

Reinforcements and Composites with Special Properties

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Abstract This chapter presents an overview of different types of composite reinforcements (fibres, textiles, nanofibres, nanotubes, particles, etc.) with special properties like piezoresistivity, self-sensing property, self-healing capability, conductivity, electromagnetic shielding, heat generation, and so on. The properties of reinforced polymers and composites have also been discussed in detail. Additionally, fundamental aspects behind these special properties are also presented in this chapter. The last section of this chapter is dedicated to novel multi-scale reinforcements and composite materials, and their properties.

1 Introduction

Composites are an important class of engineering material having wide variety of applications. The main advantage of composite is the ability of tailor making of properties to suite different application conditions. The initial development of composite was aimed at having a strong material with high strength: weight ratio and fillers of high l/d ratios are preferred so that the potential for controlled anisotropy offers considerable scope for integration between the processes of material specification and component design.

With the advancement of technology, the need for materials with functional properties is significantly increasing. Materials based on fillers having novel properties and nano-sized materials will represent an adequate solution to many present and future technological demands.

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Fillers play an important role in deciding the properties of the composite materials. When electrically conducting filler is added in sufficient quantities to a polymeric resin, a conductive composite is formed. Conductive composites are composite having significant electrical or thermal conductivity. The unique properties of such composites make them technologically superior to or more cost effective than alternative materials in a variety of applications. The inevitable link between conductive composites and the electronics industry has provided much of the impetus for their rapid development. Conductive polymeric composite finds its application in different diverse areas such as sensors, structural health monitoring system, self healing material, EMI shielding, energy storage materials, anticorrosive material, wearable electronics and materials for heat generation etc.

Structural Health Monitoring (SHM) is the process of detection, evaluation and interpretation of the damage in the engineering structure to improve its reliability. Primary goal of Structural Health Monitoring (SHM) is to replace the current inspection cycles with a continuously monitoring system. Piezoelectric and piezoresistive composite materials offer a great scope as sensors for real time monitoring of the health of structures and systems.

With the development of microelectronics, the assessment of failure and repair has become imperative for the reliability of these mass produced miniaturized devices. The high cost and difficulties involved in the repairing of such devices has led to the development of a new material capable of self healing.

The electrical and electronic devices used by us emit electromagnetic waves with frequencies that are potential hazards to health and hence the concept of EMI shielding has become practically important. Similarly sensors for soft electronics based on piezoresistive material have become potentially important.

In the present chapter, an effort has been made to discuss the structure, properties and applications of composite structures having these special properties.

2 Piezoresistive and Self-Sensing Behavior

Piezoresistive sensors translate an induced mechanical displacement into an electrical signal which is useful for monitoring minute structural deformations in composites over time. They comprise of electro-conductive fibers and fillers inside their structure to detect deformations occur. The principle of working of these sensors is the change in resistance due to applied strain between the conducting fibre/filler units. Tensile strain increases the distance between the electro-conductive fibre/filler units, thus increasing the resistivity. And inversely, compression decreases this distance, thus decreasing the resistivity. So, as an embedded circuitry, piezoresistive sensor system enables the sensing of local strain in a composite structure via connection to an external resistance meter.

2.1 Theory of Conduction Mechanism

The piezoresistivity of such composites based on conductive filler has been most successfully modeled by percolation theory and a quantum tunneling mechanism [81]. With a sufficiently large volume fraction of conductive filler material, nanojunctions will form between filler particles in which electrons can tunnel through the insulating barrier. Then an electrical network is created through the composite and it becomes conductive. The resistivity of a nanojunction can be calculated using Eq. (1).

$$\rho = \frac{h^2}{e^e \sqrt{2m\lambda}} \exp\left(\frac{4\pi\sqrt{2m\lambda}\lambda}{h} s\right) \tag{1}$$

where h is the Planck constant (Js), e is the charge of electron (C), m is the mass of electron (kg), λ is the height of tunneling barrier (J), and s is the distance between particles (m). Thus the resistivity of a nanojunction is a function of the inter-particle distance. As a composite is strained s will change and a piezoresistive signal is obtained.

Figure 1 shows the evolution of logarithm of resistivity ρ with volume fraction of conductive fillers ϕ in a polymer matrix charged with conductive fillers. This $\rho - \phi$ plot can be divided into two distinctive zones viz. the insulator regim and conductor regim. In the insulator regim, due to insufficient conductive filler (ϕ_1), few contacts will create a few charges to flow in the composite, and in the conductor regim (ϕ_2), due to abundant fillers, many contacts will create a healthy

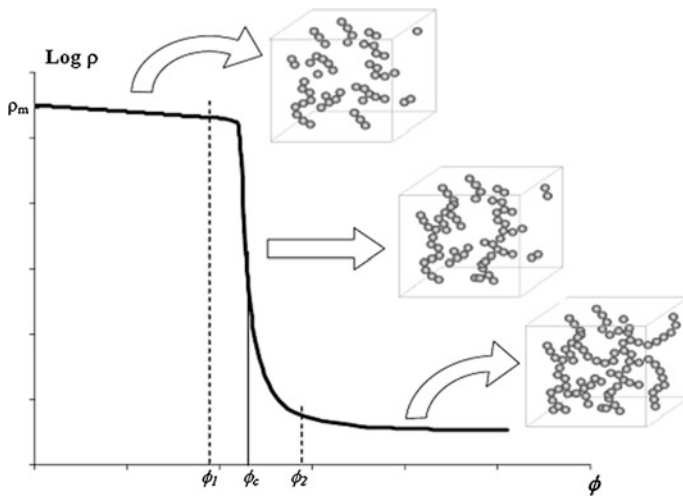


Fig. 1 Evolution of electrical resistivity in a composite with volume concentration of electric fillers [134]

conductive network for the flow of electrons and thus the electric current. The transition between the insulating and conductive regime occurs at a particular volume concentration of conductive filler. This critical concentration of conductive filler (ϕ_c) is called as percolation threshold [24]. Because of the formation of conductive networks of fillers around the percolation threshold, a sudden and rapid drop in resistivity is observed. When filler particles are in direct contact with each other then the electrical conduction is explained by metallic conduction. In metallic conduction the energy bands are overlapped which allows the electrons to flow from one site to another without any input energy. However, when there is gap or barrier between the filler particles then for conduction, the electrons need to jump from one site to another in presence of external input energy. This hopping can be either short range hopping when sites are energetically distant and geographically close or variable range hopping when sites are energetically close and geographically distant [37, 134].

The mechanism of change in electrical resistance due to reorientation of filler particles in composites structure by mechanical deformation is illustrated by Fig. 2. Beyond percolation threshold, conductivity of the filler composites obey a power law relationship which is dependent on the concentration of filler as expressed in Eq. (2).

$$\frac{\sigma}{\sigma_0} = (\phi - \phi_c)^t \quad (2)$$

where, σ is the electrical conductivity of the composite (S m^{-1}), ϕ is the volume concentration of the conductive filler, ϕ_c is the concentration of filler at the percolation threshold, σ_0 is the effective conductivity of the filler itself, and t is critical exponent [119].

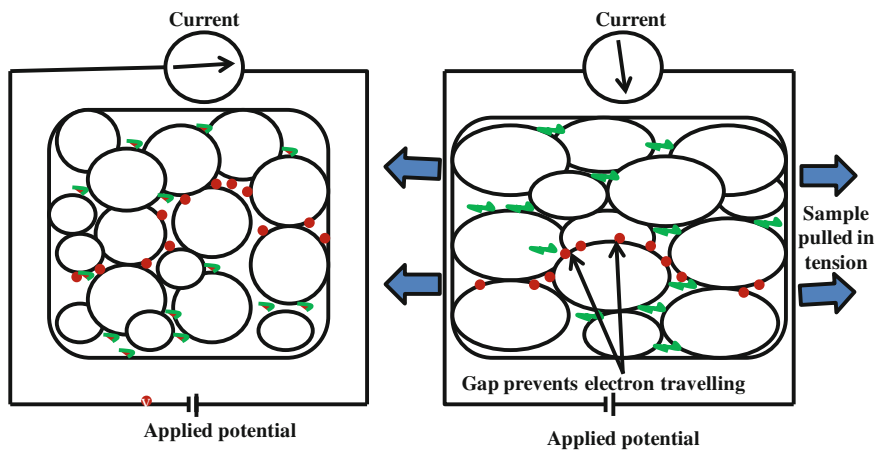


Fig. 2 Schematic representation of change of resistance of filler composites due to application of uniaxial tensile stress [119]

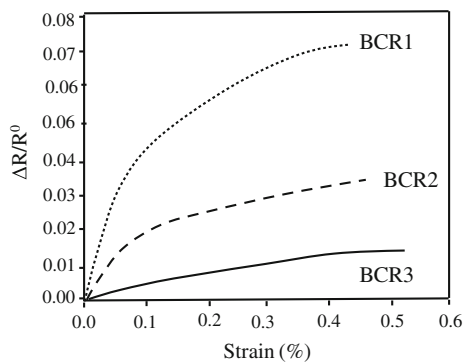
2.2 Metal-Polymer Composites as Piezoresistive Sensor

Metal-polymer composites are prepared by reinforcing polydimethylsiloxane (PDMS) polymer with copper (Cu) and nickel (Ni) particles by a method of wet mixing. These composites have high stress sensitivity which show the resistivity changes by more than 10 orders of magnitude when pressure around 4 MPa is applied. These composites are proposed as good piezoresistive sensor for practical applications in various fields like robotics, biomechanics, etc. [3].

2.3 Carbon Fibres and Carbon Black Composites as Piezoresistive Sensor

Carbon fiber is itself piezoresistive by nature, and can thus act as a strain gauge. Also, carbon black and metal nanostrand composites possess remarkable piezoresistive response [107]. Self-sensing multifunctional carbon fibre reinforced composite is prepared which has sensing function executed by its change of electrical resistance [186, 187]. But, when they are plied to prepare multifunctional laminate nanocomposites, the transverse plies of them largely short circuit their piezoresistive response. Use of insulators between the layers of the laminate helps to mitigate this problem [82]. It is discovered that direct embedding of nickel nanostrand patch into unidirectional carbon fiber laminates yields significant piezoresistive response [82, 83]. Rana et al. [154, 160] have prepared core reinforced braided composite rods (BCRs) by braiding polyester fibres around an unsaturated polyester resin impregnated core, composed of glass and carbon fibre mixture for self monitoring of deformation and damage. Their sensing behavior is characterized by monitoring the change in electrical resistance with deformation using two terminal DC methods. Three types of BRC samples are prepared altering the core materials viz. BRC1 (77/23 E-glass/carbon), BRC2 (53/47 E-glass/carbon) and BRC 3 (100 % carbon). Their piezoresistive response behavior is shown in Fig. 3. It can be seen that the

Fig. 3 Strain responses of different BCRs by change of electrical resistance [154, 160]



highest piezoresistive behavior is obtained with BCR1 and the strain sensibility decreases with increase in the carbon fibre content. It is interesting to note that the curve for BCR1 presents more non-linearity than the other BCRs. Its fractional resistance increases sharply with a linear trend up to 0.1 % strain and then more gradually at higher strains due to saturation in the electrical contacts.

An elastomer based filler composite sensor made of evoprene/carbon black nanoparticle is prepared and mounted on a thin and light nylon fabric for self-sensing. Its shows a nonlinear behaviour trend of rise of resistance at low strain level below 15 %. However, above 15 % of strain level, it shows a linear ohmic behavior [37].

Relationship between stress and strain and that between fractional resistance change ($\Delta R/R_0$) and strain during static tensile testing up to failure for a carbon fibre reinforced composite with 2.57 vol % carbon fibers (continuous, 11 mm diameter) is shown in Fig. 4. The stress–strain curve is linear up to a strain of 0.2 %, at which the resistance is increasing steadily. However, after strain level of 0.2 % resistance starts to increase abruptly.

The variation of $\Delta R/R_0$ during cyclic loading and unloading for various stress amplitudes within the linear portion of the stress–strain curve of this composite is shown in Fig. 5 [199]. The resistance increases upon loading and decreases upon unloading in every cycle and the resistance increase are not totally reversible. The gage factor, which has been commonly used as a parameter to quantify the piezoresistive sensitivity (the fractional change in reversible portion of resistance per unit strain), are found to be 28, 21 and 17 for the first, second and third cycles respectively. The decrease in gage factor with increasing cycle number is attributed to the decrease in reversibility with increasing stress amplitude.

Fig. 4 Relationship between stress and strain and that between fractional resistance change ($\Delta R/R_0$) and strain during static tensile testing for a carbon fibre reinforced composite [199]

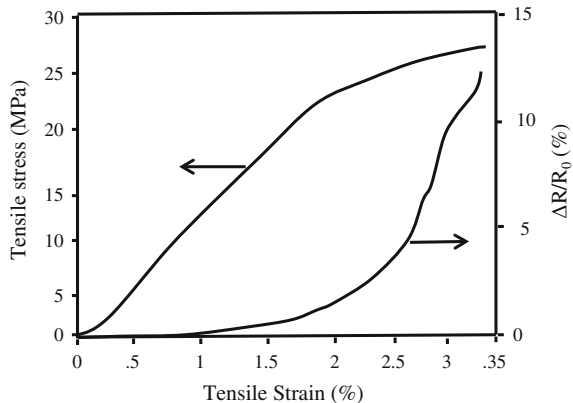
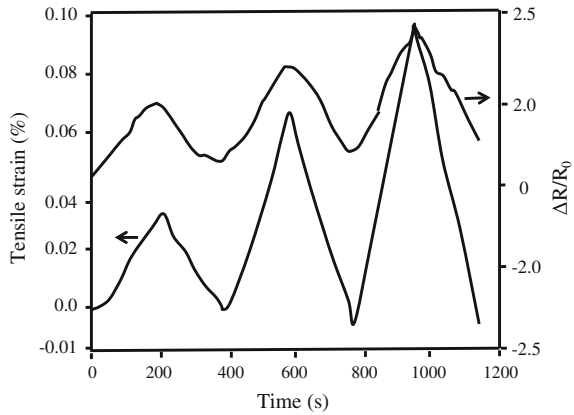


Fig. 5 Variation of Fractional change of resistance during cyclic loading for a carbon fibre reinforced composite [199]



2.4 Carbon Nanotube (CNT) as Piezoresistive Sensor

The incorporation of carbon nanotubes (CNT) into matrix of composites effectively increases the electrical conductivity of the resulting composites by several orders of magnitude and affects various other properties. This is attributed to the formation of a conductive network of the nanofillers inside the structure and it is called a percolated network. Carbon nanotubes can be fabricated in the form of single wall (SWCNT) and multi-wall (MWCNT) carbon nanotubes. SWCNTs consist of one cylindrical lattice of carbon atoms (Fig. 6a) while MWCNTs are structured by multiple helical concentrically positioned lattices (Fig. 6b) [153]. Though both the CNTs appear as hollow tubes of rolled graphene sheets, they are not produced by rolling up the sheets. Their peculiar structure is achieved under precisely controlled conditions in the presence of a catalyst. SWCNTs have diameters in the range of

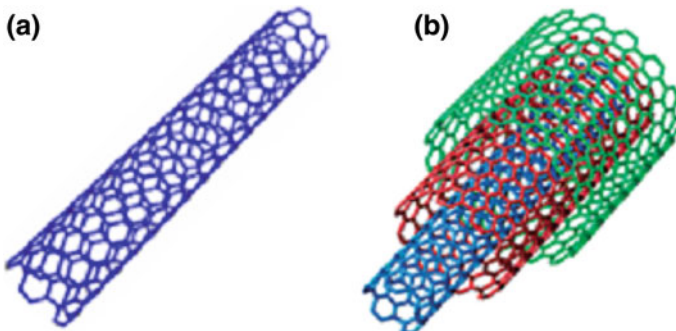


Fig. 6 Structural geometry of **a** SWCNT and **b** MWCNT [153]

0.7–1.0 nm, and they can be grown to long lengths to achieve very high length-to-diameter aspect ratios. CNTs possess very high stiffness with Young's modulus of approximately 1 TPa and a density of about 1.33 g/cm^3 . They can bear torsion and bending without breaking. The hexagonally-bonded carbon honeycomb structure of SWCNTs is responsible for their high mechanical strength up to 60 GPa, with maximum strain up to 10 %. From the electrical standpoint, CNTs can be classified as conductors or semi-conductors, depending on the orientation of the carbon atoms in the lattice structure of the tubes. The high strength, stiffness, thermal and electrical conductivities of CNTs make them promising for developing composites for a lot of applications [196].

The gauge factor of SWCNTs is in the range of ~ 400 to ~ 2900 , which is far superior to that of traditional piezoresistive materials, such as doped single-crystal silicon (gauge factor: 100–170) and metals (gauge factor: 2–5). Stampfer et al. [177] have fabricated pressure sensors based on individual SWNTs as active electromechanical transducer elements. The electromechanical measurements show a piezoresistive gauge factor of approximately 210. The change in resistance of the sensor with respect to applied strain is shown in Fig. 7. A linear response is observed in terms of increase of resistance with increase of strain.

In another study, electrically conductive rigid Poly-Urethane (PUR) composite foams are prepared by dispersing MWCNT at various concentrations. This PUR/MWCNT foams show varying electrical conductivity on a wide range of MWCNT contents and compression. Due to the application of compressive load, the electrical resistance of these foams gradually reduces as shown in Fig. 8 [10].

Composite nanomaterials with micron and submicron layers are prepared by carboxymethyl cellulose (CMC) and MWCNT. The specific bulk conductivity of the composite was found to be $\sim 40 \text{ kS/m}$ and the surface conductivity is found to be $\sim 0.2 \text{ S}$. These composites are suggested for different applications viz. flexible electronics, conductive glues, protection of electronic circuits, devices, and many more [78].

Fig. 7 The resistance change as a function of axial strain of MSWNT [177]

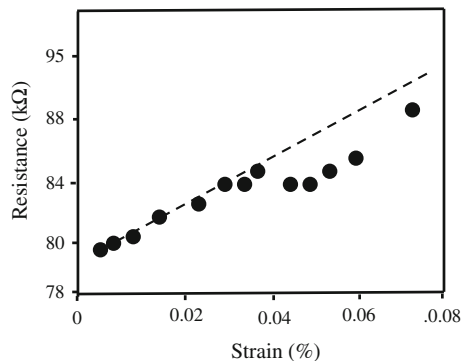
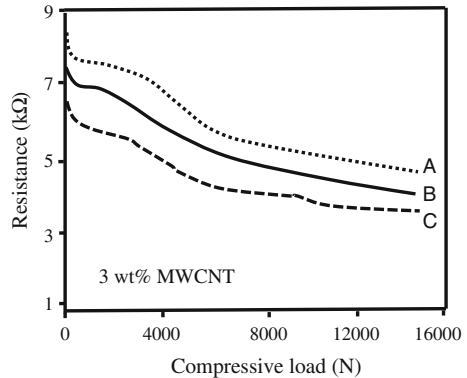


Fig. 8 Change in electrical resistance due to applications of compressive loads [10]



2.5 Conductive Polymer Composites as Strain Sensor

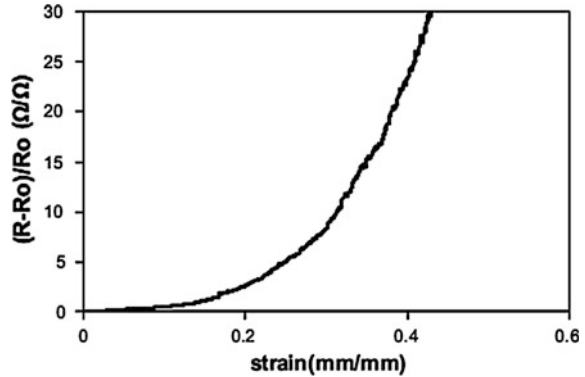
Conductive polymer composites are a well known class of composites which are being studied for its application as piezo-resistive strain sensors. Conductive polymers are used as filler material to prepare electro-conductive composites which can respond to structural deformation due to external stress or strain in terms of change in its resistivity [65].

Flexible, polymeric, and electro-conductive nanocomposite films are prepared by dispersing polyaniline (PANI) into a poly(vinyl acetate) (PVA) latex matrix. These films possess a sensitivity of 3 times larger than classical metallic gauges with certain repeatability [119]. A typical pressure sensor comprising of conductive polymer composites is prepared by sandwiching the composite in between two electro-conductive layers as electrodes. The electrodes are then covered with two layers of insulating polyester films. When a compressive force is applied to the surface of the sensor, the gap between filler particles reduces inside the matrix, resulting in an increase in conductivity of composites. This change of conductivity is detected as output of pressure sensitivity [87].

Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) based fibrous yarn sensors are developed by Trifigny et al. [189] to directly measure the mechanical stress on fabrics under static or dynamic conditions. These sensors have the ability to locally detect mechanical stresses all along the warp or weft yarn. This local detection is undertaken in real time during the weaving process [189]. In another study, polypyrrole coated lycra fibre is explored as a strain sensor. The electrical resistance of these fibres increases exponentially with the strain as shown in Fig. 9 [197, 198].

Polypyrrole/polyester textile and PEDOT/polyester textile composites exhibit a monotonic increase of the electrical resistance with the elongation up to 50%. These elastic textile composites are proposed as a strain sensor for large deformation [99]. Polypyrrole coated cotton yarn shows an increase of their resistivity due to the application of tensile strain and twist [125]. These yarns are proposed for sensory applications of strain and torsion.

Fig. 9 Typical resistance vs. strain curve of PPy-coated lycra fibers [197, 198]



2.6 Carbon Nanotubes for Structural Health Monitoring (SHM)

Over the past two decades significant efforts have been made by researchers in order to miniaturize electronic devices for SHM applications and optimize their performance. The excellent mechanical properties and the high thermal and electrical conductivities of CNTs play a fundamental role for the development of devices simultaneously showing structural and functional capabilities, including actuation, sensing and generating power. These characteristics allows the development of high performance sensors and actuators operating at low voltage. A number of such sensors have been designed by researchers. A homogeneous SWCNT film obtained through vacuum filtration of SWCNT solution has been used as a strain sensor [41]. A proper design of nanotube concentrations and polyelectrolyte matrices has yielded thin films whose electrical properties are sensitive to strain and pH changes. Layer by layer assembled carbon nanotube composites have been used as strain sensors as well as a wireless transmission systems [122]. Hybrid composites are prepared using carbon nanotubes in combination with fibers for self-sensing properties [16]. Later alternative strategies based on radial in-situ growth of CNTs on the fiber surface are attempted [152]. Also, CNTs can be fabricated as film to develop neural systems in the form of a grid attached to the surface of a structure to make a sensor network. Such an artificial neural system has potential applications in the field of monitoring of large civil structures [153]. Again, CNT/PMMA nanocomposites are prepared for electro-magnetic wave absorption and dynamic strain sensing for structural health monitoring [174]. Change in resistance (normalized resistance) of the strain sensor with respect to change of strain is shown in the Fig. 10. Slope of the curve is the gauge factor of the sensor. This sensor shows consistent piezoresistive behavior under repetitive loading and unloading and has good resistance stability.

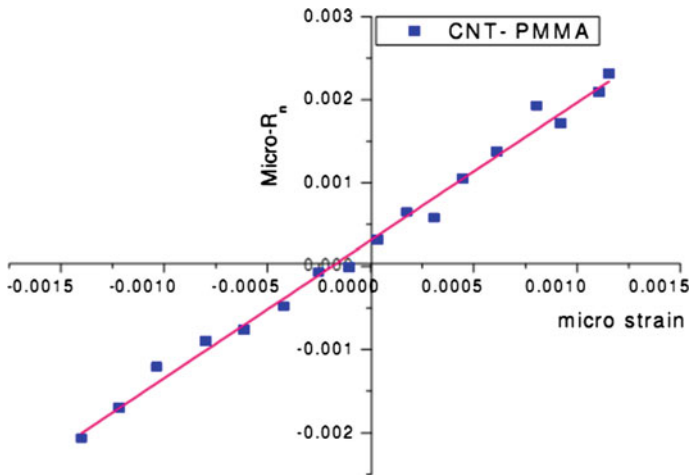


Fig. 10 Strain-Resistance behavior of CNT/PMMA nanocomposite strain sensor [174]

2.7 Piezo-Resistive and Self-Sensing Behavior of Engineered Cementitious Composites

Engineered Cementitious Composites (ECC), like concrete and other cement-based materials, act as a piezoresistive material with bulk resistivity of 101–105 Ω m which is similar to that of a semi-conductor [35]. The microstructure of ECC materials have microscopic pores, partially filled with unbound water and dissolved ions. These ions are mobile under an externally applied electric field to generate electric current. However, there is limited communication between these pores inside ECC structure which increases the resistance of current flow. Also, there exists high contact impedance between various conductive phases of these ECCs. Under applied mechanical strain, changes occur in spatial separation between conductive phases which causes a change in the bulk resistivity of ECCs. This makes the ECCs piezoresistive and self-sensing [162]. The self-sensing ability is achieved in certain ECCs by incorporating a small dosage of carbon black (CB) into the ECC system to enhance its piezoresistive behavior [121]. The significant increase in resistivity is observed when the specimens are subjected to uniaxial tension. Baeza et al. [8] develop multiple sensors based on multifunctional ECC with carbon fibers (CF) and CNF fillers and attach them to a conventional reinforced concrete beam for strain sensing. Both the admixtures, CF and CNF, are found suitable as conductive filler to fabricate cement composites capable of measuring strains on the surface of the structural beam, regardless of local stresses either tensile or compression. In another study, electrically conductive cementitious composites are prepared by adding MWCNTs to the cement matrix. The electrical resistivity of these composites changes with stress conditions with static and dynamic loads [38].

2.8 Piezoresistive Micro-Cantilever Biochemical Sensor

A compact, piezoresistive and low cost polymer nano-composite micro-cantilever sensor is prepared by Patil et al. [142], which is capable of detecting 2,4,6-trinitrotoluene (TNT), pentaerythritoltetranitrate (PETN) and 2,4,6-trinitrotoluene (RDX) vapors at low ppt level within seconds of exposure under ambient conditions. The gold coated micro-cantilevers are modified with self-assembled monolayers (SAM) of 4-mercaptobenzoic acid (4-MBA),6-mercaptonicotonic acid (6-MNA) and 2-mercaptonicotonic acid (2-MNA) in order to achieve sufficient piezo-resistivity. This nano-composite micro-cantilever is ideally suited as “electronic nose” applications. The change in resistance ($\Delta R/R$) as a function of deflection is shown in Fig. 11 The calculated deflection sensitivity is 1.1 ppm/nm and surface stress sensitivity of $7.6 \times 10^{-3} (\text{Nm}^{-1})^{-1}$ [142].

Seena et al. [170] have developed a highly sensitive piezo-resistive SU-8 nano-composite micro-cantilever sensor for detection of explosives in vapor phase. Carbon black (CB) is dispersed by 8–9 vol% in the SU-8/CB nano-composite to prepare it. The resonance frequency and spring constant are found to be 22 kHz and 0.4 N m^{-1} respectively. The force-displacement of the micro-cantilever is found to be linear with surface stress sensitivity of $7.6 \text{ ppm} (\text{mNm}^{-1})^{-1}$ as shown in Fig. 12. It can detect TNT vapor concentrations down to approximately 6 ppb with an approximate sensitivity value of 1 mV/ppb of TNT as shown in Fig. 13. The output voltage is found to increase with increase in TNT concentration.

2.9 Polymeric Filaments for Piezo-Electric Sensor

Poly(vinylidene fluoride), PVDF, is a widely studied material due to its piezo-electric properties, including in the context of integration into textiles to prepare composites for self-sensing. Piezoelectric PVDF filaments are prepared in co-axial geometry. Multilayered filaments incorporating electrically conductive layers used

Fig. 11 Change in resistance ($\Delta R/R$) as a function of deflection of polymer nano-composite micro-cantilevers [142]

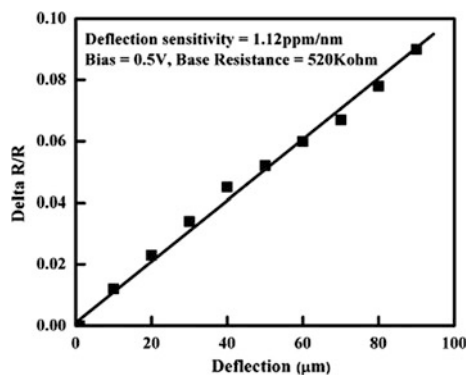


Fig. 12 Load displacement characteristics of the SU-8/CB nano-composite micro-cantilever [170]

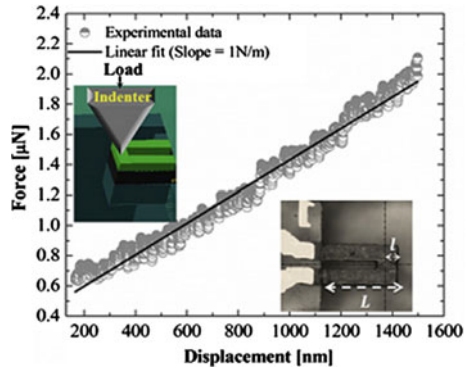
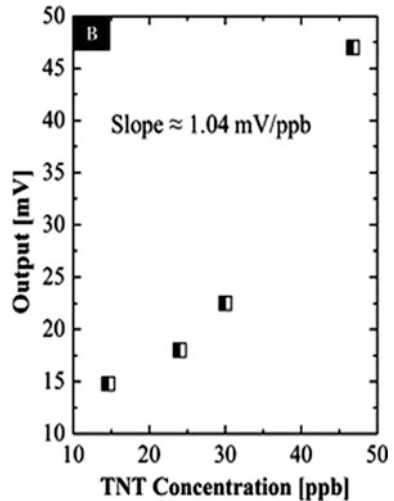


Fig. 13 TNT vapor detection sensitivity plot of SU-8/CB nano-composite micro-cantilever [170]



as electrodes, in co-axial arrangement, are produced by using single step co-extrusion technique [165]. These filament sensors are tested under bending and extension stress and found suitable for application as sensor. The sensors have a sensitivity of 2.2 nC/N.

3 Self-Healing Characteristics

Fibre reinforced composites have various applications in diversified fields such as transportation, civil, constructions, geotextiles, sports, etc. These composites are susceptible to damage due to mechanical, chemical, thermal, radiation, or any combination of these factors during their service life. This damage leads to the formation of micro-cracks in the composite structure. The micro-cracks may form

on the surface or in depth within the structure. Detection and external intervention to repair these micro-cracks within the composite structure are often difficult.

There are conventional techniques to repair visible cracks/damages of fibre composites. But, these conventional techniques are not suitable or effective for healing invisible microcracks within the structure of the composites during their service life. So, polymeric materials with self-healing capability are introduced as a means of healing invisible micro-cracks within the composite structures for extending their service life and safety [86]. Self-healing polymeric materials have a built-in capability to substantially recover their functional ability automatically after damage. Sometimes the recovery is activated by specific external stimuli such as heat, radiation etc. An ideal self-healing material can be defined as the material which is capable of continuously sensing and recovering induced damages throughout its service life without affecting its performance and base properties. These materials are contributing greatly to the safety and durability of fibre reinforced composites at cheaper costs [57]. Wool and O'Connor [201] proposed a basic method for describing the extent of healing in polymeric material by following Eq. (3).

$$\text{Healing Efficiency} = 100 \times \frac{\text{Property Value}_{\text{Healed}}}{\text{Property Value}_{\text{Initial}}} \quad (3)$$

3.1 Self-Healing of Thermoplastic Materials

A number of different mechanisms for self-healing of thermoplastic polymers as proposed by various researchers are as follows.

3.1.1 Self-Healing by Molecular Interdiffusion

Molecular interdiffusion is the process of crack healing by molecular diffusion of two similar polymers at the polymer-polymer interface when broken pieces are brought into contact above their glass transition temperature (T_g). Researchers [148, 201] proposed various models to explain the mechanism of crack healing of composites at the thermoplastic interface. The reptation model was proposed by De Gennes [40] and Doi and Edwards [44] to explain chain dynamics for self healing. In this model, motion of a polymer molecule is described as wormlike inside a strongly cross-linked polymeric gel and it is found correlated with molecular mass. Later, Wool and O'Connor [201] suggested a five stages model to explain the crack healing process such as (i) surface rearrangement of molecules, (ii) surface approaching of molecules, (iii) wetting of surfaces, (iv) diffusion between surfaces, and (v) equilibrium and randomization of molecules (Fig. 14). This theory is suitable for crack healing in amorphous polymers and polymer resins during melt

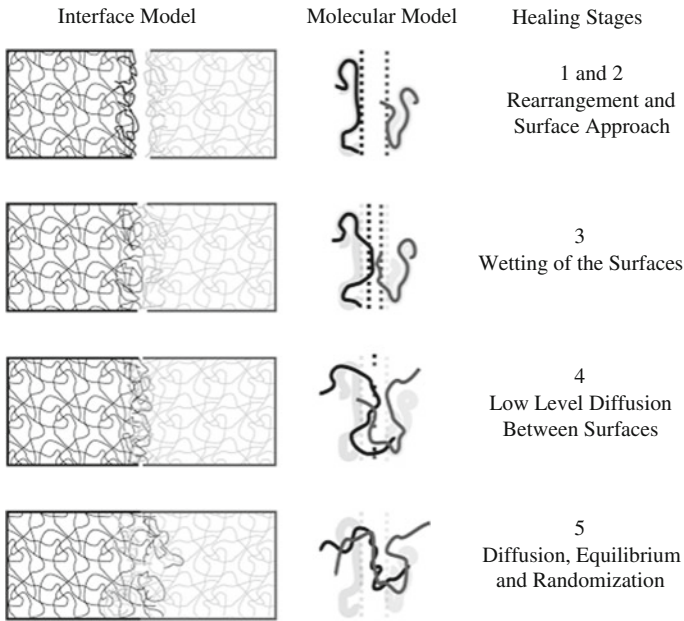


Fig. 14 Five stages model to explain the crack healing by Molecular Interdiffusion of thermoplastic composites [201]

processing. Also, Kim and Wool [102] proposed a microscopic theory of chain diffusion and randomization based on the reptation model. This theory describes the motion of chains at the damaged interface and calculates average interpenetration distance of the polymer segments as a function of time and molecular weight. Later, Kausch and Jud [91] observed that the development of the mechanical strength during the crack healing process of glassy polymers is related to inter diffusion of the molecular chains and subsequent formation of molecular entanglements.

There are various factors which affect the healing process and after healing performance of the composites such as healing time, healing temperature, clamping pressure, idle time after fracturing etc. Lin et al. [120] achieved full recovery of tensile strength of cracked poly (methyl methacrylate) (PMMA) by methanol treatment between 40 and 60 °C. But Boiko et al. [17] observed low levels of adhesion between virgin poly(ethylene terephthalate)/poly(ethylene terephthalate) and poly(ethylene terephthalate)/poly(styrene) joints even after 15 h of treatment at a temperature 18 °C higher than their T_g . Yang and Pitchumani [207] observe 100 % healing efficiency of carbon reinforced polyether-etherketone (PEEK) and polyether-ketone-ketone (PEKK) under non-isothermal conditions. Jud and Kausch [85] have also found some influence of molecular weight and degree of copolymerization on the crack healing behavior of poly (methyl methacrylate) (PMMA) and PMMA- poly (methoxyethylacrylate) (PMEA) copolymers.

3.1.2 Photo-Induced Self-Healing

It is a process of light initiated healing which only occurs upon exposure to a light of particular wave length. A mechanism of fracture and light-induced healing has been proposed by Wu et al. [202] as shown in Fig. 15. The photochemical [2+2] cycloaddition of cinnamoyl groups was chosen as the healing mechanism since photo-cyclo addition produced cyclobutane structure and the reversion of cyclobutane to the original cinnamoyl structure readily occurs in a solid state upon crack formation and propagation [34, 73, 136]. Healing of the fractures in these films is achieved by re-irradiation for 10 min with a light of $\lambda > 280$ nm. Healing efficiencies in flexural strength up to 14 and 26 % are reported using light or a combination of light and heat (100 °C). In this particular process, healing is limited to the surfaces being exposed to light. So, internal cracks or thick substrates are difficult to heal by this process.

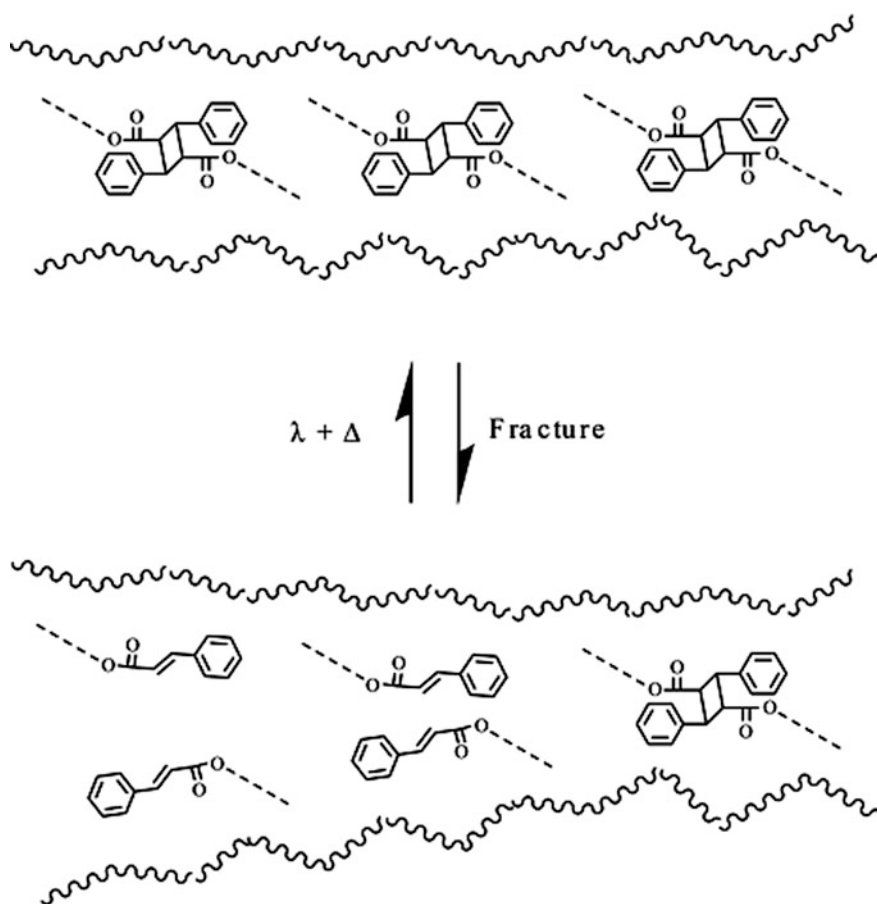


Fig. 15 Mechanism of photo-induced healing [202]

3.1.3 Self-Healing by Recombination of Chain Ends

Recombination of chain ends is a relatively new technique to heal structural and molecular damages in certain thermoplastic composites. This technique does not require external source of energy (e.g. heat, radiation etc.) for healing. Thermoplastic polymeric materials prepared by condensation reactions such as polycarbonate (PC), polybutylene terephthalate (PBT), Polyphenyl ether (PPE), polyether-ketone (PEK), polyethyl-ether-ketone (PEEK), etc. can be healed by a simple reaction that reverses the chain scission [61, 79, 129, 149, 167, 182, 183]. About 98 % of healing efficiency in recovery of tensile strength and molecular weight are achieved for PC material after a healing period of above 600 h [183]. Self healing of PC composites occurs by recombination of the phenolic end groups with phenyl end groups in presence of a small amount (0.1 ppm) of Na_2CO_3 (Fig. 17). A mechanism of the self healing reaction of these polymeric materials is proposed by Takeda et al. [182]. There are various steps for self healing via recombination of chain ends. These steps include (i) chain scissoring due to degradation; (ii) diffusion of oxygen into polymer structure; (iii) re-combination of scissored chain ends by catalytic redox reaction in presence of oxygen and catalyst; and (iv) discharging of water as a result of the self healing reaction. The self-healing process of PC and PPE are shown in Figs. 16 and 17 respectively. The kinetics of the self healing reaction depends on factors such as oxygen concentration, catalyst, chain mobility, reactant end groups etc. As the reaction progresses, the speed of the healing reaction decreases due to a reduction of the polymer chain mobility with increasing molecular weight and a gradual decrease of available hydroxyl (OH) end groups.

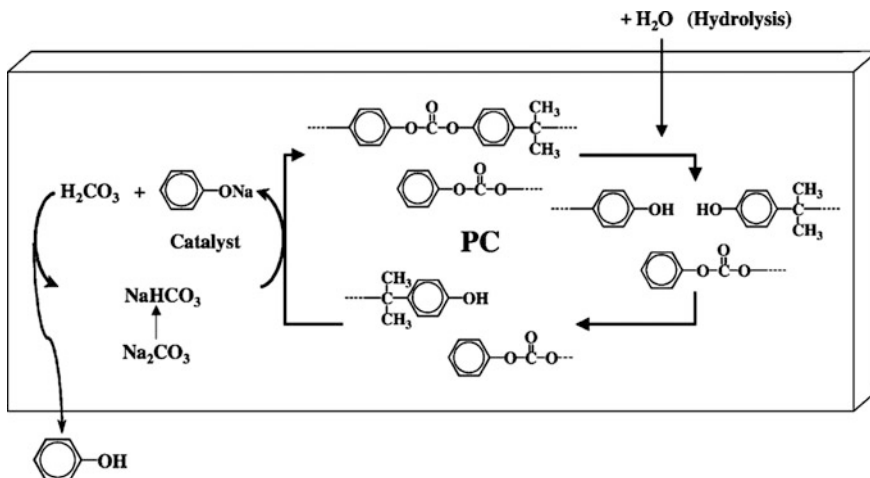


Fig. 16 Self-healing scheme in PC [182]

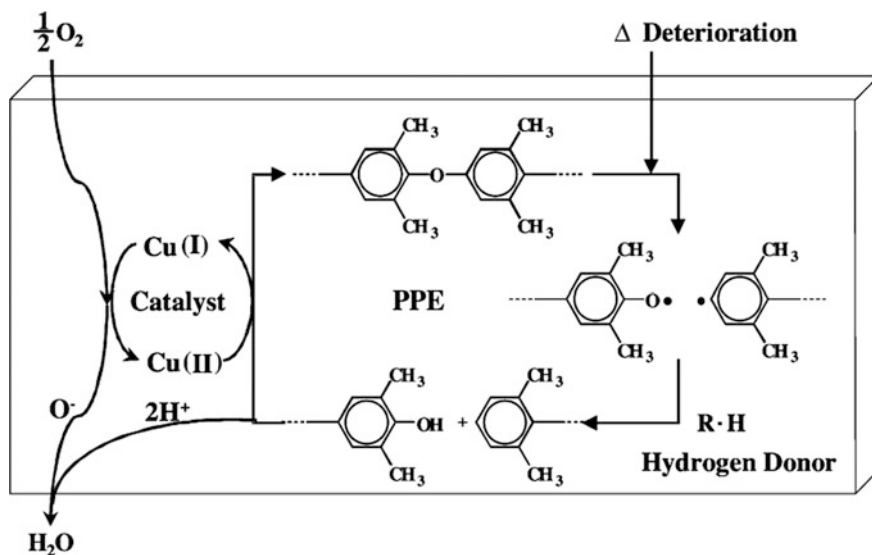


Fig. 17 Self-healing scheme in PPE [182]

3.1.4 Self-Healing by Reversible Bond Formation

Self-healing of certain thermoplastic polymers can be achieved by inclusion of reversible bonds in the polymer matrix at ambient temperatures. This technique utilizes hydrogen or ionic bonds to heal damaged polymer networks. A mechanism of molecular self healing via reversible bond formation is patented by Harreld et al. [71]. The production of polypeptide-polydimethylsiloxane copolymers as self-healing materials is depicted in Fig. 18. The silicon-based primary polymeric networks are grafted or block copolymerized with a secondary network of crosslinking peptides via hydrogen and/or ionic bonding. This hydrogen and/or ionic bondings act as intermediate crosslinks to strengthen the network and provide a good overall toughness to the material while allowing for self healing due to reversible crosslinking. Healing is initiated when the fractured surfaces come in contact either through physical closure or via a solvent induced chain mobility. The healing times can be adjusted by varying the structure of the polymer, degree of crosslinking, and strength of the crosslinks.

3.1.5 Self-Healing of Ionomers

Ionomers are defined as polymers having less than 15 % ionic groups along with polymer backbone [51]. Common ionomers are not suitable for self-healing applications. Suitable ionomers can be synthesized or modified by fillers or fibers for self-healing. Ionic content and its order-disorder transition is the driving force

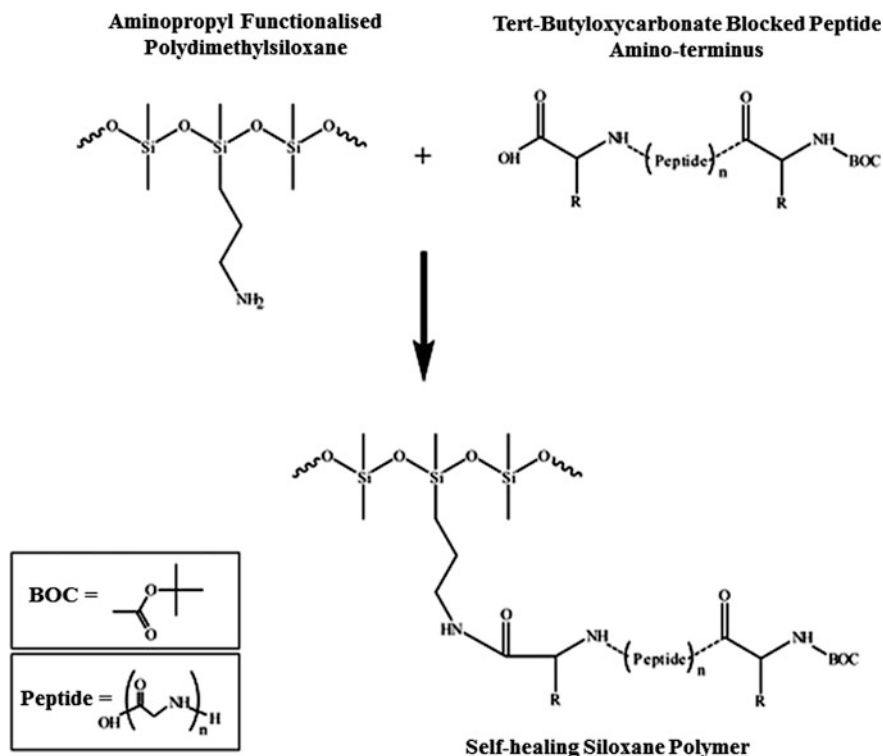


Fig. 18 Self healing of Siloxane polymer [202]

behind the healing process. self-healing behaviors of poly ethylene-co-methacrylic acid (EMAA), carbon nanotube filled EMAA composites, and low density polyethylene (LDPE) are investigated by Kalista et al. [89]. All those samples, except LDPE, exhibit the self healing behavior at room temperature. The lack of self healing in LDPE reveals the existence of the ionic functionality and/or the polar acid groups in the EMAA polymers which are essential to achieve self-healing. A new self-healing composite material is prepared by embedding carbon fibres in Surlyn ionomer [179]. Surlyn is an ethylene/methacrylic acid (E/MAA) copolymer in which the MAA groups are partially neutralized with sodium ions. This sodium ionomer is chosen as the matrix of the self healing composite. The polymer matrix made out of Surlyn melts at 95 °C from the heat generated in the carbon fiber layer and heals any surface and through thickness damage in the polymer matrix. Carbon fibers are selected as a heating element due to its low electrical resistance, resistive heating property, and reinforcement properties [179]. A two-stage theory on healing of ionic polymers by the application of heat, has been proposed by Kalista and Ward [88], and Pingkarawat et al. [145]. As temperature rises, polymer chain mobility increases which helps to complete the healing process.

3.1.6 Living Polymer Approach of Self-Healing

The living polymers are equipped with active groups at their chain ends and capable of resuming polymerization if additional monomer is added to the system. The free radical living polymerization is likely to be more suitable for self-healing considering the high reactivity and stringent conditions required for the ionic living polymerization [29]. Living polymers can be prepared with a number of macro-radicals i.e. polymer chains capped with radicals, by either ionic polymerization or free radical polymerization during which the polymer chains grow without chain transfer and termination [36, 63, 181].

3.1.7 Self-Healing by Nanoparticles

It is an interesting and new approach of self-healing to repair cracks in polymeric composites by using nanoparticles. Instead of breaking and rejoining of polymer chains like other self-healing techniques this technique involves filling and dispersing nanoparticles into cracks and flaws. The nanoparticles have a natural tendency to be driven towards the fractured or damaged area by polymer-induced attraction due to depletion at elevated temperature. The larger particles are more effective than small particles in this sense for migrating to the damaged region at relatively short time span. The system will be cooled down when particle migration will be completed. As a result, a solid nanocomposite layer is formed like a coating on the damaged surface and that effectively repairs the flaws. As an example, a 50 nm thick silicon oxide (SiO_2) layer deposited on top of a 300 nm thick PMMA film embedded with 3.8 nm CdSe/ZnS nanoparticles. The migration of the nanoparticles towards the cracks in the brittle SiO_2 layer is dependent on the enthalpy and entropic interactions between the PMMA matrix and the nanoparticles [191, 202].

3.2 Self-Healing of Thermoset Materials

Thermoset materials are rigid and thermally stable due to their cross linked molecular structure. They do not melt and even have no chain mobility due to application of heat. So, there are distinctly different approaches of self-healing of these thermoset materials.

The most common approaches for self-healing of thermoset materials involve incorporation of brittle vessels into the polymeric matrix which contain self-healing agents inside. These vessels fracture upon certain stimuli (load, strain, heat etc.) of the polymer and release low viscosity self-healing agents to the damaged sites for subsequent curing and repairing of the microcracks. This approach may differ slightly depending upon the healing functionality integrated into the composites as shown in Fig. 19. Many different self-healing approaches for thermoset materials

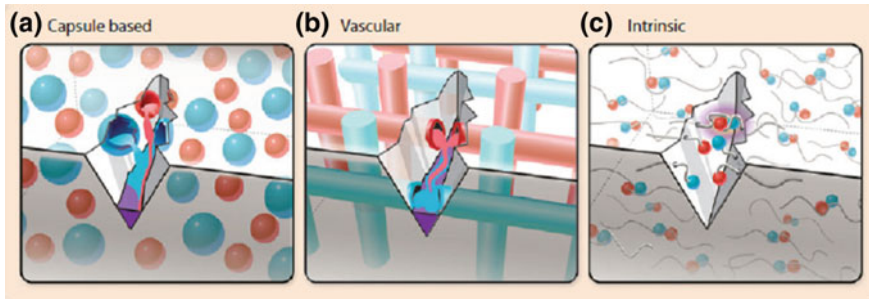


Fig. 19 Self-healing approaches of thermoset materials **a** capsule-based, **b** vascular, and **c** intrinsic methods [50]

have been reported, such as, (a) Capsule-based self-healing approach; the healing agents are stored in capsules and the capsules are incorporated into polymer matrix, which fracture upon stimuli to release self-healing agents in damaged sites (b) Vascular approach; here the healing agent is stored in hollow channels or fibers until damage ruptures the them to release the healing agent. (c) Intrinsic materials contain a latent functionality that triggers self healing of damage via thermally reversible reactions, hydrogen bonding, ionic arrangements, or molecular diffusion and entanglement. The exact nature of the self-healing approach depends on (i) the nature and location of the damage; (ii) the type of self-healing agents; and (iii) the operational environment [19, 50].

3.2.1 Self-Healing by Microencapsulation

In recent years, it is the most studied self-healing concept of thermoset materials. This particular approach involves incorporation of micro-capsules filled with healing agent and a dispersed catalyst within a polymer matrix. The microcapsules are fractured or ruptured by the propagating cracks in composites, resulting in release of the healing agent into the cracks by capillary action. Subsequent chemical reaction between the healing agent and the embedded catalyst heals the material and prevents further crack to propagate. These steps of self-healing are shown in Fig. 20 [110, 200]. Self-healing composite is prepared by blending microcapsules (<15 micron) containing various combinations of a 5-ethylidene-2-norbornene (5E2N) and dicyclopentadiene (DCPD) monomers, with (polyMelamine-urea-formaldehyde) (PMUF) shell which react with ruthenium Grubbs' catalyst (RGC) upon emergency. These self-healing materials are mixed with an epoxy resin and single-walled carbon nanotubes (SWNTs) to prepare nanocomposites which possess tremendous potential for space applications under hypervelocity impacts [5, 140]. Poly urea-formaldehyde microcapsules filled with epoxy resin 711 and E-51 healing agents are used in-situ polymerization of urea-formaldehyde in an oil-in-water emulsion has been prepared successfully for corrosion protection [118].

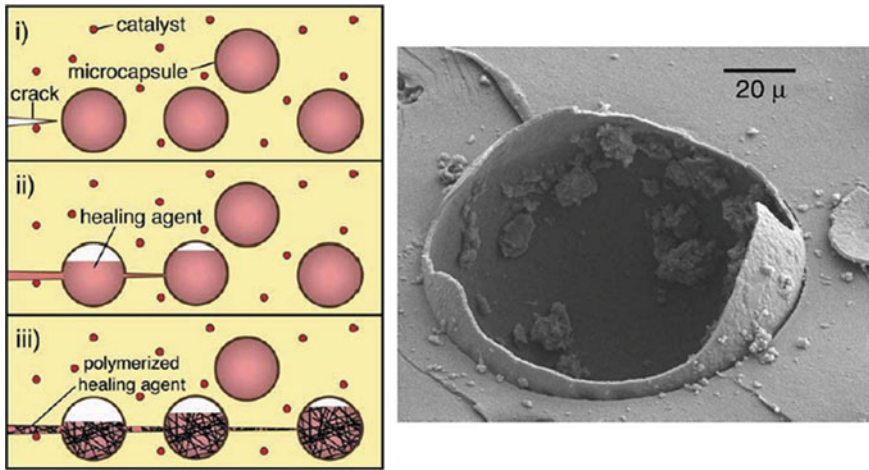


Fig. 20 Self-healing by micro-encapsulation approach, ruptured microcapsules [203]

3.2.2 Hollow Fiber Approach of Self-Healing

Dry [45–48] pioneered the concept of releasing healing chemicals stored in hollow fibers to repair damage in thermoset materials. This concept has been initially applied to cementitious materials to alter the cement matrix permeability, repair cracks, prevent corrosion, and as sensors for remedial actions. The feasibility of this approach has been subsequently extended to polymeric materials [138]. Hollow fibre approaches are used in preference to embedded microcapsules because they offer the advantage of being able to store functional agents for composite self-repair systems as well as acting as reinforcement [188]. A typical hollow fibre for self-healing used within composite structure can take the form of fibres containing a one-part resin system, a two-part resin and hardener system or one part resin system with an encapsulated catalyst or hardener contained within the matrix material as shown in Fig. 21. The exact nature of the self-healing method depends upon the nature and location of the damage, the potential of self-healing resins, and the influence of the operational environment [188].

The tough homogeneous nanofibers and core-shell healing agent-loaded nanofibers can be produced by coaxial electrospinning (co-electrospinning), emulsion electrospinning, and emulsion solution co-blowing, and several other advanced nanofabrication techniques. By these techniques low cost and continuous nanofibers for interfacial toughening and damage self-repairing of high-value advanced structural composites can be prepared. Solution co-blowing method can preferably be followed for mass production in comparison to other methods due to its higher productivity. The core of these fibers which is filled up by healing agents is surrounded by a polymer shell, which provides them with structural stability [203].

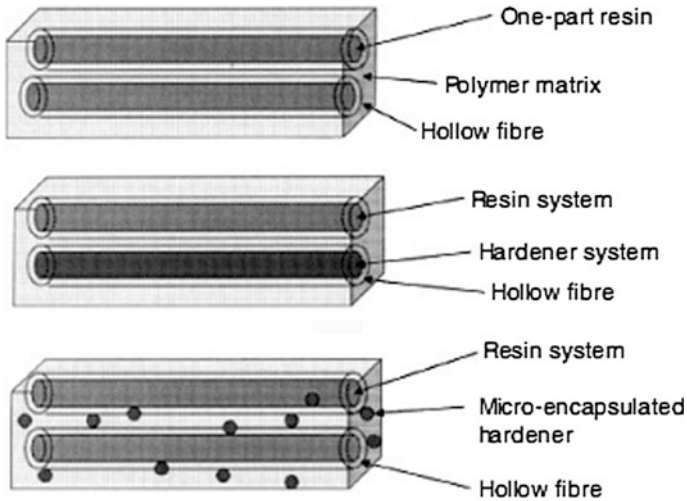


Fig. 21 Different hollow fibre approaches of self-healing [188]

3.2.3 Self-Healing of Thermally Reversible Cross Linked Polymers

Certain cross linked polymers are capable of healing internal cracks through thermo-reversible covalent bonds. This approach of thermally reversible crosslinks eliminates the need of incorporation of micro-capsules or hollow fibres filled with healing agents or catalysts in the polymeric matrix. However, heat is required to initiate the healing [25, 26, 72, 204]. This approach depends upon the nature of the fracture and can repair specific covalent bonds. Two new remendable highly cross-linked polymers, 2ME4F and 2MEP4F, are prepared by Chen et al. [26] without solvent. The study of thermal reversibility of Diels–Alder (DA) cross-linking shows that DA connections and disconnections of both polymers are thermally reversible. Cracks in these polymers can be healed effectively with a simple thermal healing procedure. These thermally reversible cross linked polymers may be suitable to fabricate fiber reinforced polymer composites for structural applications.

3.2.4 Self-Healing via Inclusion of Thermoplastic Additives

Inclusion of thermoplastic additives as self-healing agent inside the thermoset matrices enables them of re-bonding fracture surfaces on application of heat [212]. The feasibility of this technology is demonstrated using up to 40 vol % of thermoplastic epoxy particles (average diameter of 105 μm) in a glass fiber reinforced epoxy composite. Upon heating epoxy particles melted, flowed into internal cracks and healed them.

Jones and Hayes [84] describe the healing system as a “solid solution” of thermoplastic and thermoset polymers instead of the two phase system described above for self-healing fiber reinforced composites. It is specified that the matrix should contain 10–30 % (wt) of a thermoplastic polymer. Thermoplastic preferably forms a homogeneous solution with the thermoset matrix both before and after cure. There should be optimum molecular weight of the thermoplastics. Low molecular weight polymer diffuses faster resulting in quicker healing whilst high molecular weight polymer provides better mechanical properties but slower in action. Hence, there is a need to balance rapid healing and good healed mechanical properties. Healing temperature also has its influence as it is thought to be a diffusion controlled process.

3.2.5 Self-Healing via Chain Rearrangement

Healing of thermoset polymers has also been achieved by rearranging polymer chains at ambient temperature. This technique has similarity to molecular interdiffusion technology of thermoplastics. Self-healing of cracks is achieved by interdiffusion of dangling chains or chain slippage in the polymer network at ambient temperature [206]. This process does not require heating which is essential for thermoplastic additives or the thermally reversible crosslinks approach.

3.2.6 Self-Healing of Hydrogels

Concept of self-healing hydrogels is developed for repair of lightly crosslinked hydrophilic polymer gels via metal-ion-mediated reactions [192, 193]. In this technique, metal-ions are absorbed from an aqueous solution for rearrangement of crosslinked networks and then they are incorporated into the hydrogel. The metal-ion-mediated healed material has an entirely different structure and physical properties from the un-healed material.

One self-healing hydrogels system is demonstrated by Varghese et al. [192] where acryloyl-6-amino caproic acid (A6ACA) gels are synthesized. They contain flexible hydrophobic side chains with a terminal carboxyl group and undergo healing at ambient temperature through the formation of coordination complexes mediated by transition-metal ions. In another system healing of the gels is conducted by placing dried pieces of the gels together in a dilute aqueous solution of 0.1 M CuCl_2 at ambient temperature [193]. The tensile strength of the healed gels increased with time and achieved up to 75 % strength recovery after 12 h healing. The factors affecting the healing ability include the metal-binding capacity of the gel, the nature of the complexation, and the ability to deform under stress.

3.2.7 Self-Healing by Incorporating Water Absorbable Materials

Easter [49] developed a low cost cable capable of self-healing damage through expansion action of the water absorbable materials surrounding the conductor. The water absorbable material can be located in any one of the covering layers of cable. When the cable is damaged due to punctures, cracks or voids then water ingress reach to the water absorbable materials. The water absorbable materials expand and fill that cracks, punctures and voids. Thus damages are sealed in the cable. The water absorbable material is comprised of either water absorbable filler such as sodium bentonite or polyethylene oxide dispersed in a non-water absorbable polymer such as polyisobutene or polyisoprene, or a water absorbable polymer, i.e. polyethylene vinyl chloride or polyacrylic resins. This self-healing mechanism is only effective for repairing damage when water is present in the environment.

3.2.8 Self-Healing via Passivation

Passivation is a technique of light-coating on a protective material, such as metal oxide, to create a shell against corrosion. This coating material is developed to automatically heal the damage caused by exposure to UV radiation, oxygen, and in particular atomic oxygen in low earth orbit environment [166]. The self-healing polymer layer may be an organo-silicon material which operates by providing silicon to react with oxygen from the environment to form a SiO_x compound that condenses on micro-cracks, encapsulating impurities and filling the voids, fractures and other flaws. This self-healing structure can be used by itself or applied on top of a UV-sensitive substrate.

3.3 Other Approaches

When very fine polyethylene fibres are incorporated in fibre reinforced cementitious composites then self-healing capability of the composites is improved because fine polyethylene fibres form bridges over the crack which helps to attach the crystallization products [74]. Artificial skin is prepared with both pressure sensitivity and mechanical self healing properties with graphene and polymers by integrating them into a thin film which mimics both the mechanical self healing and pressure sensitivity behavior of natural skin without any external power supply [76]. Some of the self-healing materials, their system, mechanism, and assessment techniques are mentioned in Table 1.

Table 1 Self-healing materials, system, mechanism, and assessment techniques [21]

Category of materials to be repaired	Materials to be repaired	Healing system	Trigger mechanism	Healing mechanism	Assessment of healing effect
Thermoplastic	Poly(methylmethacrylate), etc.	Bulk	Heating or solvent induced	Chain interdiffusion and entanglements	Compact tension (CT) test or photography
Thermoplastic	Poly(ethylene-comethacrylic acid)	Bulk	Thermo-mechanically induced melting	Chain interdiffusion and entanglements	Visual inspection after sawing, cutting and puncture
Thermoplastic	Polycarbonate	Bulk (weak alkali/hydrolyzed chains)	Steam	Weak alkali catalyzed polymerization	Molecular weight and mechanical strength
Thermoplastic	Poly(phenylene ether)	Bulk (copper ion/oxygen/scission chains)	Heating	Copper ion catalyzed polymerization	Molecular weight
Thermoset	Epoxy	Bulk	Heating	Post-curing of residual functional groups	Impact strength
Thermoplastic/thermoset semi-interpenetrating network	Poly (bisphenol-A-co-epichlorohydrin)/epoxy	Bulk	Heating	Chain interdiffusion and entanglements	CT and impact tests; photography
Thermally reversible crosslinking network	Crosslinked multifuran/multimaleimide	Bulk	Heating	Diels-Alder reaction	CT and double cleavage drilled compression
Thermoset	Epoxy, fiber/unsaturated polyester, and fiber/epoxy	Cyanoacrylate, epoxy, unsaturated polyester, etc.	Crack induced breakage of hollow tubes containing healant	Curing of healant	Tensile, flexural and impact tests; photography; ultrasonic C-scan
Thermoset	Epoxy	Dicyclopentadiene/Grubbs' catalyst	Crack induced damage of 3D microvascular networks, releasing healant	Ring-opening metathesis polymerization of healant	Four-point bending

(continued)

Table 1 (continued)

Category of materials to be repaired	Materials to be repaired	Healing system	Trigger mechanism	Healing mechanism	Assessment of healing effect
Thermoset	Unsaturated polyester	Styrene or epoxy	Crack induced rupture of microencapsulated healant	Polymerization or curing of healant	Mechanical strength and visual inspection
Thermoset	Glass fiber/epoxy	Epoxy granules	Heating	Curing of healant	Three-point bending and tensile fatigue
Thermoset	Epoxy and woven glass fiber/epoxy	Epoxy/latent hardener	Crack induced rupture of microencapsulated epoxy	Curing of healant	Single edge notched bend (SENB) and double cantilever beam (DCB) tests
Thermoset	Epoxy, fiber/unsaturated polyester, and fiber/epoxy	Dicyclopentadiene/Grubbs' catalyst	Crack induced rupture of microencapsulated healant	Ring-opening metathesis polymerization of healant	Tapered double cantilever beam (TDCB), DCB and fatigue tests
Thermoset	Unsaturated polyester	Phase-separated polysiloxane droplets/tin catalyst	Crack induced rupture of microencapsulated catalyst	Polycondensation of polysiloxanes	TDCB
Elastomer	Silicone rubber	Polysiloxane/platinum catalyst/initiator	Crack induced rupture of microencapsulated healant and initiator	Polycondensation of polysiloxanes	Tear strength
Thermoset	Epoxy	Solvent (chlorobenzene)	Crack induced rupture of microencapsulated solvent	Solvent induced crosslinking of incompletely cured resin	TDCB

4 Heating Properties

A resistor can generate heat when it is connected with an external voltage supply. This phenomenon of heat generation is well explained by Joule's law. A composite material can act as a resistor with certain level of electrical conductivity to generate heat through Joule's effect. Electrical conductivity in composites can be achieved by incorporation of various conductive materials in their structure by various means. However, self-heating phenomena is noticed in certain composite materials which are particularly used in automobiles and aircraft structures. When dynamic loads are introduced in these composites, energy is starting to dissipate through its matrix, which is transformed into heat. The evolved heat accumulates in the structure if matrix material has small values of heat transfer coefficients. However, the evolved heat can dissipate through the structure when matrix has high heat transfer coefficient. When the evolved heat and the thermal dissipation conditions are balanced, a self-heating effect of the composite in the steady-state can be observed. The self-heating effect could be used in problems of the damage detection and evaluation in polymer-based composite structures [90].

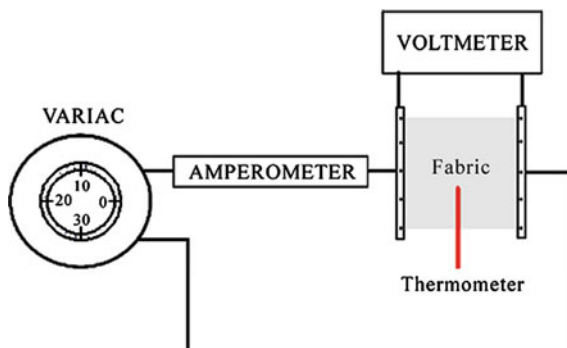
4.1 *Metal Fibres and Wires Used in Composites for Heat Generation*

Structures prepared with highly conductive metals alone such as copper, steel, aluminum etc. are not suitable for heat generation. Because, for Joule's effect of heat generation, a material requires a moderate electrical resistivity. That's why, metal are blended with textile fibres by various means to develop hybrid electro-conductive composite yarns or fabrics for heat generation [27, 213]. A stainless steel multifilament and a carbon yarn can be produced having moderate resistance that may be suitable for heat generation [106, 168, 169]. It is found that each of the selected electro-conductive yarns/wire exhibits particular brittle characteristics and poor bending properties that are not typical of yarns for textiles applications [147]. A flexible knitted fabric made of silver and elastomeric yarn can generate sufficient heat to warm up the body. This fabric can be used to manufacture personal heating garments that can generate heat on application of external voltage [69].

4.2 *Conductive Polymer Coated Composites for Heat Generation*

Conductive polymers such as polyaniline, polypyrrole, polythiophene etc. are coated/applied on the surface of textile yarns/fabrics by various means to prepare electro-conductive composites. These non-metallic polymeric composites are found

Fig. 22 Experimental set-up diagram for measuring the heating effect of a textile composite [176]



suitable for potential application of heat generation. Compared to other heating materials, the merits of these heating fabrics are their temperature homogeneity, low power density on large surface area, light-weight, their suppleness and fineness. They can be sewed up, cut off or pasted on substrates for a large range of applications [21].

Dall'Acqua et al. [39] have prepared textile composites by embedding polypyrrole in natural and manmade cellulosic fibres, such as cotton, viscose, cupro and lyocell, by in situ vapour phase polymerization and they are found suitable for application of heat generation. In another study, polypyrrole is incorporated in cotton woven fabrics and various properties such as anti-static, anti-microbial, heat generation is investigated [171]. A possible application of the polypyrrole coated composite fabric is demonstrated as heating devices as shown in Fig. 22 [176]. A square shape fabric (6 cm × 6 cm) is positioned between two pressed electric contacts. The temperature rise is measured using an Omega infrared thermometer, placed at the center of the sample.

The temperature-current ($T-I$) and voltage-current ($V-I$) characteristics of this textile composite are shown in Fig. 23. The $T-I$ characteristic follow an exponential trend and $V-I$ characteristics follow a power law. According to the power law, maximum theoretical power achieved from the fabrics is: $P = VI$, where P is the power developed and V, I the voltage and current. In Fig. 24, the power and the impedance as a function of current are shown.

In another study, when a constant voltage of 9 V is applied to cotton/polypyrrole fabric for 10 min, its surface temperature raised up to 90 °C and for many numbers of repeating cycle performance of the fabric does not deteriorated. The voltage-temperature ($V-T$) characteristic of the fabric is shown in Fig. 25. Initially temperature is rising sharply with time at a fixed applied voltage and then level off at a particular temperature. These conductive fabrics can be used as heating pads which are more comfortable to use than metal incorporated fabrics [171].

The behavior of temperature versus voltage of viscose/polypyrrole fabrics prepared by in situ vapor phase polymerization (VPV) with different FeCl_3 concentration, are fitted by exponential curves with the following general Eq. (4).

Fig. 23 Behavior of the voltage and temperature of the PPy coated sample as a function of the current [176]

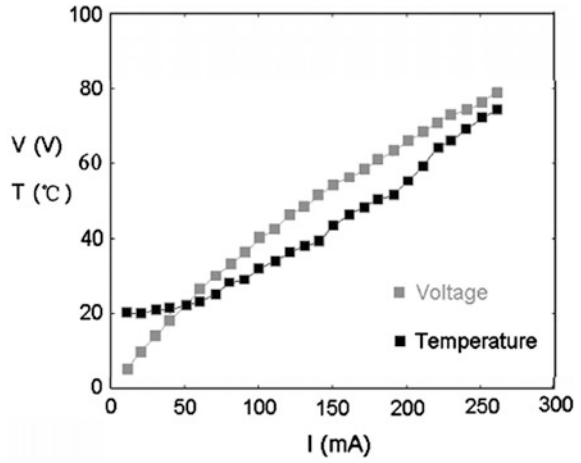


Fig. 24 Behavior of the impedance and power developed by PPy coated textile composite as a function of the current [176]

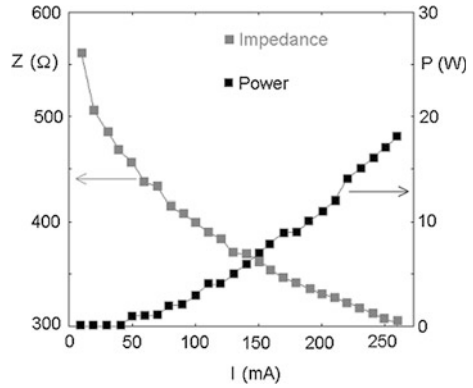


Fig. 25 Voltage-temperature characteristics of Cotton/polypyrrole fabric [171]

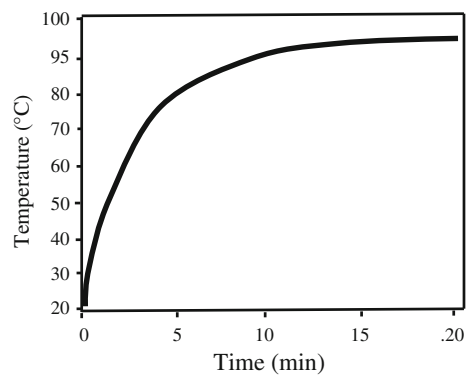
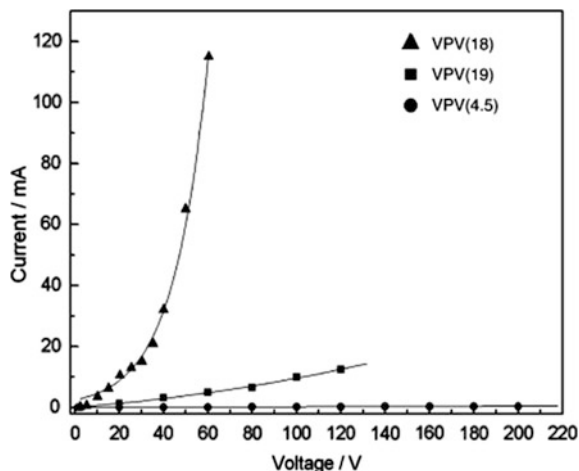


Fig. 26 Plot of temperature vs. applied voltage for different VPV samples [39]



$$T = T^0 + ae^{-kV} \quad (4)$$

where, V is the applied potential, T^0 the initial temperature and T is the final temperature. The resulting current–voltage characteristics of viscose fabric prepared by in situ vapor phase polymerization depends on FeCl_3 concentration as shown in Fig. 26. It shows a linear fit until FeCl_3 concentration of 9 gl^{-1} , and an exponential fit for higher FeCl_3 concentrations [39].

It is suggested by Sparavigna et al. [176] and Macasaquit and Binag [123] that 100 % polyester fabrics can easily be made electrically conductive by polypyrrole coating and they are practically useful for many applications, including flexible, portable, surface-heating elements for medical or other applications. Polypyrrole coated polyester/lycra woven composite fabrics exhibit reasonable electrical conductivity and effective heat generation capacity where temperature reaching up to $40.55 \text{ }^\circ\text{C}$ at 24 V [94]. For all these composites the rate of change of temperature has two distinct phases, an initial sharp rise and followed by a leveling-off to plateau, similar to cotton/PPy composites [68]. Rodriguez et al. [163] have observed that electrical resistivity and heating effect of PPy composites depends on the doping anion present, whether it is chloride (Cl^-) or other. Nylon/polypyrrole composite fabric with electrical resistance of $5 \text{ } \Omega/\text{square}$ is prepared by sequential high temperature high pressure (HTHP) chemical and electrochemical polymerizations [117]. Surface temperature of this fabric is increased very quickly from room temperature to about $55 \text{ }^\circ\text{C}$ within 2 min due to application of 3.6 V from a commercial battery. The heat generating property of the fabric is so stable that it exhibits similar behaviors for at least 10 repeated cycles [117]. PPy coated E-glass fabric exhibits reasonable electrical stability, and is found effective in heat generation. By application of a constant voltage across the fabric, surface temperature increases whereas power consumption is found to be decreasing [1]. Polypyrrole coated electro-conductive woven, needlepunched nonwoven and spunlace

Fig. 27 V-T characteristics of Polyester fabric/polypyrrole composites [126]

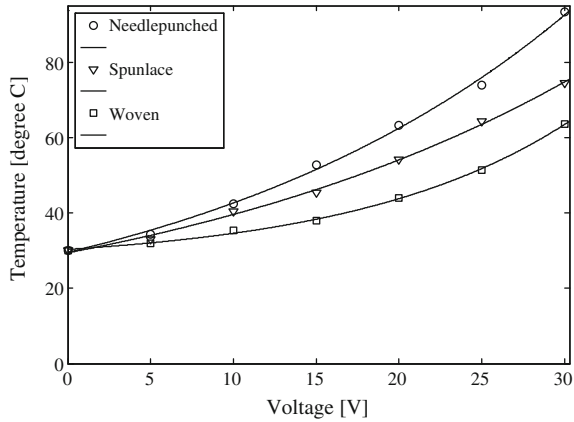
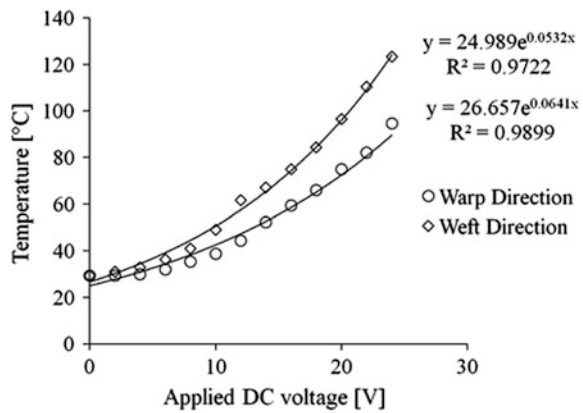


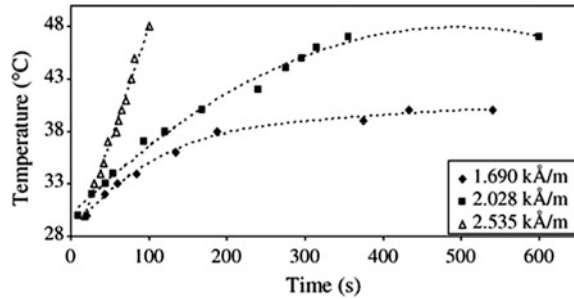
Fig. 28 V-T characteristics of Silk fabric/polypyrrole composite [128]



nonwoven fabric composites are prepared and characterized for heat generation [126]. Their $V-T$ characteristics are shown in Fig. 27. All these fabrics follow an exponential trend of heat generation due to application of voltage in the form: $T = ae^{bV} + c$, where T is the measured temperature, V is the applied voltage, a , b and c are coefficients, exponent and constant respectively. Among these fabrics needlepunch nonwoven fabric shows highest rate of heat generation.

Silk/Polypyrrole electro-conductive composites are also prepared for the application of heat generation [20, 128]. Figure 28 shows the heat generation behavior of silk/polypyrrole composite woven fabrics. It can be seen that as voltage is increasing, surface temperature of the composite is increasing exponentially when tested in both warp and weft direction [128].

Fig. 29 Induction heat generation behavior of $\text{Fe}_3\text{O}_4/\text{PVA}$ composites [114]



4.3 Composites for Induction Heating

Idea of using induction heating technology for the processing of fibre reinforced polymer composites is a recent approach. Induction technology is suitable for the processing of thermoplastic and thermoset polymer materials but requires special additives (conductive materials) either in the form of structured fibres and fabric or particulate that can transform the electromagnetic energy into heat. This approach is found suitable for thermoplastic composite welding, thermoset curing, selective material heating and fast mould heating technologies [11, 56]. The magnetic particles can be used as filler of the composite and are stimulated by the applied electromagnetic field and act as heat sources during the induction heating procedure. Micro-sized Fe_3O_4 particles are dispersed in polyvinyl alcohol hydrogel or other substrate to prepare composites for hyperthermia applications [114, 214]. Induction heating behavior of such composites is shown in Fig. 29. Maximum temperature achieved by applying alternating magnetic field 1.7 kV/m is 40 °C which is sufficient for application in hyperthermia [114].

5 Electromagnetic Shielding

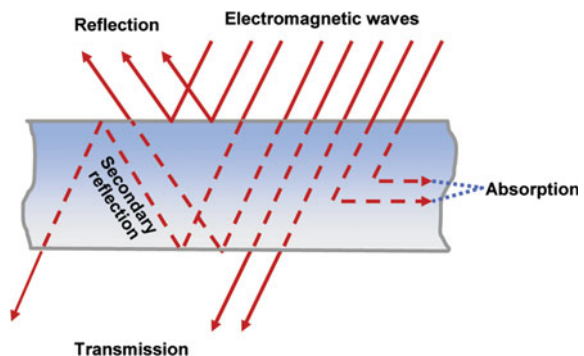
Electromagnetic Interference (EMI) shielding is a process of restricting the penetration of electromagnetic waves into a medium or object by blocking them by a barrier made of electro-conductive material. It is a very popular method of protecting electronic and electrical equipments and even human beings against electromagnetic radiation. The barrier or protector which protects a body, environment or a circuit from harmful electromagnetic radiation is called a shield. It is well known that exposure to long term or acute electromagnetic radiation can have harmful effects on human tissue [4, 59, 105, 112, 124] and furthermore, electromagnetic radiation can interfere with certain bio-electronic devices such as pacemakers [184], and affects the lives of people. The recent proliferation of electronic devices, such as cell phones, and computer equipment, that emit low levels of electromagnetic radiation, or interference, has significantly increased the problem

and created a need for everyday shielding garments. In this regard, a variety of electromagnetic shielding composites have been produced to prevent electromagnetic radiations [108, 164, 215].

5.1 Mechanism of Electromagnetic Shielding

When electromagnetic waves pass through a medium or object they interact with molecules of the medium or object and waves are attenuated in certain amount depending upon the medium or object. This phenomena of interaction can be divided in two major steps such as (a) Attenuation due to absorption, and (b) Attenuation due to reflection [164]. As the waves strike a conductive object, the charges in the object are forced to oscillate at the same frequency of the incident wave. These forced oscillating charges behave like antenna and cause reflection from the surface. The signal wave may reflect in many directions depending upon the pattern associated with a signal oscillating charge. Hence, the signal is scattered and there is some signal loss. This mode of signal loss is called attenuation due to reflection. There are also successive losses of signal into the depth of the layer of the medium. It is called attenuation due to successive internal reflections. Again, the forced oscillating charge losses some energy in the medium in terms of heat. This mode of signal loss is known as attenuation due to absorption. Thus, electromagnetic shields work on the basis of the two above mentioned major electromagnetic mechanisms such as reflection from a conducting surface, and absorption in a conductive volume [130, 144, 164]. The combined effect of these losses (reflection and absorption) determines the effectiveness of the shield as shown in Fig. 30. Reflection from an electromagnetic shield occurs when the impedance of the wave in free space is different from the impedance of the electromagnetic wave in the shield. This phenomenon is independent of the thickness of shield and is a function of conductivity, magnetic permeability, and frequency of the shield [18, 130]. Whereas, electromagnetic shields made of electromagnetic absorbers attenuate undesirable electromagnetic waves and substantially dismiss electromagnetic radiation.

Fig. 30 Schematic representation of shielding phenomena



Shielding efficiency of this type of shield depends upon factors such as type of material, its thickness, size, shape, orientation of apertures etc. [18, 113, 132].

5.2 Electromagnetic Shielding Efficiency

Electromagnetic Interference Shielding Efficiency (EMISE) value expressed in dB is defined as the ratio of the incident to transmitted power of the electromagnetic wave [42, 144]. Mathematically,

$$SE = 10 \log \left| \frac{P_1}{P_2} \right| = 20 \log \left| \frac{E_1}{E_2} \right| \text{ (decibels, dB)} \quad (5)$$

where, $P_1(E_1)$ and $P_2(E_2)$ are the incident power (incident electric field) and the transmitted power (transmitted electric field), respectively.

By measuring the reflectance (R_e) and the transmittance (T_r) of the material, the absorbance (A_b) can be calculated using Eq. (6).

$$A_b = 1 - T_r - R_e \quad (6)$$

where, R_e and T_r are the square of the ratio of reflected (E_r) and transmitted (E_t) electric fields to the incident electric field (E_i), respectively, as represented in Eqs. (7) and (8).

$$R_e = \left| \frac{E_r}{E_i} \right|^2 \quad (7)$$

$$T_r = \left| \frac{E_t}{E_i} \right|^2 \quad (8)$$

5.3 Preparation Methods of Composites for EMI Shielding

We can protect ourselves from electromagnetic radiation by covering us with an electro-conductive media which can generate and transport free charges. Metals are conventional conductive media but metal sheet or foils are not flexible enough to cover easily a complex three dimensional contour of a body or device to be protected. Even if, when metal powder or other conductive particles (such as carbon or conductive polymers) are incorporated as filler material in a polymeric matrix, a rigid or semi flexible composite structure is produced and which will not effectively solve the problem. If textile fabric as a flexible substrate can be made electro-conductive then flexible, moldable, light-weight, composites can be developed for a more versatile application. It is known that synthetic textile fibers such as

polyester, polyamide, acrylic, cellulose-acetate etc. exhibit a very poor electrical conductivity and are hydrophobic in nature. When these fiber mass are rubbed, static electricity is generated and accumulates on the fibers [9, 178]. Natural fibers, such as cotton, wool and silk, exhibit a relatively high hydrophilic property and have relatively higher electric conductivity in favor of static charge dissipation. They are suitable for static charge dissipation but do not serve as effective electromagnetic shield [185]. For this purpose, metallic fibers, or fibers coated with a metal, as an electrically conductive material are commonly used [23, 27, 130, 143, 164, 194, 213]. These metallic fibers are not proved to be satisfactory for practical use due to their poor recovery from bending and breakage [108]. The breakage results in a decrease in the conductive effect of the metallic fiber. Also, it is difficult to mix spin, mix weave or mix knit the metallic fibers with organic polymer fibers. In case of textile fiber, yarn or fabric coated with a metal layer by electro-plating technique, it is required to form a uniform and continuous layer on the textile surface. In order to satisfy the above-mentioned requirement the surface of the fiber is required to be smooth and highly polished. Also, intensive care is required during coating operation to coat a continuous layer of metal with uniform thickness leading to substantial enhancement of the cost of the coating. Also, the metal-coated fiber has demerits in terms of easy peeling off from the fiber during processing or use [30]. The fiber coated with a polymer dope containing an electrically conductive material, such as carbon black, CNT, silver particles etc. is also found unsatisfactory because the coating operation is expensive and the coated layer is easily peeled off from the fiber during processing [13, 135]. When carbon black is used in dope mixing with polymer to spin a conductive filament then at least 15 % of carbon black is required based on the weight of the fiber matrix polymer. This large amount of carbon black causes the fiber-forming process to be difficult, complex and expensive. Also, it is impossible to contain the carbon black in the inside of the natural fibers. Many such limitations associated with processability, flexibility, durability etc. could be successfully overcome by coating/applying conducting polymers such as polyaniline, polypyrrole, polythiophene etc. on textile substrates [109]. These conductive polymer coated textile composites, owing to their flexibility, durability, ease of preparation and application, are considered promising for shielding of electromagnetic radiation [58, 108, 111, 176].

5.4 Textile/Metal Composites for EMI Shielding

Textile fabrics have been coated with metals such as aluminium, copper, nickel, silver and combination of them in industrial scale to prepare electro-conductive composites [7, 108]. The coating methods used are electroless plating, laminating with aluminium foils, dyeing with copper sulfide, vapor deposition etc. Electroless metal plating is a non electrolytic method of deposition of metal from solution by process of oxidation and reduction [70]. This method has some advantages such as coherent metal deposition, excellent conductivity and shielding effectiveness. It is

also applicable to complex shaped insulating textile materials [70]. Vapor deposition coating of woven or nonwoven fabrics are important step for producing a variety of new thin film composites for new applications. Depending on the evaporation conditions, these coated composite fabrics can present quite different surface properties [43]. The shielding efficiency of these metalized textile fabrics mainly works in principle of energy reflection and not its absorption. In many cases, such a phenomenon is not satisfactory. Hence, there have been searches for materials with greater capability of absorbing electromagnetic radiation. In recent years, some patents have appeared which deal with the problem of producing textile composites with ferromagnetic properties. Such products can be applied as flexible screens for attenuating electromagnetic radiation, to produce cores in transformers, motors, generators, etc., and to produce filters to remove substances showing magnetic properties from air and water [108]. The process of coating on the surface of textile fabrics with layers of ferromagnetic powder can give a way to products of such quality composites. Nonwoven materials with ferromagnetic coating showed EMSE of about 30–35 dB for frequency range of 1000–2000 MHz [108]. Those materials are proposed for applications of the camouflage of military objects, restricting the range of fields emitted by devices such as shortwave and microwave diathermy. Textile materials embedded with metallic wires and fibres are also explored as EMI shield. Knitted fabric forms a good conductive network which can better stop the electromagnetic radiation and achieve the shielding effectiveness [216]. They have good impact energy absorption characteristics. Electro-conductive composites are prepared by using polypropylene (PP) matrix and knitted glass fibers as the reinforcement [28]. Copper wires are incorporated as conductive fillers into knitted structure to provide desired EMISE in composite structure. The EMISE of these knitted composites is greatly influenced by the amount of copper, which can be varied by changing the knit structure, stitch density and linear density of yarns used for knitting [28, 137, 175]. The copper and stainless steel wires are wrapped with polyamide filaments to produce a hybrid conductive yarn which is co-woven-knitted to produce fabrics for EMISE [22]. Here a multilayer structure of various thickness and stainless steel (SS) fiber content are responsible for blocking the electromagnetic interference in different frequency. Also, different compositions of Cu/Zn/Sn coated polyester nonwoven (CNW) and Ni/Cu coated polypropylene nonwoven (SNW) show various EMISE depending on incident frequency as shows in Fig. 31. Coated CNW fabric shows higher EMISE due to its higher thickness than that of the coated SNW fabric [22]. In another study, the effect of single and multilayer fabrics made of stainless steel/polyester (40/60) spun yarn on shielding effectiveness has been investigated and the results are shown in Fig. 32. Also, polypropylene and polyamide filaments are wrapped on copper wire to produce conductive yarn. This yarn is utilized as warp and weft identically for manufacturing woven fabric to obtain isotropic shielding behavior [23]. It is observed that the EMSE of these woven fabrics increases with increase of copper wire content and as well as with the density of warp or weft at all frequencies of incident radiation. The shielding effectiveness of these fabrics of a single layer is barely sufficient for general applications and the multi-layers provide adequate shielding

Fig. 31 Shielding effectiveness of various metalized nonwovens [22]

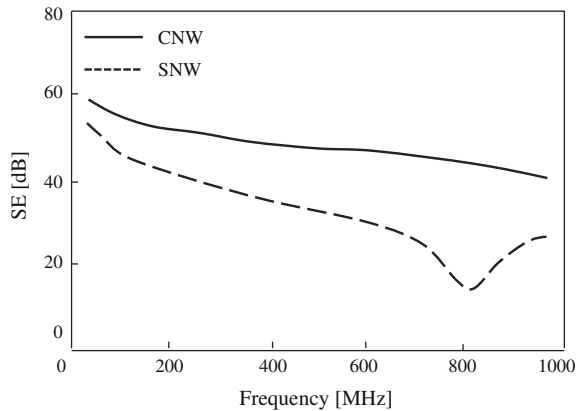
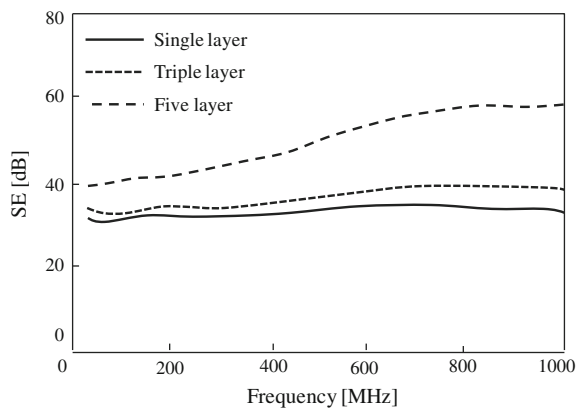


Fig. 32 Shielding effectiveness of laminated SS/PET (40/60) woven fabrics [22]

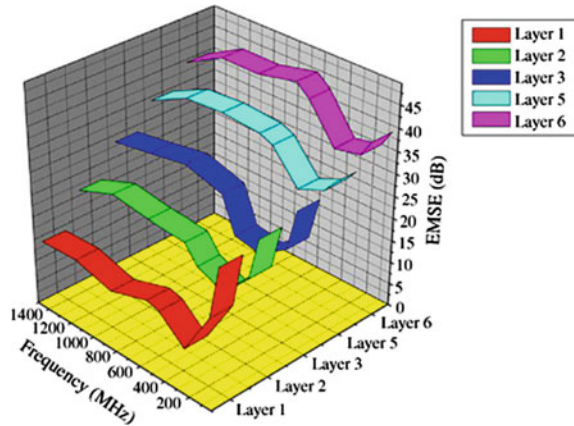


effectiveness (20–55 dB) when the wave is normally incident on fabric of thickness higher than 1.6 mm. The EMISE increases with increase of fabric thickness as the number of conductive layers increases as shown in Fig. 33 [23].

5.5 Conductive Polymer Coated Textile Composites for EMI Shielding

Coating of conducting polymers on insulating fabrics produces novel composites for potential applications of EMI shielding [53, 66, 96, 100, 127, 208]. Various composite textiles are prepared by coating different textile substrates, such as cotton, wool, viscose, cupro, lyocell, polyester, nylon etc. with conducting polymers by means of in situ polymerization [1, 15, 31, 39, 54, 92, 93, 97, 133, 141, 197, 198, 205, 209]. These composite textiles show better performance than metal fibre and filler composites which are susceptible to galvanic corrosion or loss of

Fig. 33 EMSE of woven fabric at various layers [23]



conductivity due to friction [7]. The conducting polymers reflect less and largely absorb electro-magnetic radiation [7]. It has been reported that textile fabrics coated with polypyrrole by chemical polymerization are suitable for EMI Shielding [1, 53, 93, 100, 109]. The desired value of electrical resistivity of an electromagnetic shield is less than $100 \Omega/\text{cm}^2$ [42, 131, 173]. Polyaniline coated polyester fabric of resistivity $5 \text{ k}\Omega/\text{Y}$ has been found suitable for EMI shielding [111].

5.5.1 Conductive Polymer Coated Woven Fabrics for Electromagnetic Shielding

The polymerization of aniline pyrrole and thiophene on insulating fabrics such as polyester, glass and high silica cloth is carried out by in situ chemical polymerization [42]. In the radio frequency range from 100 to 1000 MHz, conducting polyaniline-coated polyester fabrics show a shielding effectiveness in the range 30–40 dB as shown in Fig. 34. The reflectance studies show that the polyaniline-coated polyester fabrics can absorb about 98 % and can reflect only about 2 % of the energy. In case of polypyrrole coated polyester fabrics, 96 % of energy is absorbed and 4 % is reflected back, whereas in case of polythiophene coated polyester fabric, 82 % of the energy is absorbed and 18 % is reflected back [42]. An effective shield should absorb all the energy and nothing should reflect back. The shielding effectiveness of polypyrrole coated nylon/lycra fabric prepared with an anthraquinone-2-sulfonic acid (AQSA) dopant is reported as 89.9 % at 18 GHz [67]. In another study, polypyrrole is polymerized chemically and electrochemically in sequence on a polyester woven fabric, for preparation of a composite with very low electrical resistivity of $0.2 \Omega \text{ cm}$. EMISE of this composite is about 36 dB over a wide frequency range up to 1.5 GHz as shown in Fig. 35. It can be seen that the composite restricts electro-magnetic waves in large by absorption and in small by reflection. Overall EMISE increases with increase of electrical conductivity [96]. PPy films with high conductivity and good adhesion are generated on the surface of

Fig. 34 Shielding effectiveness of polyaniline-coated fabrics in the frequency range 100–1000 MHz [42]

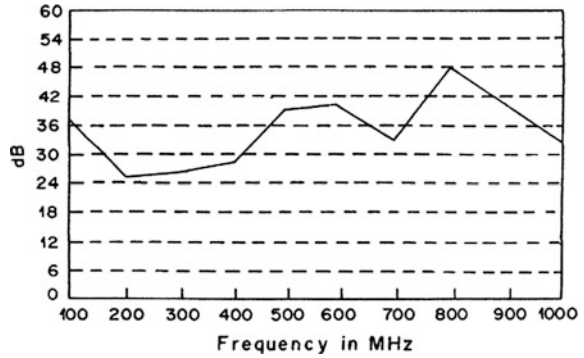


Fig. 35 EMISE absorbance (A), and reflectance (R) of PET fabric/PPy composites with various specific volume resistivity [100]

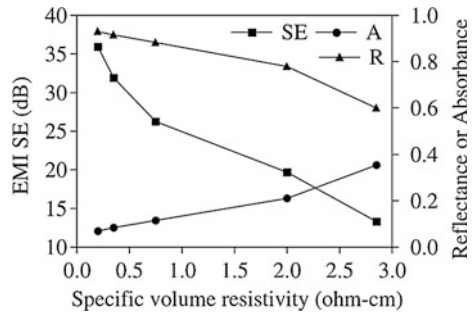
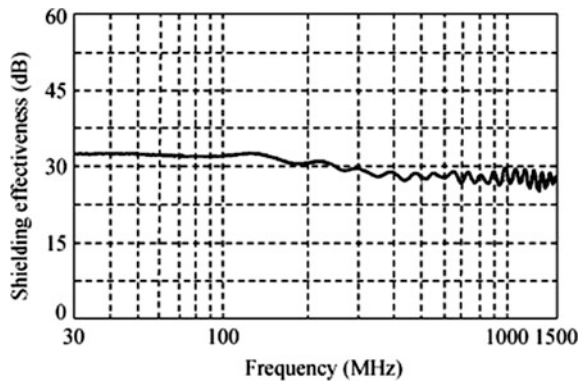
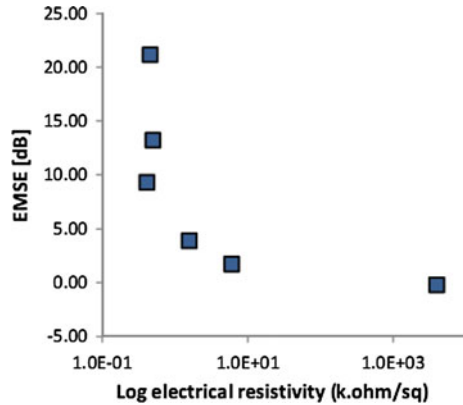


Fig. 36 Shielding effectiveness of PPy film [150]



insulating epoxy resin substrates using chemical polymerization. Those films show EMISE of about 30 dB over a wide frequency range from 30 MHz to 1500 MHz as shown in Fig. 36 [150]. PPy coated polyester and silica fabric show EMISE of 21.48 dB and 35.51 dB respectively at frequency of 101 GHz [99]. Polypyrrole coated glass fabrics having resistivity below $500 \Omega/\gamma$ exhibit 98.67–99.23 % signal loss in the frequency range of 800–2,400 MHz [1]. These samples with low resistivity show high shielding effectiveness compared to those samples with high

Fig. 37 EMSE of PPy coated glass fabric as a function of electrical resistivity [1]



resistivity as shown in Fig. 37. These fabrics are proposed for applications as shield for house hold appliances, FM/AM radio broadcast sets, wireless phones, cellular phones, computers, buildings, secret rooms and various electronic gadgets that operate up to 2.4 GHz frequency [1].

In another study, silver (Ag) is thermally vacuum evaporated on the surface of polypyrrole–polyester complexes. The EMISE of fabric complexes increases as the area of Ag evaporation layer increases. When the Ag is partially (~37 %) evaporated on one side of fabric complexes, the EMISE is 29 dB at 0.5 GHz, and while Ag is evaporated on total area of the sample the EMISE obtained is 33 dB at the same frequency range [75]. Also, PPy/Al₂O₃ textile nanocomposite is found suitable for effective EMI shield in the range of 8–12 GHz frequency and could be able to absorb more than 53 % of microwave radiation [190].

5.5.2 Conductive Polymer Coated Nonwoven Fabrics for Electromagnetic Shielding

EMISE of PPy coated hydro-entangled polyester nonwoven textiles is studied in the frequency range 100–800 MHz [6]. A positive correlation between the SE and the surface conductivity of those nonwoven textiles is found. EMISE of 37 dB was found for the sample with the lowest surface was resistivity of 3 Ω/square [92]. In another study, PPy coated polyester nonwoven composite fabrics shows effective EMISE of 20 dB in 1 GHz frequency [116]. For these nonwoven fabrics coating with Ag particles enhances the EMISE up to 55 dB and for multilayer complexes of those fabrics had EMISE of about 80 dB. PPy coated nonwoven fabrics are proposed for excellent radio frequency and microwave absorber because of high absorbance and low reflectance [197, 198]. It is reported that polypyrrole coated textile fabrics of high conductivity show reflection dominant EMISE and that of low conductivity showed absorption dominant EMISE [99, 101]. EMISE of some conductive textile materials proposed as effective shield, as cited in literature, are tabulated in Table 2.

Table 2 Shielding effectiveness of various conductive textiles

Material	Resistivity	Testing frequency	EMSE [dB]	References
Metallized fabrics	–	100 kHz–1 GHz	67, 75–80	Koprowska et al. [108]
PPy-coated fabrics	Surface resistivity $3 \Omega/\gamma$	800 MHz	37.02	Avloni et al. [6]
PPy-coated polyester fabrics	Volume resistivity $0.2 \Omega \text{ cm}$	1500 MHz	36.6	Kim et al. [100]
PPy-coated polyester fabrics	Volume resistivity $0.3 \Omega \text{ cm}$	1500 MHz	35 dB	Kim et al. [99]
PPy or poly (3,4-ethylenedioxythiophene coated polyester woven fabric	Volume resistivity $0.3 \Omega \text{ cm}$	1500 MHz	36	Abbasi and Militky [1]
PPy coated glass fabrics	Surface resistivity $460 \Omega/\gamma$	800 MHz	18.75	Abbasi and Militky [1]
PPy coated glass fabrics	Surface resistivity $460 \Omega/\gamma$	2.4 GHz	21.16	Abbasi and Militky [1]
Ag/PPy coated fabric complex	–		80	Lee et al. [115]
PPy coated cotton fabric	Surface resistivity $1.18 \text{ M}\Omega/\gamma$	2500 MHz	01	Yildiz et al. [210]
Polyaniline-coated polyester fabrics	Volume resistivity $10\text{--}60 \Omega \text{ cm}$	101 GHz	21.48	Dhawan et al. [42]
Polyaniline-coated silica fabrics	Volume resistivity $10\text{--}28 \Omega \text{ cm}$	101 GHz	35.61	Dhawan et al. [42]
Co-weaved/knitted fabrics	–	100 kHz–1 GHz	40–50	Chen et al. [22]
Metalized nylon	Surface resistivity $0.09 \Omega/\gamma$	800 MHz	67.04	Avloni et al. [6]
Twill PPy coated	Surface resistivity $40 \Omega/\gamma$	800 MHz	16.8	Avloni et al. [6]
PPy/chitosan composite film	Linear resistivity $0.0145 \Omega \text{ cm}^{-1}$	1200 MHz	32.15–35.66	Abdi et al. [2]
PPy blended hot melt adhesives	Linear resistivity $0.2 \Omega \text{ cm}^{-1}$	300 MHz	30	Pomposo et al. [146]
Boron and carbon fabrics	–	1200 MHz	30	Mistik et al. [130]

6 Multi-scale Reinforcements and Composites

Like all other materials, nanotechnology has been extensively applied in composite materials with the aim to overcome some existing drawbacks or to introduce some special features. Laminated composites are the most widely used type of composite materials which are applied in various advanced applications including aerospace, automobiles, civil engineering, etc. Common problems of these composites are the poor z-directional properties and delamination between the different layers under loading conditions. The approaches that have been explored to overcome these problems are ply stitching or the use of 3 dimensional fabrics in which all the fabric

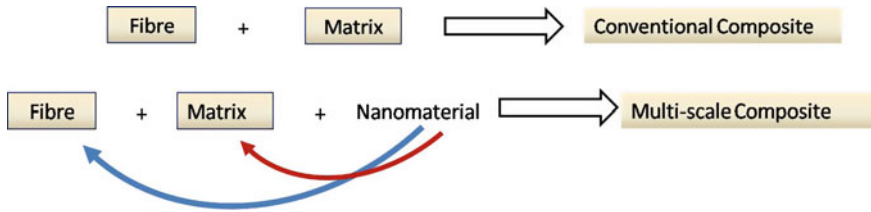


Fig. 38 Concept of developing multi-scale composites

layers are integrated using through-the-thickness yarns. However, these methods usually lead to reduced properties in in-plane direction. The most recent approach to solve this ever existing problem of laminated composites is to apply nanomaterials between the different plies of composites. The deposition of nanofibres and nanotubes between the plies could greatly enhance the inter-laminar shear strength of composites [80, 195]. Further, techniques to grow nanotubes (CNT) vertically between the plies have also been developed in order to stitch the different layers with nanotubes [52]. Nanostructures, specially nanofibres and nanotubes have nano-diameters, high aspect ratio, huge surface area and extraordinary mechanical properties and therefore, stitching plies with nanomaterials is far more effective than conventional stitching methods. Moreover, nanomaterial addition does not affect the in-plane mechanical properties of composites. Besides nanomaterial deposition between plies, they can be also introduced within the surface of the fibres or within the matrix of composites [14, 95, 155, 156, 158–161, 197]. In both cases, significant improvement in the inter-laminar shear strength has been noticed, along with improvements in in-plane mechanical strength and stiffness and toughness. Moreover, when nanomaterials like CNTs are introduced, they composite possesses some additional special features such as electrical and thermal conductivity, self-sensing behaviour, electromagnetic shielding and so on. These special features are highly important for advanced technical applications.

The incorporation of nanomaterials within conventional composites originated a special class of composite, known as multi-scale composites. Similarly, when nanomaterials are introduced within the fibres prior to composite reinforcement, the fibre systems are known as multi-scale reinforcements. These materials are called multi-scale as they are composed of materials from two different length scales. So, these composites are a special class of hybrid composites and sometimes, also called hierarchical composites. The concept of multi-scale composite is presented in Fig. 38.

Although different types of nanomaterials have been explored to develop multi-scale composites such as nano TiO_2 , nano Al_2O_3 , nano clay, polymeric nanofibres, CNF, CNT, etc., most of the research studies have been focused on CNF and CNT due to their exceptional mechanical, thermal and electrical properties. However, these nanomaterials with remarkable properties also led to a number of processing difficulties, mainly their agglomeration problems.

As discussed above, multi-scale composites can be developed by mainly three ways: (1) introducing nanomaterials within fibres (i.e. multi-scale reinforcement),

(2) introducing nanomaterials within matrix and (3) introducing nanomaterials within plies. The method of introducing nanomaterials on the surface of the fibres avoids the difficulty in dispersing them within the matrix. However, as nanomaterials are present on the fibre surface or at the interface region, the improvement in the matrix dominated properties such as fracture toughness is less likely to occur. One of the most studied approaches to introduce nanotubes on the fibre surface is through their growth directly on the fibre surface using CVD technique. For this purpose, the fibre substrate is first impregnated into the catalyst solution prior to introducing into the CVD chamber. A hydrocarbon gas is then passed through the CVD reactor maintained at very high temperature (~ 1000 °C), which breaks down the hydrocarbon gas and initiates the growth of CNTs on the fibre substrate containing catalyst. CNTs can also be grown vertically aligned through this process. One major problem of this process is the high temperature, which the conventional polymeric fibres do not sustain. So, another approach to avoid this problem is to first grow the nanotubes on a metal fabric such as alumina cloth, next to windup the cloth on a roller which, subsequently, transfers the nanotubes on a tacky fibre prepreg through application of pressure (this process is known as transfer printing). Coating of fibre surface with nanomaterial solution or simple spraying of the nanomaterial solution on to the fibre surface are other simple approaches followed for developing multi-scale reinforcements. Electrophoretic deposition of CNTs on to the carbon fibre surface has also been reported. In this process functionalized CNTs with negative charge are deposited on to carbon fibres which are used as the positive electrodes in the electrophoresis process. Grafting chemically functionalized CNTs on to surface activated carbon fibres is another reported technique.

The other most common approach of fabricating multi-scale composite is through dispersion of nanomaterials within the composite matrix. This process is very challenging due to very high agglomeration tendency of nanomaterials, especially for CNTs [139, 155, 157]. A number of physical and chemical techniques have been used for dispersing nanomaterials in various matrices. The most common physical approach is the ultrasonication technique, which creates a number of shock waves in the nanomaterial solution, separating the nanotubes and distributing within the matrix. Further, the use of surfactants assists in separating the nanomaterials and the stabilization of their dispersion through steric/electrostatic stabilization mechanisms. Other mechanical techniques which are used to disperse nanomaterials within thermosetting matrices are high speed mechanical stirring, calendaring, ball milling, etc. which have been also used, sometimes, in combination with ultrasonication to reduce the period of ultrasonic treatment and associated problems (nanomaterial damage, process time and cost). In case of thermoplastic polymers, the efficient route of dispersing nanomaterials is through twin screw extrusion process.

The process of fabricating multi-scale composites is similar to the conventional composites, once the nanomaterials have been incorporated within the fibre or matrix system. Commonly, vacuum assisted resin transfer moulding (VARTM) and compression moulding are used. However, the composite fabrication system should not allow much resin flow, as it favours nanomaterial re-agglomeration.

Multi-scale composites possess enhanced mechanical properties as compared to the conventional composites. Improvements in in-plane mechanical strength and stiffness, inter-laminar shear strength, fracture toughness, impact performance, fatigue resistance, dynamic mechanical performance, etc. have been reported. The main factors responsible for enhanced mechanical performance of multi-scale composites are improved fibre/matrix interface, reinforcing effect as well as other energy absorbing effects of nanomaterials such as crack-bridging, nanomaterial pull-outs, crack pinning, etc. Besides mechanical properties, some nanomaterials with excellent thermal and electrical conductivity like CNT and CNF can produce conducting composite materials. Electromagnetic shielding, piezoresistivity and sensing behaviour are other important benefits of multi-scale composites. Table 3 lists some recently developed multi-scale composites and their various properties.

Table 3 Different types of multi-scale composites and their properties

Type of nano filler and concentration	Fibre/matrix and composite fabrication method	Property improvement
Nano Al ₂ O ₃ 10 vol% [77]	Carbon fibre/epoxy, Filament winding technique	Young's modulus, flexural strength, interlaminar shear strength and fracture toughness improved significantly
Nanoclay 1–3 wt% [33]	Carbon fabric/epoxy, Vacuum assisted resin infusion molding	Maximum improvement of 9.3 and 13.7 % in flexural modulus and strength, 52.4 % in storage modulus (35 °C), 30.2 % in shear strength at 2 wt% nanoclay
Graphite nanoplatelets 3 and 5 wt% [30]	Carbon fibre/epoxy, vacuum assisted wet layup	Maximum improvement of 18 and 11 % in in-plane shear modulus and strength and 16 % in longitudinal compressive strength at 5 wt%
Amino functionalized DWCNT, 0.1 and 0.3 wt%, dispersed in resin [64]	Glass fabric/epoxy, Resin transfer molding	No significant change in Young's modulus and tensile strength. Improvement of 20 % in interlaminar shear strength
MWCNT, thin-MWCNT, amine functionalized double walled CNT 0.5 wt%, dispersed in resin [62]	Carbon fibre/epoxy, Preparation of prepreg in drum winder and laminates in vacuum bag	No major improvement in modulus and strength. Fracture toughness improved by 80 % for MWCNTs and modifying epoxy by compatibilizer
MWCNT functionalized and non-functionalized 1 wt%, dispersed in resin [151]	Glass fibre/epoxy, vacuum assisted resin transfer molding	Improvement of 14 % in tensile strength, 20 % in Young's modulus, 5 % in shear strength
Silane functionalized MWCNTs, 1 wt%, Dispersed in resin [104].	Basalt/epoxy, VARTM	Flexural modulus and strength increased by approximately 54 and 34 %, respectively

(continued)

Table 3 (continued)

Type of nano filler and concentration	Fibre/matrix and composite fabrication method	Property improvement
Silane and acid functionalized MWCNTs, 1 wt% [103]	Basalt/epoxy, autoclave processing	Flexural modulus, strength and fracture toughness of silane-treated CNT based composites were 10, 14 and 40 % greater than those of acid-treated CNT based composites
DWCNT-NH ₂ , 0.025–0.1 wt%, dispersed in resin [55]	Carbon fibre/epoxy, Vacuum Infusion Technique	Enhancement in flexural modulus by up to 35, 5 % improvement in flexural strength, 6 % improvement in absorbed impact energy, and 23 % decrease in the mode I interlaminar toughness
Amine functionalized MWCNTs, 1 wt%, dispersed in resin [172]	Carbon fibre/epoxy, Hand Layup-Vacuum bag processing	Increase in Young's modulus, inter-laminar shear strength, and flexural modulus by 51.46, 39.62, and 38.04 %, respectively
SWNT, 0.1 wt%, dispersed in matrix [155]	Carbon fabric/epoxy, Hand layup- compression moulding	Improvements of 95 % in Young's modulus, 31 % in tensile strength, 76 % in compressive modulus and 41 % in compressive strength
SWNT, 0.1 wt%, sprayed on to fibres in midplane ply [80]	Glass/vinyl ester, VARTM	Up to 45 % increase in shear strength over control samples
Vertically aligned CNT on prepreg surface for ply stitching, 1 vol%, transfer printing method [52]	Carbon fibre/epoxy, Autoclave processing	Increase in fracture toughness by 1.5–2.5 times in Mode I, and 3 times in Mode II
MWCNT, 1–2 vol% in composite, grown on surface of the fibres [180]	Alumina fibre/epoxy, Vacuum bag processing	Improvement of steady-state toughness by 76 %, in-plane tension-bearing stiffness by 19 %, critical strength by 9 %, and ultimate strength by 5 %
CNT, 1–3 vol% in composite, grown on fibre surface [60]	Alumina fibre/epoxy, Vacuum bag processing	Enhancement of 69 % in interlaminar shear strength
MWCNTs, 0.25 wt% on fibre surface, electrophoretic deposition [12]	Carbon fibre/epoxy, VARTM technique	Enhancement of the interlaminar shear strength by 27 %

7 Conclusions

The initial development of the composite was a result of the quest for a strong at the same time light material. However, with change and advancement of technology, the material requirements have also changed drastically. This has led to the development of a new breed of composite having various functional properties. These new composites with special properties have potential for many critical and demanding applications. Some of these special composites have already become a

reality and are being used commercially either in high end or routine applications, but many are still in growing stage. The advent of nano materials and nano technology has opened up new vistas for the development of composites with special properties. The challenge is in the selection and processing of these materials to tailor make a specialised composite structure. The biggest challenge is the technology transfer and commercialisation of process to benefit the mankind and society at large.

A dream is the bearer of a new possibility, the enlarged horizon, the great hope
—Howard Thurman

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