, metal-matrix composites, carbon-matrix composites, and ceramic-matrix composites. The latter includes polymer-based pastes, silicate-based pastes, and solder. Polymer-matrix composite materials for microelectronics are designed for high thermal conductivity, low CTE, low dielectric constant, either high or low electrical conductivity, and processability (e.g., printability). Applications include heat sinks, housings, printed wiring boards, substrates, lids, die attach, encapsulation, interconnections, thermal interface materials, and EMI shielding. Combinations of properties are usually required. For example, for heat sinks and substrates, the combination of high thermal conductivity and low CTE is required for heat dissipation and thermal stress reduction. In the case of aerospace electronics, low density is also desired. Polymer-matrix composites for microelectronics include those with continuous and discontinuous fillers. They can be in the form of an adhesive film, a stand-alone film, or a bulk material, and can be electrically isotropic or anisotropic.

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