

POLYPYRROLE BASED NANOCOMPOSITES AS RADIATION SHIELDING MATERIALS: A MINI REVIEW

R.G. Mahloniya,

Email: rmahloniya@gmail.com

Associate Professor, Department of Basic Science, Technocrats Institute of Technology - Science,
Bhopal, India

ABSTRACT:

Conducting polymers having numerous applications in the field of electronics and antistatic textiles, some of which have military applications. Among the main importance of conducting polymers as a nanocomposites in light-emitting devices (LEDs), replacing silicon as the conventional substrate material for clock radios, audio equipment, televisions, cellular telephones, automotive dashboard displays, and aircraft cockpit displays. Conducting polymer nanocomposites provide benefits to industries such as electronics by shielding against electromagnetic interference (EMI). Conductive polymer nanocomposites are being used in devices that detect environmentally harmful chemicals, factory emissions, and flavors or aromas in food products. Currently, their conductivity is being increased in electrostatic materials, conducting adhesives, electromagnetic shielding, artificial nerves, aircraft structures, diodes, and transistors. The present article reviews various aspects of conducting polymers and focus on potential of polypyrrole as shielding materials.

KEY WORDS: *Conducting polymers, nanocomposites, radiation shielding, polypyrrole*

1. INTRODUCTION

Conductive polymers or, specifically, intrinsically conducting polymers (ICPs) are organic polymers that have the property to conduct electricity. The biggest advantage of conductive polymers is their processibility, mainly by dispersion.

Conductive polymers are generally not plastics, i.e., they are not thermoformable. But, like insulating polymers, they are organic materials (Fig. 1). They can offer high electrical conductivity to substrate but do not show mechanical properties as other commercially used polymers do. The electrical properties of conducting polymers can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques [1-6].

Polypyrrole (PPy) is one of the most popular and promising conducting polymers using in the field of sensors as the monomer pyrrole (Py) which is water soluble, commercially available and can be easily oxidized. Apart from this PPy possesses good environmental stability, excellent redox properties and high electrical conductivity [7]. In general, the PPy films are synthesized either by chemical or electrochemical approaches [8, 9].

Although, The oxidation reaction of Pyrrole can be controlled in the electrochemical method, it requires intricate equipments at high cost. On the other hand, by adjusting the process conditions like concentration, synthesis time, etc. in chemical synthesis, the oxidation reaction can be controlled easily [10-13].

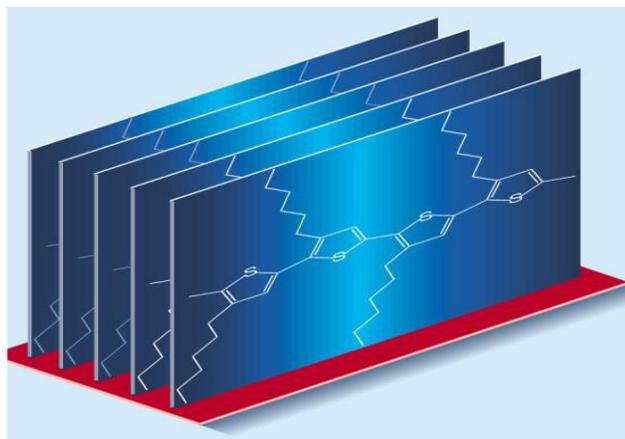


Fig. 1 Polymeric conductors

2. TYPES OF CONDUCTING POLYMERS

Conducting polymers are different types on the basis of mechanism of conduction that offers electrical conductivity to polymers. Conducting polymer composites, Organometallic polymeric conductors, Polymeric charge transfer complexes and Inherently conducting polymers. Brief description of the conducting materials has been given here.

2.1 CONDUCTING POLYMER COMPOSITES

Most commercially applicable composites use a polymer matrix material often called a resin solution. There are many different polymers available based upon the raw ingredients. There are several broad categories, each with numerous variations. The most common ones are known as polyester, vinyl ester, epoxy, phenolic, polyimide, polyamide, polypropylene and others. The reinforcement materials are often fibers, conducting polymers, carbon but sometimes commonly ground minerals are also used. The various methods are developed to reduce the resin content of the final product, or the fibre content is increased. By incorporating reinforcement materials such as glass, carbon, or a polymer to another polymer, it is often possible to obtain unique combinations or levels of properties. Typical examples of prepared polymeric composites are glass-, carbon-, or polymer-fiber-reinforced thermoplastic or thermosetting resins, carbon-reinforced rubber, polymer blends, silica- or mica-reinforced resins, and polymer-bonded or -impregnated concrete or wood. It is often applicable to consider composite materials as coatings (pigment-binder combinations) and crystalline polymers (crystallites in a polymer matrix) (Fig.2). Methods for the synthesizing of conducting polymers nanocomposites have been reviewed [14-16]. Conducting polymers such as polypyrrole (PPy) have potential applications in electromagnetic radiation shielding, microwave absorbent and battery [17-21]. Among all the conducting polymers, PPy has been an object of intense investigation due to its good conductivity, stability in air, interesting electrochemical behavior, corrosion protection, and ease of preparation [22-24].

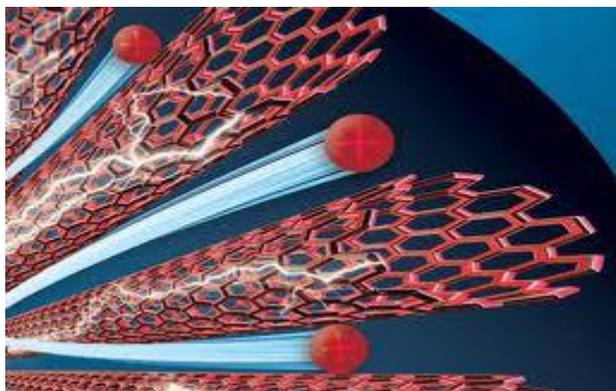


Fig. 2 Conducting polymer composites

2.2 ORGANOMETALLIC POLYMERIC CONDUCTORS

On addition of organometallic groups to polymer molecules gives organometallic polymeric conductors. In its mechanism the d- orbital of metal may overlap with orbitals of the organic structure and thus increasing the electron delocalization. The d orbital may also bridge adjacent layers in crystalline polymers to give conducting property to it [25]. Sturge et al.[26] prepared organometallic polymers and linear mono-, bi-, and trimetallic Octafluoro-p ,p'-biphenylene-Bridged Complexes of Bis (methylphenylphosphine) nickel and confirmed by structural analysis technique Ni (PMePh₂)₂, (4,4'-C₁₂F₈,H) Br and Ni (PMePh₂)₂, (4,4'-C₁₂F₈H)₂.

2.3 POLYMERIC CHARGE TRANSFER COMPLEXES

Polymeric charge transfer complexes (CTC) are obtained when acceptor like molecules are added to the insulating polymers. In the literature, Many charge transfer complexes are reported e.g. CTC of tetrathiafulvalene (TTF) with bromine, chlorine etc is a good conductor. The cause for high conductivity in polymeric charge transfer complexes and radical ion salts are still somewhat obscure. In polymeric materials, the donor – acceptor interaction increases orbital overlapping, which contributes to modify molecular arrangements and enhanced electron delocalization process. Molecular electronics based on charge transfer complexes (CTC) have considerable attention in recent years [27, 28]. Their unusual electrical, magnetic, and optical properties are reported in fabrication of devices [29]. However, the mechanical properties of polymeric materials is very low, which restrict their application [30]. By preparing their composites with insulating materials, Mechanical strength of these CTC can be improved [31]. Such prepared composite materials have enhanced mechanical strengths, but retaining their other properties, e.g. electrical conductivity, optical, and magnetic properties. Such electrically conducting polymer composites can be synthesized by using fillers like graphite, carbon black, metal powders, and flakes to insulating polymer materials [32, 33].

2.4 INHERENTLY CONDUCTING POLYMERS

The conjugated polymers are known as the intrinsically conductive polymers and their conductivity arises due to a special type of metallic bonding in which valence electrons are completely delocalized and move almost freely through the crystal lattice. It is therefore necessary for the polymer backbone to behave as an electrical conductor. Shira kawa and his group found drastic increase in the

electrical conductivity of polyacetylene films when exposed to iodine vapor. This research made inherently conducting polymer center of attraction to the researchers [34]. The electrical conductivity of highest crystalline variety of the polyacetylene had the order of 10^{-5} S/cm and was in all possibility the trans-form of polyacetylene. Shirakawa and his group started the new era of research and many small conjugated molecules were being polymerized, obtained polymeric materials were either insulating or semiconducting in their oxidizing or doping state. The delocalization electrons in conjugated polymers are cause for electrical properties. This delocalization of electrons may occur through the interaction of n-bonded electrons in a highly conjugated chain or by a similar interaction of n-electrons with non bonded electrons of electron rich hetero-atoms (e.g. S, N, etc.) in the backbone. The delocalization of the electrons in a conjugated polymeric chains may be good when the molecular structure of the backbone is planar and there is no torsion at the bonds, which would decrease the delocalization of the electron system. Some of the examples of conjugated polymers and large number of application areas using inherently conductive polymers have been developed and tested. Each is based on properties that are specific to these materials. Due to the High demand of air-stable highly conductive polymers, and the remarkable entry of these products into the commercial sectors, several applications have already been possible, and numerous others are going to be easily realized. The unique properties of inherently conductive polymers like the possibility of fine-tuning the conductivity by adjusting the amount of dopant incorporated within the polymer, doping/un-doping reversibility, and the optical absorption characteristics in the UV, visible and near infrared as well as its electromagnetic absorption characteristics.

Several polymers have been tested and proved to work in a variety of applications including batteries, capacitors, smart windows, light emitting diodes, transistors, photovoltaics, microlithography, corrosion control, conductive adhesives and inks, static dissipation, EMI shielding, radar/microwave absorption, direct plating, electrostatic powder coating, clean room applications, sensors, and drug delivery systems.

During the last two decade, the research on inherently conductive polymers such as polyaniline (PANi), polypyrrole (PPy) and polythiophene (PTh) have been increased intensively due to their special properties [35, 36,37]. Among intrinsically conductive polymers, polypyrrole (PPy) has many special properties such as ease to synthesize, high processing flexibility and also good mechanical strength and remarkable stability [22]. Different methods can be used to synthesize polypyrrole such as chemical, electrochemical, vapor phase and enzymatic routes [38]. One of the key problems relating to the potential applications of electroactive polymers is their poor processability and inadequate mechanical properties; some of them (for example, polypyrrole) are not capable of film formation. The most promising approach to the solution of this problem is to prepare composite. Materials such as blends, filled polymers, and multilayer materials using conventional thermoplastic polymers [39]. Examples of some polymers are shown in Fig. 3.

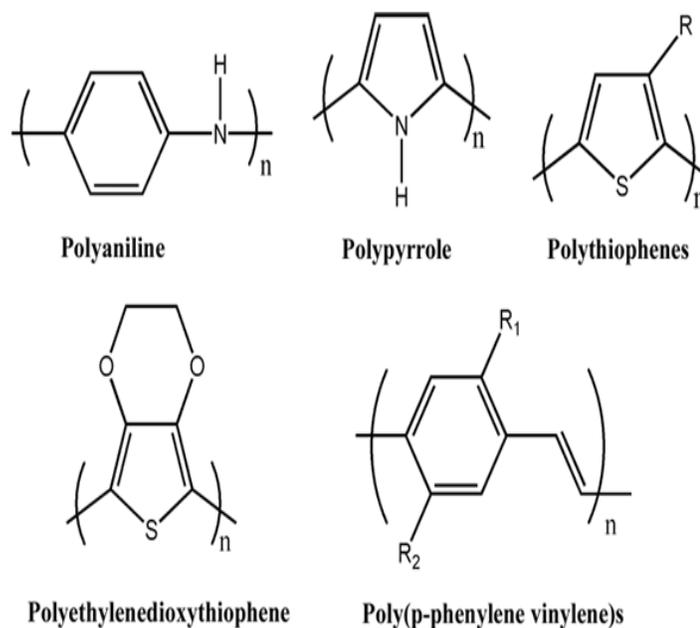


Fig. 3 Examples of some polymers

3. ELECTROACTIVE POLYMERS

Electroactive Polymers (EAPs) are polymers that show a variation in size or shape on stimulating by an electric field. The most promising applications of EAPs are in actuators and sensors. A typical characteristic property of an EAPs is that they undergo a large amount of deformation on sustaining large forces.

EAPs having some remarkable characteristics like softness, flexibility, and low-density that provide reversible mechanical deformation by electric fields. The electromechanical response of EAPs is because of either electrostatic force (dielectric EAPs) or displacement of ions inside the polymer (ionic EAPs (IEAPs)). IEAPs are particularly attractive due to their lower density, higher resilience, higher deformation and lower operating voltage compared to other types of electroactive materials [40-42]. On comparing with electroactive ceramics (EACs), dielectric EAP, and shape memory alloys (SMAs), IEAPs are significantly more efficient. The soft and elastic IEAPs exhibit mechanical strain up to two orders of magnitude larger than that generated by fragile and rigid EACs under application of several hundred volts under application of few volts (≈ 4 V) [43,44]. IEAPs also have significantly higher resilience and lower density compared to SMAs [45].

4. CONDUCTING AND ELECTROACTIVE POLYMERS

4.1 POLYMER NANOCOMPOSITES

Composites are prepared from combinations of two or more compounds by a suitable technique, in order to get materials having unique physiochemical properties and large potential for application in different fields.

Novel properties of composites material can be obtained from the combination of the matrix into a single material. Traditional polymers usually serve as the matrix, in order to obtain a special class of hybrid

materials termed “polymeric nanocomposite”. Composite material having different physical and chemical properties with respect to matrix and hence it is useful for many applications in different fields [22, 46-47]. Recently, Nanocomposites of conducting polymers and metal nanoparticles are considered as a new era of research due to its potential possibilities to create suitable materials for microelectronic devices, chemical sensors and electrocatalysis [48]. Polymer composites of electrically conducting particles become important for a variety of applications in science or technology (Fig 4). Owing to their high mechanical and chemical stability, unique dielectric and electric properties, they can be used as smart materials in the field construction of various components of electronic appliances [49]. A diverse of their applications offer protection against radiation, e.g. microwave absorbers [50, 51], for electromagnetic interference shielding of various devices [52]. Composites consisting of conventional polymer matrix filled with anisotropic particles such as metal [53, 54] or carbon fibres [55, 56] have been reported in the past. Conducting polymers, as polypyrrole (PPy) or polyaniline (PANI) have shown unique properties and emerged as a new class of materials in the last decades. Due to their high electrical conductivity and ease of preparation [57-59], potential applications of these materials such as microwave absorbers were reported [60]. The electromagnetic interference shielding applications of conducting polymers composites were studied for chitosan/polypyrrole composite [61] where shielding by reflection prevails over absorption by the composite.

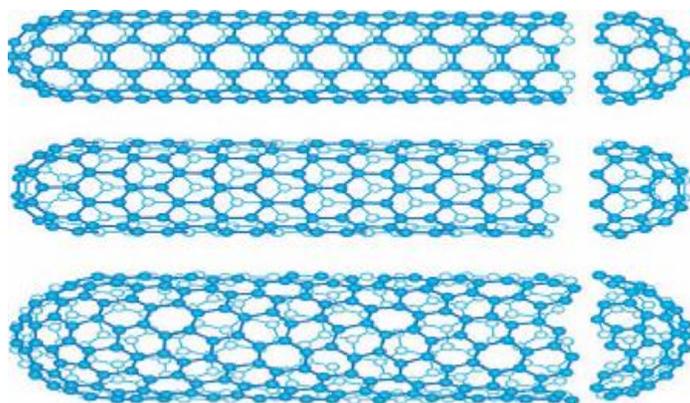


Fig. 4 Schematic of nanotube morphologies (a) Armchair, (b) zig-zag, and (c) chiral

4.2 HOMOPOLYMERS

Homopolymer, consisting of a single type of building unit or identical monomers, is a large molecular weight compound produced by polymerization. [62- 64]. Pyrrole and aniline had been prepared by chemical synthesis in an equimolar proportion at three different temperatures [65]. Copolymerisation is an easy, facile method to combine the different kind of monomeric units and it is a common approach to obtain materials with tailored properties [66-68]. Usually these properties are determined by the structure, ratio, and sequence of the repeat units derived from the co-monomers [69]. The copolymers are shown their solubility in basic media and thin films can be prepared, onto glassy carbon electrodes, by evaporation of the solution [70, 71].

4.3 POLYMER BLENDS

Polymer blends or polymer mixtures are materials analogous to metal alloys, in which at least two polymers are blended together to get a new material having different physical properties. Polymer blends can be mainly classified into following categories. Immiscible polymer blends or heterogeneous polymer blends: If the blend is made of two polymers, two glass transition temperatures will be observed. Compatible polymer blends: Immiscible polymer blends having macroscopically uniform physical properties. The macroscopically uniform properties are usually generated by adequate strong interactions between the component polymers. Miscible polymer blends or homogeneous polymer blends: Polymer blends they are a single-phase structure. Here, one glass transition temperature will be reported. The term polymer alloy for a polymer blend is discouraged, as the former term includes multiphase copolymers but excludes incompatible polymer blends.

5. ELECTRICAL PROPERTIES OF CONDUCTING POLYMERS

It is only the doping which makes most of the conjugated polymers conducting from their insulating to semiconducting or conducting state. Although the charged species are impregnated by doping and the electrical conductivity is due to electrons. The Electronic conduction of conducting polymers is tuned by numerous factors. Significant among these are: i) Nature or chemical reactivity of the dopant ii) Process of doping iii) Doping level iv) Method and condition of polymer synthesis v) Processing of the polymer Chemical reactivity of the dopant is of prime importance to obtain a conducting polymer. All dopants are not equally capable to oxidize a polymer chain. Iodine is one of the dopant for increasing the electrical conduction in polyacetylene by 13 orders of magnitude but is too weak for oxidizing PPy or PANI. Similarly HCl is used to impart conductivity to PANI. The electrical conduction in polyaniline hydrochloride observed is $4.4 \pm 1.7 \text{ S cm}^{-1}$. Doping conditions also play an important role. Electrical conductivity usually increases with the help of doping level due to increase in charge carriers concentration. Rapid increase in mobility of the charge carriers may be responsible for this high rate of increase in conductivity. Development of quantitative model for conduction is hampered by the fact that there are at least three elements contributing to the carrier mobility: Single chain or intramolecular transport and Interchain transport Interparticle contact Electrical conduction is very much dependent on the synthesis of polymer, purification of the polymer, physical treatment of the polymer etc. besides nature of the dopants and the process of doping.

6. APPLICATIONS OF CONDUCTING POLYMERS

6.1 BIOMEDICAL APPLICATIONS

A numerous of biomedical applications of CPs are currently being reported, including the development of artificial muscles (Fig. 5) [72], controlled drug release [73-75, 67], tissue engineering [76], biosensors [77], neural recording [78] and the stimulation of nerve regeneration [79]. Moreover, electrically active tissues including the brain, heart [69] and skeletal muscle [80], provide opportunities to couple electronic devices and computers with human or animal tissues to create therapeutic body-machine interfaces [81]. The CPs has both conductive and semiconducting properties, making them an important class of materials for a wide range of applications. Conducting Oligomers of pyrrole and thiophene connected by ester bonds have been reported for the creation of temporary scaffolds for cell attachment, biodegradable scaffolds [82] and proliferation for tissue engineering.



Fig. 5 Artificial muscle

6.2 ELECTRONIC APPLICATIONS

Since the discovery of conduction in conjugated polymers, a great interest has been paid to these materials and has been extensively explored as alternative to metals or inorganic semiconductors in fabrication of optoelectronic, microelectronic and microelectrochemical devices [83-85]. Polypyrrole (PPy), one of the most studied conducting polymers, have potential uses in sensors (Fig 6) [86], and corrosion protection [87]. Polymer composites of electrically conducting particles have great importance for a diverse of applications in science or engineering. Owing to their unique electric and dielectric properties and mechanical and chemical stability, they can be worked as smart materials in the field construction of various components of electronic appliances [88]. A wide range of their applications offers protection against radiation, e.g. microwave absorbers [89,90] for electromagnetic interference shielding of various devices [52]. Composites of conventional polymer matrix of anisotropic particles such as metal and some non metals [91 92] or carbon fibres [93, 94] have been reported in the last decades. Conducting polymers, as polypyrrole (PPy) or polyaniline (PANI) have been emerging as a new class of materials in the last decades. PNCs have numerous applications (Fig. 7) in wind mills, solar cells, attery manufacturing, electronic circuit boards, transistor, micro chips, etc. ,Nanocomposites comprising of spatially confined liquid crystals are of great important because of the prospects of their application in photonic crystals, optoelectronic devices, depolarizers, information storage, scattering displays and recording devices such as compact disk, universal serial bus storage, and windows with adjustable transparency [95].

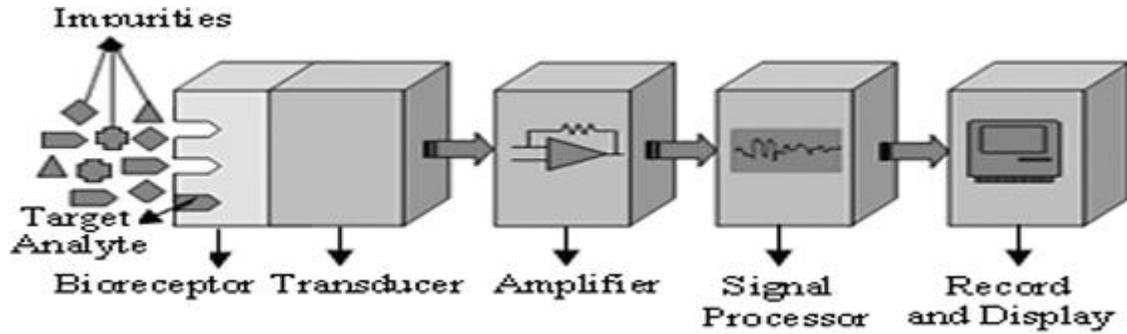


Fig. 6 Biosensors

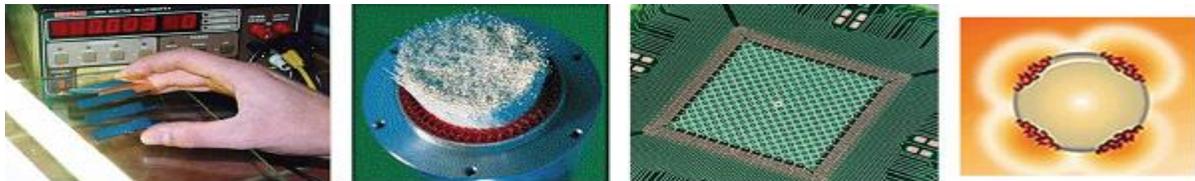


Fig. 7 Commercial applications: photovoltaic solar cell, hollow fibers for gas separation, e-beam lithography, and chemical and biological sensors.

7 CAUSES OF CONDUCTIVITY

7.1 CONJUGATED STRUCTURES POLYMERS (PLASTICS)

Conducting polymers are polymer materials have conjugation in their structure with metallic and semiconductor characteristics, a combination of properties not exhibited by any other known material. A key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double. Since the electrons in a conjugated system are only loosely bound, electron flow may be possible. Every bond contains localized “sigma” electrons which form a strong covalent chemical bond and also contains a less strongly delocalized “pi” bond which is weaker than “sigma”. The “pi” electrons are delocalized over the whole system and shared by many atoms. This means that the delocalized electrons may move around the whole system. However, conjugation is not enough to make the polymer material to be conductive. That is why, the polymer material needs to be doped for electron flow to occur. Doping can be done either the addition of electrons (reduction reaction) or the removal of electrons (oxidation reaction) from the polymer. By doping of iodine, an oxidation can be done (removal of electrons). The iodine attracts an electron from the polymer matrix from one of the bonds. Once doping has been completed, the electrons in the -bonds are able to “jump” around the polymer chain and move along the molecule, electric conduction occurs. For better conductivity the molecules must be well ordered and closely packed to limit the distance “jumped” by the electrons. The conduction of conducting polymers can be increased by change of chemical compositions of the polymer backbone, by the nature of the dopant, by the degree of doping, and by blending with other polymers [96].

7.2 FACTORS AFFECTING CONDUCTIVITY

Various factors that affect the conduction in conducting polymers include: Conjugation length: Presence of conjugation is one of the structural features common to all the conducting polymers. It has been observed that it is the conjugation length of the polymer chain, and not its chain length that is important for its high electrical conduction in polymer material. The conjugation length of a polymer chain is the average distance between two defects that interrupt the conjugation experimentally; it has been observed that conductivity decreases sharply with decreasing conjugation length. Temperature: Conductivity of polymers generally decreases with decrease of temperature. This temperature dependence of conductivity varies according to two factors: Doping level: The conductivity of conjugated polymers is found to increase with increase in the doping level of the polymers. The doping level of the polymer is examined by the dopant concentration expressed in mol %. Frequency Dependence: The electrical conductivity of conducting polymers can be decomposed into a d.c. part and an a.c. contribution. The d.c. contribution is frequency independent because in this case, current path involves several long distance hops resulting in low d.c. conductivity. The a.c. contribution, on the other hand, increases linearly with frequency because electric field reverses sign while electron is waiting to hop.

8. SYNTHESIS OF CONDUCTING POLYMERS

Conductive polymers with high conductivity and stability can be synthesized either by chemical oxidation in the presence of a strong oxidant, for example FeCl_3 , or by electrochemical oxidation in the presence of a supporting salt which strongly affects the conduction in the polymer.

8.1 CHEMICAL SYNTHESIS

Polypyrrole (PPy) and its derivatives can be obtained by simple chemical or electrochemical methods [97-103]. In Chemical polymerization process there is no need of special instruments because it is simple and fast process. However, the chemical polymerization process have certain limitations because limited conducting polymers can be obtained since only a limited number of counter ions can be incorporated in polymer matrix. The chemical polymerization of pyrrole appears to be a general and useful tool for the preparation of conductive composites [104, 105] and dispersed particles in aqueous media [106, 107]. During chemical polymerization of pyrrole, electroneutrality of the polymer matrix can be maintained by incorporation of anions from the reaction solution. The counter ions in this proces are usually the anion of the chemical oxidant or reduced product of oxidant. For example, when FeCl_3 or Cl_2 are used as oxidants, Cl^- ion is incorporated as counter ion or when I_2 is used as oxidant, I^{3-} ions are incorporated into the polymer matrix.

8.2 ELECTROCHEMICAL SYNTHESIS

The electrochemical preparation of conducting polymer dates back to early attempts of Dall'olio and coworkers [108], who obtained "pyrroleblack" as it was called at that time, on electrochemical oxidation of pyrrole in aqueous sulphuric acid as a powdery, insoluble precipitate on a platinum metal electrode. Electrochemical polymerization of conducting polymers is a simple and novel method. The beauty of this method is that polymerization in suitable electrolytic medium gives directly the directly doped polymer as a flexible free standing film. In this method, films of conducting polymer are produced

on the metal electrode surface by oxidative coupling. In this respect this method is somewhat identical to the electrochemical deposition of metal. The first electrochemical synthesis of polyemeraldine salt was studied by Letheby [109] in the year 1862. In the year 1962 Mohilner et al [110] reported the mechanistic aspects of aniline oxidation. Major interest in the electrochemistry of polyaniline was created only after the discovery that aromatic amine, pyrrole, thiophene, furan, indole and benzene can be polymerized anodically to conducting film. Electrochemically prepared polyaniline is the preferred method to obtain a clean and better ordered polymer thin film.

8.3 SYNTHESIS BY RADIATION DOPING

The initiation of polymerization reaction and its mechanism can be explained by Ionizing radiation method. The radiation initiated polymerization have Some advantages over the conventional methods such as (i) polymerization at low temperature or in solid state, (ii) absence of foreign matter, like initiator, catalyst, etc., (iii) the initiating radicals can be produced uniformly by irradiation and (iv) rate of the initiation step can easily be controlled by varying dose rate,. Polyaniline (PANI) is an important conducting polymer, with numerous applications. PANI was synthesized by radiation polymerization [111]. Its characterization can be done by optical absorption, TEM and light scattering techniques. The conductivity of conducting polymers have been further increased by irradiation with x-rays [111, 112], gamma radiation [113].

8.4 CONDUCTING COPOLYMERS

It has been observed that the structural properties of polymer play a major role in the conductivity of polymers, whilst the effects of molecular weight and crystallinity are less pronounced [114]. The structural properties of a conducting polymer such as chain can be controlled in different ways: (1) variation in the protonation, (2) by the change in constitutional units in the PANI, (3) by the change in co-monomers in copolymerization of CPs. Recently, a great efforts has been given to prepare aniline-based copolymers. A possible reason is probably attributed to great difficulty to obtain new conducting polymers with high stability and electric properties better than PANI and PPy. The copolymerization process of aniline and other monomers have a possibility to synthesize a new PANI type of copolymer that not only retains the good properties of PANI itself but also possesses new properties of other ingredients. However, Fusalba et al. [115] expalined that the main motive to prepare copolymer composites lies in the possibility that these materials overcome the limitation of the rareness of new conjugated p-bond-containing monomers. It is assumed that copolymerization of a repeating units of polymer will lead to an increase in the number of conductive polymers that can be made from the same set of monomers [116]. The Preparation method and morphological evolution, optical and structural properties of poly (aniline-co-pyrrole) have been reported [117].

9. ELECTROMAGNETIC INTERFERENCE SHIELDING

The blocking of electromagnetic radiation so that the radiation essentially cannot pass through the blocking medium (or shield) are referred as electromagnetic interference shielding. The interference of computers and other electronic devices are caused by radiofrequency radiation (such as that emitted by a cellular phone), there is a growing need for developing materials for such radiation shielding. The main mechanisms of shielding are reflection and absorption. Electrical conductors such as metals and non

metals such as carbons are shielded by reflection of the radiation while magnetic materials are shielded by mechanism of absorption of the radiation. In order to choose materials used for shielding must have electrical conductivity rather than their magnetic behavior.

Polymer composites of electrically conducting particles become significant for numerous applications in science or technology. They are being used as smart materials in the construction of various components of electronic appliances due to their unique electric ,dielectric properties, mechanical and chemical stability [118], they can be used as a wide range of their applications offers protection against radiation, e.g. microwave absorbers [119-121], electromagnetic interference shielding devices [122, 52]. In this respect, composites of conventional polymer matrix of anisotropic particles such as metal [123, 124] or carbon fibres [125, 126], conducting polymers, as polypyrrole (PPy) or polyaniline (PANI) have been reported in the last decades because of their high electrical conduction and ease of preparation meyhod [127, 128]. Polymer composites have potential applications such as microwave absorbers [129], the electromagnetic interference shielding properties where shielding by reflection prevails over absorption by the composite[130].In nanocomposites of propylene– ethylidene-norbornene rubber/polyaniline/organoclay the absorptions peak frequency can be easily manipulated by changing the thickness of the microwaves absorber[131]. Polymer composites materials of short carbon fibres coated with polyaniline significantly influenced the shielding properties of conducting polymer layer [132]. Polymeric materials offer a wide range of radiation effects. The irreversible effects have been observed as account of formation of new chemical bonds after irradiation. In general, these irreversible effects have been observed as changes in appearance, chemical and physical states, mechanical, electrical, and thermal properties. However, not all polymeric properties are changed to the same degree by radiation. The radiation stability of a polymer materials depend upon the structural properties of the material because the excitation by radiation is not coupled to the entire chemical structure, but is often observed at a specific part of polymer. On the addition of energy-absorbing aromatic rings or conjugation to the chemical structure, the radiation stability significantly increases of some polymers by aiding in the redistribution of the excitation energy throughout the polymeric material. In contrast, polymeric materials have aliphatic structures (e.g., ethers and alcohols) exhibit the least resistance to radiation. On irradiation of polymers generally undergo two types of reactions: chain scission and cross linking. Chain scission or fracture of polymer molecules lowers the molecular weight and increases solubility. The cross-linking process results in formation of new chemical bonds between two adjacent polymer molecules and increases the molecular weight of the polymer until the material is eventually bound into an insoluble three-dimensional network. Both the reactions significantly modify the physical properties of a polymer. However, the change in properties is not at the same extent for all polymers.

9.1 MECHANISM OF ELECTROMAGNETIC SHIELDING

When electro-magnetic rays are passed through an object or medium then these rays are getting interacted with molecules of the object or medium. The interaction of radiation with polymeric materials can be categorized in different steps. There is attenuation of radiation due absorption, reflection and successive internal reflections as the rays in forms of wave impinge the surface of the object, it forces charges in the object to oscillate at the same frequency of the incident wave. This forced oscillating charge observed as an antenna and thus reflection. The signal loss had been observed on account of the partial signal reradiation in the direction of the incident wave. The observed field pattern is scattered with a signal charge oscillating antenna. On forcing the charge, it vibrates in the medium and energy loss is

observed in the form of heat. This mode of signal loss in the form of heat is known as attenuation due to absorption. Thus, electromagnetic interference shielding can be explained on the basis of the above mentioned two major electro-magnetic mechanisms such as reflection from a conducting surface, and absorption in a conductive volume. The metallic surfaces exhibit both types of loss on account striking electro-magnetic wave. Some of the part of the wave is reflected, while the rest is transmitted and attenuated as it passes through the media. The effectiveness of the shield is determined by the combined effect of these losses (reflection and absorption) as shown in figure 8. The difference in the impedance of the electromagnetic wave in the free space and in the barrier results in reflection from an electromagnetic shield. This phenomenon depends upon of the material's conductivity, magnetic permeability, and frequency and it is independent on the barrier thickness. On Absorption mechanisms, electromagnetic energy is transformed into thermal energy by electromagnetic shielding materials. The electromagnetic absorbers attenuate undesirable electromagnetic radiations and thus dismiss electromagnetic radiation. The coupling of radio waves, electromagnetic fields and electrostatic fields can be reduced by EM shielding, while static or low-frequency magnetic fields such as conductive enclosure used to block electrostatic fields is known as a Faraday cage. The following factors are responsible for the amount of the reduction. i) The nature of material, ii) The thickness of material, iii) The shielded volume of material, iv) The size and, shape as well frequency of the fields of interest, v) the Apertures Orientation in a shield to an incident electromagnetic radiation

9.2. ELECTROMAGNETIC SHIELDING EFFICIENCY

The efficiency (EM SE) value of electromagnetic interference shielding is expressed in dB and defined as the ratio of the incident to transmitted power of the electromagnetic radiation.

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

The incident power (incident electric field) and the transmitted power (transmitted electric field), are represented by P1 (E1) and P2 (E2) respectively. In order to calculate the absorbance (Ab) by using the following equation with the help of the Measuring of the reflectance (Re) and the transmittance (Tr) of the material.

$$A_b = 1 - T_r - R_e$$

Where, Re and Tr represent the square of the ratio of reflected (Er) and transmitted (Et) electric fields to the incident electric field (Ei), respectively, as following.

$$R_e = \left| \frac{E_r}{E_i} \right|^2 = |S_{11} \text{ (or } S_{22})|^2$$

$$T_r = \left| \frac{E_t}{E_i} \right|^2 = |S_{21} \text{ (or } S_{12})|^2$$

These S factors can be obtained by instruments to evaluate absorbance.

9.3 EXPERIMENTAL SHIELDING EFFECTIVENESS

Experimentally, by the help of instruments named network analyzer shielding is measured. The amplitude of signals can be measured by scalar network analyzer (SNA) while magnitude as well as phases of various signals can be measured by vector network analyzer (VNA). Consequently, SNA can not measure complex signals (e.g. complex permittivity or permeability). Therefore, despite of some limitations of VNA such as its higher cost, still it is the most widely used instrument. The incident and transmitted waves in a two port, VNA can be mathematically represented by complex scattering parameters (or S-parameters) i.e. S11 (or S22) and S12 (or S21) respectively which in-turn can be conveniently correlated with reflectance (R) and transmittance (T) i.e. $T = |E_T/E_I|^2 = |S_{12}|^2 = |S_{21}|^2$, $R = |E_R/E_I|^2 = |S_{11}|^2 = |S_{22}|^2$, giving absorbance (A) as: $A = (1-R-T)$. When SEA is greater than 10 dB, SEM becomes negligible (~ -1.0 dB) and can be neglected [133] so that SET can be expressed as: $SET = SER + SEA$. In addition, the intensity of the EM wave inside the shield after primary reflection is based on quantity $(1-R)$, which can be subsequently used for normalization of absorbance (A) to yield effective absorbance $\{ A_{eff} = [(1-R-T)/(1-R)] \}$ so that experimental reflection and absorption losses can be expressed as [133 -135]. _ Therefore, from the knowledge of reflected and transmitted signals i.e. R and T, VNA can easily compute reflection and absorption loss components of total shielding.

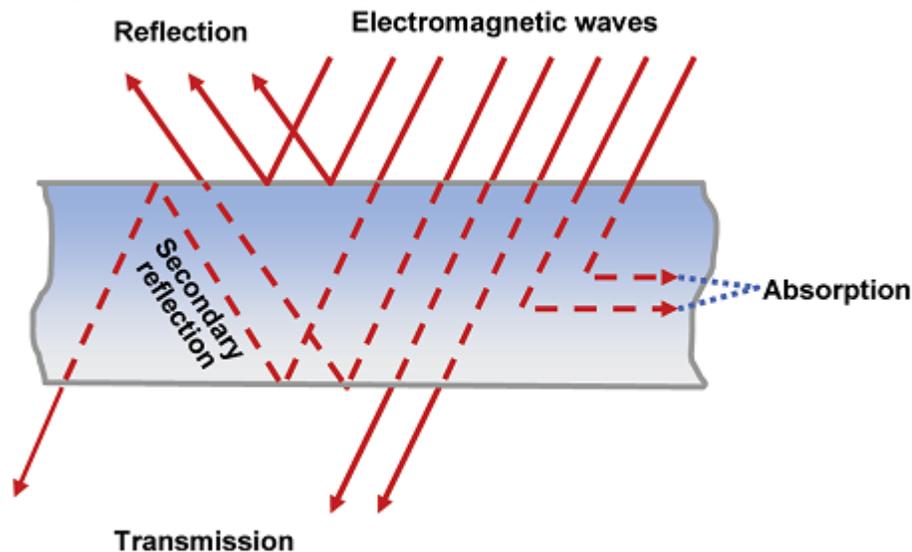


Fig. 8 Schematic representation of shielding phenomena

9.3 ELECTRICAL PROPERTIES OF ICP BASED NANOCOMPOSITES

As already mentioned and shown in Fig. 8, the primary shielding mechanism is reflection. The reflection depends free charge carriers (electrons/holes) of shielding material which can interact with incident EM field. On increasing the concentration of dopant, the concentration and mobility of proto-generated charge carriers increase and thus enhancement of conductivity. Furthermore, Enhancement in conductivity strongly depends on nature and concentration of dopant and in some case conductivity well

exceeds the required limit [133] to exhibit good radiation shielding effectiveness. The ICPs particles (guests) are added as conducting filler to polymer matrices (hosts) leads to formation of nanocomposites which have high value of electrical conductivity due to the formation of percolation networks [136]. It is reported, when ICPs are combined with other conducting fillers (e.g. Polyaniline with MWCNT, [133] significantly increase in shielding performance due to higher conductivity and reduction in percolation threshold, as compared to pristine (unfilled) ICPs. Polymers have conjugation can be used as matrix in place of insulating polymers. On incorporation of conducting fillers (e.g. carbon black, metal particles, graphite or CNTs) into undoped (poorly conducting) ICP matrices, the electrical conductivity increases and follows typical percolation behaviour.

Such improvement in electrical conductivity can be explained by the help of granular metal/inhomogeneous doping model [137] which considered that ICPs consists of highly conducting metallic islands dispersed within low conductivity amorphous matrix. The nature, concentration and aspect ratio of filler particles as well as type and morphology of host ICP matrix are the factors deciding the conductivity improvement.

Nevertheless, the establishment and enhancement of electrical conductivity are playing a significant role because it results in parallel enhancement of reflection and absorption loss component beam lithography, and chemical and biological sensors. Interestingly, absorption loss (SEA) increases by much larger magnitude (with conductivity) compared to corresponding reflection loss (SER) component. For a nonmagnetic material, this can be explained on the basis of logarithmic [i.e. $\log(s)$] and square root [i.e. $(s)^{1/2}$] conductivity dependence of SER and SEA respectively.

9.4 DIELECTRIC AND MAGNETIC PROPERTIES OF ICP BASED NANOCOMPOSITES

Absorption is a secondary mechanism of shielding, depends upon electric or magnetic dipoles. These dipoles can be interacted with transverse electric (E) and magnetic (H) vectors of the incident EM radiation to introduce losses into the system. It is observed that pure (without any filler) conjugated polymers exhibit poor magnetic and dielectric properties. However, Dielectric properties of polymeric material can be improved by controlled doping (e.g. dielectric constant/real permittivity, imaginary permittivity/dielectric losses), while magnetic properties (e.g. real and imaginary magnetic permeability) can not be improved. Doping of ICPs leads to formation of polarons/bipolarons that produces pronounced polarization/relaxation effects [138, 135, and 133]. Therefore, observed improvement in dielectric properties with doping level can be attributed formation and increase in concentration of above localized carriers. Interestingly, ICPs also have dielectric properties due to doping induced polarization filler and induced interfacial polarization. For example, ICPs matrices are impregnated with conducting fillers like metal particles, graphite or CNT.

Such a polarization, on account of electrical conductivity differences between ICP and metallic fillers result in charge localization at interfaces via Maxwell-Wagner-Sillars [139, 140] interfacial polarization phenomenon. Energy storage and losses are based upon the polarization and related relaxation phenomenon. Nevertheless, ICPs still have poor magnetic properties while dielectric properties are significantly improved. In principle, high conducting materials, must possess conductivity (s) and magnetic permeability (μ), and ratio (i.e. s/μ) determines the reflection loss (SER) while their product (i.e. $s \cdot \mu$) [133] the absorption loss (SEA). In contrast, Permittivity (ϵ), besides s and μ also plays a significant role in deciding absolute values of SER and SEA in moderately conducting materials (e.g. ICPs) [141]. As most are non magnetic nature ($\mu_r \approx \mu_i \approx 0$), observed attenuations are mainly governed by s and ϵ only.

Now, it is cleared that absorption loss along with parallel reduction of reflection loss can be improved by improving magnetic properties of ICPs. In addition, ICP composites of high dielectric constant materials like BaTiO₃, ZnO, TiO₂ etc. are expected to further improve the absorption of microwave radiations. These composites must have moderate polarization or/and magnetization along with good microwave conductivity so as to introduce absorbing properties into the material. They display dynamic dielectric and/or magnetic losses, upon impingement by incident electromagnetic waves. In order to EMI shielding of ICP based nanocomposites doping is applied which produces localized defects (polarons / bipolarons) that are responsible for polarization and electrical conductivity. On increasing dopant concentration, doping level are increased and lead to enhancement of polaronic concentration as well as related conductivity/permittivity, and thus leads to improvement of shielding effectiveness). Conducting polymer (PANI) blended with polyvinyl chloride (PVC) or Nylon were shown EMI shielding behavior with EMI SE value (~0.1-20 S/cm over a frequency range of 1 MHz to 3 GHz also observed theoretically under both near and far field regimes [142, 143]. The graphically presentation of results showed that both near and far field SE followed the DC electrical conductivity and exhibit rapid initial rise followed by slow increment at higher conductivity. Far field SE of -70 dB was obtained for the melt blend of polyaniline (again at higher loading level of 30 wt. %) with PVC which agreed well with the theoretical calculations as per expressions derived by authors. Polypyrrole have prepared with oxidant of FeCl₃ and its conducting adhesives have prepared by melt mixing of ethylene-co-vinyl acetate (EVA) copolymer and PPY. The Shielding properties of the adhesives have found to increase with the loading of PPY at both near and far field EMI at room temperature. Near field SE in excess of -80 dB was reported at 1MHz and above -30 dB at 300 MHz, though a decreasing with increasing of frequency. Far field SE values of -22, -27 and -30 dB were observed (in the 1 to 300 MHz frequency range) for PPY loadings of 15, 20 and 25% respectively. Also demonstrated that better SE value upto -50 dB can be realized by stacking several polymeric sheets of different thicknesses or by sandwiching a lossy dielectric between two sheets of the same thickness. It has been found that the high shielding effectiveness of polymeric materials can not only depend on the electrical conductivity but also other factors play role [141] and good attenuations can be also improved by moderate conductors with good dielectric properties. Furthermore, it is expected that the orientation of ICPs at micro level have played role to improve SE. The higher SE have reported by the PPY impregnated polyethylene membranes (-40 to -45 dB) than that of the impregnated polyurethane membranes (-20 to -25 dB), despite the much lowered thickness (1/5th) which was due to the more oriented PPY produced in polyethylene than that in polyurethane. Synergistic coupling of fillers can give unique combination of properties [135] like enhanced conductivity, better dielectric/magnetic traits and improved processability/thermal conductivity that can not be achieved by individual fillers. An effective solution to realize a lightweight, mechanically strong, processable and economically viable shielding material suitable for commercial and defence sectors, the very specific combination are needed like thin film/membrane technologies, porous structures, negative permittivity materials (or left handed materials), multilayered structures and hybrid fillers based on broad range of ICP filler. For many applications e.g. radar absorbers or stealth technology, the sample should reflect as low energy as possible. However, The Composites of conducting filler have significant reflection which is primary shielding mechanism along with absorption which is secondary EMI shielding mechanism. The shields with electric and/or magnetic dipoles which interact with the electromagnetic fields in the incident radiation have reduced reflection loss and significant absorption of the radiation. Now it is possible to introduce dielectric (BaTiO₃, TiO₂ etc.) or magnetic (γ -Fe₂O₃, Fe₃O₄, BaFe₁₂O₁₉ etc.) materials within various ICP matrices as filled inclusions [144 -149].

10. RECENT SURVEY ON CONDUCTING POLYMERS

Conducting polypyrrole was synthesized by chemical polymerization method and characterization of synthesized Polypyrrole was done by Fourier transform infrared spectrometer and its conductivity was measured by a resistometer. Then, the incorporation of PPy into high density polyethylene/montmorillonite nanocomposites was done by varying PPy concentration in the range of 5 to 20% by weight in nanocomposites using melt mixing followed by compression molding. The change in thermal and electrical properties of nanocomposites due to effect of PPy concentration was investigated. Now, it is proved by thermal gravimetric analysis and differential scanning calorimeter that the thermal stability can be improved by the incorporation of PPy in nanocomposite. The conductivity of nanocomposites can be increased by the raising the amount of PPy and it can be measured by two probe conductivity measurements method [133]. The electrosynthesis of PPy films on conductive tin oxide substrates were produced by potentiostatic deposition in various aqueous electrolyte solutions including naphthalenesulfate, p-toluenesulfonate, tetrafluoroborate, nitrate and perchlorate anions.

Its characterization such as electrical and structural studies were measured by using Van der Pauw method, atomic force microscopy, scanning electron microscopy and optical profilometry. The Factors which affect the structural characteristics and conductivities of so-prepared polypyrrole films were concentration of the pyrrole and the electrolyte as well as experimental parameters including applied electro deposition potential. The highest conductivity and the lowest conductivity were shown by p-toluenesulfonate doped polypyrrole film and perchlorate doped films respectively. On the contrary, the electrical conductivity can not be affected by the film thickness. The globular-shaped topographic structures with different sizes of globules and aggregates were reported for nearly all the polymer films. The roughness along with morphological characteristics was also proved to be very dependent from the electro polymerization parameters [134]. Polypyrrole and polyaniline based composites can be prepared by two-step electrochemical polymerization method and the morphological and structural features of the composites can be confirmed by techniques of fourier transform infrared spectroscopy, scanning electron microscope, and thermal gravimetric analysis. In order to investigate electrochemical properties of the composite, cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy can be implemented. It is observed that composites of polyaniline-polypyrrole conducting polymers have advanced electrochemical capacitive performance than polypyrrole and polyaniline. The composite electrode has specific capacitance 523 F/g at a current of 6 mA /cm² in 0.5 M H₂SO₄ electrolyte [135]. The electrical conductivity have also become important in the field of textile industries due to the numerous applications such as electromagnetic interference shielding, antistatic applications, electrostatic dissipating, gas sensors, biomechanical sensors and microwave reduction. Conductive polymers more specifically polypyrrole is one of the most promising conducting polymer because of its high electrically conductive and good chemical stable features, however it has some limitation such as poor processability. In order to get combined properties of polyurethane with polypyrrole [136], films and nanofibers of Polyurethane –Polypyrrole were produced successfully. The effect of polypyrrole content on thermal, mechanical, dielectric and morphological properties of prepared composites were performed by using Dynamic Mechanical Analyzer, Dielectric Spectrometer, UV – Vis spectrophotometer and the Scanning Electron Microscope.

The composites of multiwall carbon nanotubes with conducting polypyrrole have obtained by mixing both via an in situ chemical oxidative preparation method. The structural, morphological and

thermal properties of the prepared composites have been revealed by X-ray diffraction, field emission scanning electron microscope, Fourier transform infrared, and thermogravimetric analyses respectively [137]. An advanced approach to obtain ultrathin and thickness-tunable polypyrrole films onto multiwall carbon nanotubes has been investigated [138]. It is demonstrated for controlling the morphology and thickness of Polypyrrole film have been controlled and demonstrated by a facile procedure adding ethanol in the reaction system and the coating formation mechanism is proposed. By addition of ethanol and adjusting a mass ratio of pyrrole to MWCNTs, the coated Polypyrrole films can be easily tuned. Moreover, the electronic conductivity and capacitive behavior of the PPy/MWCNT composites significantly depends upon the thickness of PPy film. Composite electrodes of polypyrrole (PPy)/carbon nanotube (CNT) composite electrodes were fabricated on ceramic fabrics for electrochemical capacitor applications [139]. In order to grow CNTs on the ceramic fabrics, the chemical vapour deposition (CVD) method is applied and subsequently by chemical polymerization method PPy is coated on them. Now, composites have high energy storage capacity because of the large surface area and high conductivity of the CNTs on the porous ceramic fabrics. Due to PPy, composites not only have additional capacitance which make material active, but also have improved adhesion property between the CNTs and ceramic fabrics. In addition, PPy connect every individual CNT to increase the capacitance, and thus work as conducting binder. The confirmation of morphology of the PPy–CNTs on the ceramic fabrics is reported by SEM and TEM, and Cyclic voltammetry and galvanostatic charge–discharge tests confirms electrochemical characteristics.

In order to synthesis Mesoporous carbon/conducting polymer composites, adsorption of different monomers (aniline, pyrrole, thiophene and 3-methylthiophene) in the gas phase onto the carbon surface is applied, followed by oxidative chemical polymerization [140]. The materials were observed as electrode material for electrochemical capacitors. On examining, the porous structure of the composites by N₂ isotherm adsorption at low temperature, the decreasing of the BET surface area and the pore volume were observed. The pore size distribution was unaltered independently of the polymer nature and concentration decides Electrochemical performance of the composites was studied by cyclic voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectroscopy in 2.0 mol l⁻¹ H₂SO₄. All composite electrodes show a stable cycle life in the potential range of 0 to 1.0V, the specific capacitance of carbon/polypyrrole composite electrode (83.8 F·g⁻¹) being slightly higher than that obtained for the pristine mesoporous carbon electrode (77.9 F·g⁻¹). The remaining carbon/polymer composites show lower specific capacitance than carbon only, due to their higher internal resistance. The aim possible use of conductive polymer composites (CPC) as thermoelectrical material for energy harvesting from temperature gradient was examined [141]. Their ease of processing, low cost and environmental impact compared to typical thermoelectric semiconductor materials were found to have more advantages for large scale production. The results show that expanded graphite- carbon nanotubes (eGR-CNT) hybrid fillers are the most effective to enhance the CPC electrical conductivity up to $\sigma=4123 \text{ S.m}^{-1}$, but that eGR is more effective to improve both thermal conductivity ($\lambda_c=5.5 \text{ W.m}^{-1}.\text{K}^{-1}$) and SEEBECK coefficient ($S=17 \mu\text{V.K}^{-1}$), whereas finally CNT give the best compromise to reach the highest $ZT=7\times 10^{-5}$ at room temperature. This finding was attributed to the ability of CNT network to allow electron circulation by tunneling, when junctions are separated by an insulating polymer film (even of some nm thick), whereas photon scattering at nano interfaces will prevent their effective transmission through the CPC. Although the intrinsic individual physical properties obtained (σ, λ_c, S) with the different kinds of carbon filler were good, it was not possible to completely uncouple them to maximise ZT.

We believe that this value of ZT, too low for commercial application, can be enhanced by

increasing the confinement of conducting fillers with exclusion volumes and by decreasing the thermal conductivity of the matrix with voids. SnO₂-based composite coaxial nanocables with multi-walled carbon nanotube (MWCNT) and polypyrrole (PPy) have been successfully synthesized via a simple one-pot chemical route [142]. Such novel nanostructures can not only provide a high conductivity, but also effectively suppress mechanical stress and prevent aggregation of SnO₂ nanoparticles, leading to the improvement in the electrochemical utilization and cycling stability of SnO₂ during Li-storage reaction. As anode materials, the as-obtained coaxial nanocables show a reversible capacity as high as 600 mAh g⁻¹ and a coulombic efficiency close to 100%, which is potential for practical application in lithium-ion batteries. A fiber optic reflectance sensor (FORS) using Polypyrrole (PPy) conducting polymer to detect volatile organic compounds (VOCs) was demonstrated [143]. The conventional interfacial polymerization method is used to synthesize a sensitive polypyrrole membrane, which shows relatively low roughness and high reflectivity. In general the changes in electrical properties of conductive polymers are explored in sensing applications, however their optical properties have been less explored.

The optical properties of PPy and transfer on the end face of polymer optical fiber (POF) for the detection of VOCs. The change in the reflected optical signal from PPy upon interaction with the VOCs is systematically evaluated. The fabricated PPy FORS shows the excellent sensitivity to the VOCs under test with the detection limit up to 1 ppm. Carbon nanotube/polypyrrole/antibodies polymer films were synthesized successfully on microelectrodes by electrochemical deposition [144]. Electropolymerization was performed at optimal range between -0.8 and +0.8 V at a scan rate of 50 mV s⁻¹ in an electrochemical mini-cell containing monomer pyrroles, carbon nanotubes, and goat IgGs. The conducting polymer films were characterized by Fourier transform infrared spectrometry, Raman spectra, and Field emission scanning electron microscopy. And then, it was prepared for immunosensor application to determine anti-goat IgGs. The results show that a linear range between 0.05 and 0.7 µg ml⁻¹ for anti-goat IgGs detection was observed for immunosensor, a detection limit as low as 0.05 µg ml⁻¹ and a response time of 1 min. The effect parameters of electropolymerization process on immunosensor response are also studied. It was found that the immunosensor well active in 1.5 mg ml⁻¹ CNT concentration, 2.5 mM pyrrole, 10 µg ml⁻¹ goat IgGs. Tailoring polypyrrole (PPy), an electroactive polymer, with functional groups to which a variety of bioactive molecules can be tethered is highly attractive for building biological structures on conducting surfaces for a range of biomedical applications [145]. In this respect the authors, investigated the effects of three independent electrosynthesis parameters, namely the applied potential, the composition of the comonomer solution and the film thickness on the incorporation of carboxylic acid-functionalized pyrrole units (Py-COOH) into polypyrrole/Py-COOH copolymer films. FT-IR, XPS and fluorescence microscopy results show that a larger Py-COOH content is inserted in films electrosynthesized at low potential, that the surface functionality of the copolymer films increases with the molar percentage of Py-COOH in the comonomer solution, and that Py-COOH units are preferentially incorporated in the earlier stage of the electrosynthesis process. The method was further adapted for preparing functionalized PPy copolymer nanotubes with potential application in drug delivery.

Bootha and co-worker described uses of the conducting polymer polypyrrole as both a sensing element and transducer of sensing events – namely the hybridization of complementary target oligonucleotide to probe oligonucleotide [146]. Detection was performed using electrical impedance spectroscopy. Initially sensor development was performed, wherein demonstrated an improvement in stability and sensitivity as well as reduction in non-specific DNA binding for fabricated sensors, through

use of a specific dopant and post-growth treatment. Subsequently, it was shown that longer target DNA strands display increased response, as do sensors containing longer probe DNA strands. It was suggested that these results are a feature of the increase in negative charges associated with the longer DNA strands. The results of this comparative study were aimed to guide future design of analogous sensors. Conducting polymers with pendant functionality are advantageous in various bionic and organic bioelectronic applications, as they allow facile incorporation of bio-regulative cues to provide bio-mimicry and conducive environments for cell growth, differentiation and function. In this work [147], polypyrrole substrates doped with chondroitin sulfate (CS), an extracellular matrix molecule bearing carboxylic acid moieties, were electrochemically synthesized and conjugated with type I collagen. During the coupling process, the conjugated collagen formed a 3-dimensional fibrillar matrix in situ at the conducting polymer interface, as evidenced by atomic force microscopy (AFM) and fluorescence microscopy under aqueous physiological conditions.

Cyclic voltammetry (CV) and impedance measurement confirmed no significant reduction in the electroactivity of the fibrillar collagen-modified conducting polymer substrates. Rat pheochromocytoma (nerve) cells showed increased differentiation and neurite outgrowth on the fibrillar collagen, which was further enhanced through electrical stimulation of the underlying conducting polymer substrate. The study demonstrates that the direct coupling of ECM components such as collagen, followed by their further self-assembly into 3-dimensional matrices, has the potential to improve the neural-electrode interface of implant electrodes by encouraging nerve cell attachment and differentiation. The use of fibril materials as substrate for reinforcing polymers has wide industrial applications. Shivakumar et al. [148], discussed polyaniline and polypyrrole as conducting polymers to provide electronic conductivity in E-glass fabric reinforced conducting composite with varied degree of composition and conductivity using industrially important polymers polymethylmethacrylate and polyvinyl chloride as a host matrix. Aromatic sulphonic acids such as PXSA, OXSA, PSA, PDSA, RDSA, OCPSA and MCSA were used as a dopant. The influence of the aromatic ring substituents in these dopants over the conductivity and processibility due to various interactions has been studied. The study shows that due to bulk nature of conductivity, shielding effectiveness (SE) increases with increase in conductivity and thickness of a composite. The test samples were characterized by conductivity and electromagnetic interference shielding effectiveness (EMI SE). The electromagnetic shielding effectiveness was measured by co-axial transmission line method in the frequency range of 0.01–1000 MHz. These composites with both side shielded by polypyrrole offered a uniform shielding effectiveness of 69 dB.

Conducting polymers (CPs) have been widely applied for fabricating various electrochemical devices such as sensors, actuators, solar cells, etc. To extend the functions or improving the performances of the devices, CPs frequently have to be blended with other functional materials to form composites. Graphene, a oneatom layer of graphite with unique two-dimensional structure and excellent mechanical and electrical properties, has become an increasing star in material science. Chemically converted graphene (CCG) prepared by reducing graphene oxide has satisfied processing property and complementary properties with CPs. Therefore, CCG is an important functional component for preparing high-performance CP-based composites. In this critical review, we mainly summarize the recent advancements in our group on the synthesis of CP/CCG composites and their electrochemical applications including supercapacitors, solar cells and electroanalysis [149]. The synthesis of a series of praseodymium oxide/polypyrrole ($\text{Pr}_6\text{O}_{11}/\text{PPy}$) nanocomposites, and their application in the

electrochemical energy storage [150]. The Pr₆O₁₁/PPy nanocomposites were synthesized by the in situ surface-initiated polymerization technique based on the amine-functionalized Pr₆O₁₁ nanoparticles. The nanocomposites exhibit the well-defined core/shell structure observed by transmission electron microscopy (TEM) and scanning electron microscope (SEM). Thermo gravimetric analysis reveals a significantly enhanced thermal stability with the addition of the amine-functionalized Pr₆O₁₁ nanoparticles. Furthermore, they possess weak temperature dependence of the conductivity and the highest specific capacitance of 400 F g⁻¹ at the charge–discharge current density of 10 mA cm⁻² in 1.0 M NaNO₃. Electrical conductivity and dielectric properties have been studied for two types of polypropylene composites containing conducting phase. One type comprised of conducting polymer–polypyrrole while the second employed montmorillonite particles coated with conducting polymer–polypyrrole.

Composites' shielding properties were estimated based on their previously determined electromagnetic characteristics. Unlike a basic binary polypropylene/polypyrrole composite, the ternary sample with multi component montmorillonite particles exhibited higher dielectric losses and consequently a significant rise in shielding efficiency in the radio-frequency range of 0.1–1.5 GHz. This stems from the presence of highly polarizable multicomponent montmorillonite anisotropic lamellar particles with polypyrrole conducting layer, which considerably increases the complex permittivity of the composite [151]. The use of different polymers as both reducing agent and stabilizers has gained wide attention for its simplicity and impressive efficiency when being applied to synthesis noble metal nanoparticles. An-Qi Zhang et al. [152] reports published recently on specific polymers used to reduce metal precursors and protect metal nanoparticles. The control of the size and morphology of nanoparticles tuned by changing the polymer structure and experiment conditions has been concluded and the possible redox mechanisms of different polymer-metal systems have been illustrated.

Electromagnetic interference is a cause of concern when emitted electromagnetic fields interfere with operation of other electronic equipments. Given rapid development in commercial, military, scientific electronic devices and communication instruments operating in microwave frequency range (GHz), there has been an increased interest in development of such materials that could shield against electromagnetic radiation to protect interference. Conducting polymers can be used as microwave absorbing materials with or without fillers. Vaishali Bhavsar et al. [15] report the complex permittivity measurements of pure PVC and PVC doped with varying concentrations of PPy films at microwave frequency of 9.37 GHz (X-band) using microwave bench at room temperature. Further the microwave absorption properties of these films of various thicknesses have been investigated. The maximum absorption coefficient of 118 m⁻¹ was obtained for film of average thickness 850 μm and with 16% concentration of PPy in PVC films. A facile and original method of deposition of polyaniline (PANI) and polypyrrole (PPy) by reactive ink-jet printing on different textile fabrics is proposed. Polyaniline- and polypyrrole-coated conducting fabrics were obtained by chemical oxidation of aniline hydrochloride or pyrrole by ammonium peroxydisulfate on polyacrylonitrile (PAN), cotton, poly(ethylene terephthalate) (PET), cotton/PET, wool, and cotton/wool fabrics. The conducting fabrics were characterized chemically by means of Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and energy-dispersive spectroscopy (EDS). The morphology of the coatings was observed by optical microscopy and scanning electron microscopy (SEM).

The conducting properties (surface resistance) of the fabrics were measured by means of the four-probe method. The optimal conditions of the PANI and PPy deposition on textiles by reactive ink-jet

printing were established. The obtained results prove that the proposed method is very simple, practically could be carried out on the basis of water-containing inks, giving a very good adhesion of the in-situ formed conductive polymer to the substrate and ensuring a very low surface resistance. The variation of the surface resistance vs. concentration of aniline hydrochloride or pyrrole for different textile fabrics was obtained. The mechanism of the PANI and PPy deposition and adhesion on textiles based on the electrokinetic phenomena is proposed and proved by the changes in relative resistance of PANI/PAN and PPy/PAN composites during the multi-cyclic flexing, washing and dry-cleaning processes, and re-doping with HCl. An application of PANI and PPy conductive textiles in electromagnetic interference (EMI) shielding is proposed [121]. The results showed that PANI/PAN and PPy/PAN composites achieved very good and moderate EMI shielding effectiveness, respectively.

The protection against electromagnetic radiation (EMR) emitted by operating electrical and electronic devices, the shielding materials based on woven fabrics coated with the highly conductive layers were designed and investigated [153]. The electrostatic charge dissipation properties and EMR shielding properties within certain frequency bands were investigated and compared with such properties of textile fabrics with incorporated conductive metal fibres. Also the influence of washing on electrical properties of developed fabrics was examined. This study presents technological guidelines for designing coated textile fabrics, which are able to safeguard high electrostatic charge dissipation properties and to provide effective protection against EMR, using two types of electrically conductive coatings. The results of EMR shielding measurements, especially within the range of 2 GHz to 20 GHz, showed that fabrics with conductive coatings exhibit certain advantages over fabrics with incorporated metalized yarns. Whereas shielding properties at the low frequency range of 20 kHz to 50 kHz for all investigated conductive fabrics are similar despite the type of conductive additive.

Methods for measurement of electrostatic properties, reflection and transmission as well as the assessment of EMR shielding effectiveness (SE) are also presented. Highly adherent and homogeneous polypyrrole thin films were deposited on copper from sodiumoxalate solution for different molar concentration. The electromagnetic reflection, absorption, permittivity and conductivity studied in the frequency range 8- 12 GHz is reported. Polypyrrole increases the reflection of copper but decreases the microwave absorption [154]. The absorption is highly dopant concentration dependent. As dopant concentration increases the permittivity and microwave conductivity increases. The development of flexible polymer monofilament fiber strain sensors has many applications in both wearable computing (clothing, gloves, etc.) and robotics design (large deformation control). For example, a high-stretch monofilament sensor could be integrated into robotic arm design, easily stretching over joints or along curved surfaces. As a monofilament, the sensor can be woven into or integrated with textiles for position or physiological monitoring, computer interface control, etc.

Commercially available conductive polymer monofilament sensors were tested alongside monofilaments produced from carbon black (CB) mixed with a thermo-plastic elastomer (TPE) and extruded in different diameters. It was found that signal strength, drift, and precision characteristics were better with a 0.3 mm diameter CB/TPE monofilament than thick (~2 mm diameter) based on the same material or commercial monofilaments based on natural rubber or silicone elastomer (SE) matrices [155]. Amarjeet et al. [156] prepared Polypyrrole (Ppy) nanoparticles by surfactant directed chemical oxidation method. The synthesis of Ppy nanoparticles were confirmed by Fourier transform infrared spectroscopy

and transmission electron microscopy. The prepared samples were tested for electromagnetic interference (EMI) shielding. It has been observed that the particle size of the PPy nanoparticles decreases (53, 42, 28 nm) while the dc conductivity (3, 7, 22 S/cm) and total shielding effectiveness (23, 46, 49 dB) increases with surfactant concentration for the PPy samples (P1, P2, and P3).

Morphology and microwave absorbing properties of polypyrrole nanoparticles have been studied by Shamuddin et al. [157]. Hakansson et al. [158] studied electromagnetic interference shielding and radiation absorption in thin polypyrrole films. The author doped PPy with anthraquinone-2-sulfonic and applied on textile fibers irradiated the materials in the frequency range 1-18 GHz. Liu and coworker [159] designed carbon nanotube – polyurethane composite evaluated EMI shielding of the prepared materials. They observed that the prepared composite exhibited a reflection dominant mechanism. It was also observed that on increasing the amount of single walled carbon nanotube the mechanism changed into mode. The role of carbon based materials in EMI shielding was reviewed by Chung [160], considering composite materials based on colloidal graphite and flexible graphite. Highly adherent and homogenous polypyrrole thin films were deposited on copper substrate by Jamadade et al. [161] from sodium oxalate solution of different molar concentration. The EM reflection, absorption, permittivity and conductivity was studied in the frequency range 8-12 GHz. The authors noticed that PPy increases the reflection of copper but decreases the microwave absorption. The absorption was found to be highly dependent on dopant concentration.

Roy et al. [162] prepared novel electrically conducting nanocomposite materials comprising of poly (pyrrole) (PPy) nanoparticles dispersed homogeneously in a poly (vinyl alcohol)-g-poly (2-acrylamido-2-methyl-1-propanesulphonic acid-co-acrylonitrile) matrix by in situ polymerization of pyrrole. Radiation shielding potential of so designed polypyrrole based nanocomposites was studied by exposure of polymer materials to gamma radiation under varying experimental conditions and structural and morphological changes in irradiated materials were examined by FTIR) and SEM techniques.

11. CONCLUSIONS

To realize the advantages of conducting polymers having a rare combination of electrical, electrochemical and physical properties, it is very essential to increase their processability, environmental and thermal stabilities. From the recent studies on the polypyrrole, it has been demonstrated that these polymers could be highly promising for many technological uses because of their chemical versatility, stability, processability and low cost. Another versatile area from the technological point of view is the studies on composites containing conductive polymers and an inert polymer matrix. Moreover, there is very great potential to use conductive polymers in virtually unexplored biochemical, electronics, electrical and Electromagnetic interference (EMI) shielding applications.

REFERENCES

- [1] MacDiarmid, A.G., *Angew. Chem. Int. Ed.*, 40, 2581–2590 (2001).
- [2] Heeger, A.J., *Synth. Met.* 125, 23–42 (2001).
- [3] Heeger, A.J., *Chem. Soc. Rev.* 39, 2354 (2010).
- [4] Blodgett, M.P., Ukpabi, C.V., Nagy, P.B., *Mater. Eval.* 61, 765 (2003).

- [5] Naarmann, H., *Polymers to the Year 2000 and beyond*, John Wiley & Sons Chapter 4, (1993).
- [6] Wallace, G.G. and Spinks, G. M., *Intelligent Material Systems*, 2nd Edn., CRC Press, 1.
- [7] Kharat, H.J., Kakde, K.P., Savale, P.A., Datta, K., Ghosh, P., Shirsat, M.D., *Polym. Adv. Technol.* 18, 397 (2007).
- [8] Lee, Y.S., Joo, B.S., Choi, N.J., Lim, J.O., Huh, J.S., Lee, D.D. *Sens. Actuat. B*, 93, 148 (2003).
- [9] Shirale, D.J., Gade, V.K., Gaikwad, P.D., Kharat, H.J., Kakde, K.P. Savale, P.A., Hussaini,S.S., Dhumane,N.R., Shirsat, M.D., *Mater. Lett.* 60, 1407 (2006).
- [10] Murugendrappa, M.V., Khasim,S., Prasad, M.V.N.A., *Mater. Sci.* 28, 565 (2005).
- [11] Omastova, M., Trchova, M., Pionteck, H., Prokes,J., Stejskal, J., *Synth. Met.* 143, 153 (2004).
- [12] Zhang, S., Lv, G., Wang, G., Zhu, K., Yu, D., Shao, J., Wang, Y., Liu, Y., *J Photoch. Photobio. A*, 309, 30 (2015)
- [13] Richard, B., Nigel, J. C., Sarah, H. C., *Acta Biomater.* 10, 2341 (2014).
- [14] Gangopadhyay, R. and De, A., *Chem. Mater.* 12, 608 (2000).
- [15] **Bhavsar, V. and Tripathi D.**, *Adv. Electron. Electr. Eng.* 4, 417(2014).
- [16] Almeida, A.K.A., Dias, J. M.M., Silva, A.J.C., Santos, D.P., Navarro, M., Tonholo, J., Goulart, M.O.F., Ribeiro, A.S., *Electrochim. Acta* 122, 50 (2014).
- [17] Liu, Y., Chu, Y., Yang, L., *Mater. Chem. Phys.* 98, 304 (2006).
- [18] Kang, T.S., Lee, S.W., Joo, J., *Synth. Met.* 153, 61 (2005).
- [19] Liu, L., Zhao, C.J., Zhao, Y.M., *Eur. Polym. J.* 41, 2117(2005).
- [20] Mabrook, M.F., Pearson, C., Petty, M.C., *Sens. Actuat. B* 115, 547 (2006).
- [21] Mario, C.,Clara, M.G. and Andrés C., *Mater.* 7, 6701(2014).
- [22] Liu, Y.C., Lee, H.T., Yang, S.J. *Electrochim. Acta*, 51, 3441 (2006).
- [23] Pfaendner, R., *Polym. Degrad. Stab.* 95(3), 369 (2010).
- [24] Wanga, N., Lia, G., Yua, Z., Zhanga, X., Qib, X., *Carbohydr. Polym.* 127, 332 (2015).
- [25] Francesco, B., Gianluca, M., Farinola and Francesco, N., *J. Mater. Chem.* 14, 11(2004).
- [26] Sturge, K.C., Hunter, A. D. McDonald, R., Santarsiero, B.D., *Organomet.* 11, 3056 (1992).
- [27] Li, X., Gui, J., Yang, H., Wud, W., Li, F., Tian, H., Huang, C., *Inorg. Chim. Acta.* 361, 2835 (2008).
- [28] Song, H.K., Park, Y.H., Han, C.H., Jee, J.G., *J. Ind. Eng. Chem.* 15, 62 (2009).
- [29] Ulanski, J., *Synth. Met.* 39, 13 (1990).
- [30] Gupta, R.K., Singh, R.A., *Mater. Chem. Phys.* 86, 279 (2004).
- [31] Margolis, J.M., *Conducting Polymers and Plastics*, Chapman and Hall, New York. (1989).
- [32] Skotheim, T.A., *Handbook of Conducting Polymers*, Marcel Dekker, New York (1986).
- [33] Ashwell, G.J., *Molecular Electronics*, John Willey & Sons Inc., New York (1992).
- [34] Shirakawa, H., Louis, E.J., Gau, S.C., MacDiarmid, A.G., Chiang, C.K., Fincher, C.R., Jr., Park, Y.K., Heeger, A.J., *Phys. Rev. Lett.* 39, 17 (1997).
- [35] Schulz, B., Orgzall, I., Díez, I., Dietzel, B., Tauer, K., *Sci. Direct. J. Physicochem.*, 354(1-3), 368 (2010).
- [36] Shanshaz, M., Seidi, S., Ghorbani, Y., Shoja, S.M.R., Rouhani,S., *Spectrochim. Acta A*, 149, 481 (2015).
- [37] Hatchett, D.W., Josowicz, M., *Am. J. Chem. Soc.* 108, 746 (2008).
- [38] Pina, C.D., Falletta, E., Rossi, M., *Gold Bull.* 42, 1 (2009).
- [39] Elyashevich, G.K., Rosova, E.Y., Sidorovich, A.V., Kuryndin, I.S., Trchov, M., *Eur. J. Polym.* 39: 647 (2003).
- [40] Oguro, K., Kawami, Y., Takenaka, H., *J. Micromachine Soc.* 5, 27 (1992).
- [41] Sadeghipour, K., Salomon, R. Neogi, S., *Smart Mater. Struct.* 1, 172 (1992).
- [42] Akle, B., Bennett, M., Leo, D., *Sens. Actuat. A* 126, 173 (2006).

- [43] Bar-Cohen, Y., Leary, S., Yavrouian, A., Oguro, K. Tadokoro, S., Harrison, J., Smith, J., Su, J., Proc. SPIE 3987, 140 (2000).
- [44] Bar-Cohen, Y., Xue, T., Joffe, B., Lih, S., Shahinpoor, M., Simpson, J., Smith, J., Willis, P., Proc. SPIE 3041, 697 (1997).
- [45] Shahinpoor, M., Bar-Cohen, Y., Simpson, J., Smith, J., Smart Mater. Struct. 7, R15 (1998).
- [46] Guo, H., Chen, J., Xu, Y., Synth. Met. 205, 169 (2015).
- [47] Su1, Z., Pan, D., Han, H., Lin, M., X., Hu, M., Wu, X., Int. J. Electrochem. Sci. 10, 2413 (2015).
- [48] Huang, K., Zhang, Y., Han, D., Nanotechnol. 17 (1), 283 (2006).
- [49] Lopatin, A.V., Kazantseva, N.E., Kazantsev, Y.N., D'Yakonova, O.A., Vilcakova, J., Saha, P. J., Commun. Technol. Electron.53, 487 (2008).
- [50] Abbas, S.M., Chandra, M., Verma, A., Chatterjee, R., Goel, T.C., Appl. Sci. Manuf. 37, 2148 (2006).
- [51] Saib, A., Bednarz, L., Daussin, R., Bailly, C., Lou, X., Thomassin, J.M., IEEE Trans Microw. Theory Tech. 54, 2745 (2006).
- [52] Kaiser, K.L., 1st Ed. New York: Taylor & Francis Group chap.2 (2006).
- [53] Ahmad, M.S., Abdelazeez, M.K., Zihlif, A.M., J. Mater. Sci. 25, 5019 (1990).
- [54] Madani, M., Aly, R.A., Mater. Des. 31, 1444 (2010).
- [55] Huang, C.Y., Mo, W.W., Surf. Coat. Technol. 154, 55 (2002).
- [56] Vilcakova, J., Saha, P., Quadrat, O., Eur. Polym. J. 38, 2343 (2002).
- [57] Stejskal, J., Gilbert, R.G., Pure. Appl. Chem. 74, 857 (2002).
- [58] Omastova, M., Trchova, M., Kovarova, J., Stejskal, J., Synth. Metal. 138,447 (2003).
- [59] Abdullah, Z., Othman, A.L. Alam, M.M., Naushad, M., Bushra, R., Int. J. Electrochem. Sci. 10, 2663 (2015).
- [60] Truong, V.T., Riddell, S.Z., Muscat, R.F., J. Mater. Sci. 33, 4971 (1998).
- [61] Abdi, M.M., Kassim, A., Mahmud, H., Yunus, W.M.M., Talib, Z.A., Sadrolhosseini, A.R., J. Mater. Sci. 44, 3682 (2009).
- [62] Yee, L., Mei-Kassim, A., Mahmud E.H.N.M., Sharif, A.M., Haron., M.J., Malaysian J. Anal Sci. 11(1), 133 (2007).
- [63] Tuncer C., A., Mehmet, S.E.I., Olgum, G.V., J. Appl. Polym. Sci. 69, 1551 (1998).
- [64] Zhou, Y., Hall, C.K., Karplus, M., Phy. Rev. Lett. 77(13), 2822 (2007).
- [65] Wasnik H.R., Keller, D.S., Int. Conf. Adv. Mate. Compo. (ICAMC-2007) 24 (2007).
- [66] Silva, A.J.C., Nogueira, V.C. Santos, T.E.A., Buck, C.J.T., Worrall, D.R., Mortimer, T., Ribeiro, A.S., Sol. Energy Mater. Sol. Cells, 134, 122 (2015).
- [67] Krukiewicz, K., Stokfisz, A., Zak, J.K., Mater. Sci. Eng., C 54, 174 (2015)
- [68] Silva, A.J.C., Ferreira, S.M.F., Santos, D.P., Navarro, M.,Tonholo, J., Ribeiro, A.S., Sol. Energy Mater. Sol. Cells, 103, 108 (2012).
- [69] Zhang, Q., Prabhu, A., San, A., .Al-Sharab, J.F., Levon, K., Biosens Bioelectron 72, 100 (2015).
- [70] Salavagione, H.J., Acevedo, D.F., Miras, M.C., Barbero, C., *Portugaliae Electrochim. Acta*, 21, 245 (2003).
- [71] Strobl, G.R., *Springer-Verlag*. Section 3.2 Polymer Mixtures. (2003)
- [72] Otero, T. F. and Sansinena, J. M., Adv. Mater. 10, 491 (1998).
- [73] Abidian, M. R., Kim, D. H., Martin, D. C., Adv. Mater., 18, 405 (2006).
- [74] Abidian, M. R. and Martin, D. C., Adv. Funct. Mater. 19, 573 (2009).
- [75] Rogina, A., Appl. Surf. Sci. 296, 221 (2014).

- [76] Balint, R., a, Cassidy, N. J., Cartmell, S.H., *Acta Biomateri.* 10, 2341 (2014).
- [77] Voitechovic, E., a, Bratov, A., Abramova, N., Razumien, J., Kirsanov, D., Legin, A., Lakshmi, D., Piletsky, S., Whitcombe, M., Ivanova-Mitseva, P.K., *Electrochim. Acta*, 173 (2015) 59–66
- [78] Abidian, M. R., Ludwig, K. A., Marzullo, T. C., Martin, D. C., Kipke, D. R., *Adv. Mater.* 21, 3764 (2009) .
- [79] Schmidt, C. E., Shastri, V. R., Vacanti, J. P., Langer, R., *Proc. Natl. Acad. Sci. USA*, 94, 8948 (1997).
- [80] Zhou, Z., Zhub, W., Liao, J., Huang, S., Chen, J., He, T., Tan, O., Ning, C., *Mater. Sci. Eng. C*, 48, 172 (2015).
- [81] Warren, L. F., Walker, J. A., Anderson, D. P., Rhodes, C. G., Buckley, L. J., *J. Electrochem. Soc.* 136, 2286 (1989).
- [82] Rivers, T. J., Hudson, T. W., Schmidt, C. E., *Adv. Funct. Mater.* 12, (2002)
- [83] MacDiarmid, A. G., *Synth. Met.* 125, 11 (2001).
- [84] Zhang, Z. M., Wei, Z. X., Wan, M. X., *Macromolecules*, 35, 5937 (2002).
- [85] Hepel, M., *J. Electrochem. Soc.* 145, 124 (1998).
- [86] Buckley, L.J., Eashoo, M., *Synth. Met.* 78, 1 (1996).
- [87] Zhao, C., Wang, H., Jiang, Z., *Appl. Surf. Sci.* 207, 6 (2003).
- [88] Lopatin, A.V., Kazantseva, N.E., Kazantsev, Y.N., D'Yakonova, O.A., Vilcakova, J., Saha, P. J., *Commun. Technol. Electron.* 53, 487 (2008).
- [89] Abbas, S.M, Chandra, M., Verma, A., Chatterjee, R., Goel, T.C., *Compos Part A – Appl Sci Manuf.* 37, 2148 (2006).
- [90] Saib, A., Bednarz, L., Daussin, R., Bailly, C., Lou, X., Thomassin, J.M., *IEEE Trans. Microw Theory Tech.* 54:2745 (2006).
- [91] Ahmad, M.S., Abdelazeez, M.K., Zihlif, A.M., *J. Mater. Sci.* 25, 5019 (1990).
- [92] Madani, M. and Aly, R.A., *Mater. Des.* 31, 1444 (2010).
- [93] Huang, C.Y., Mo, W.W., *Surf. Coat. Technol.* 154, 55 (2002).
- [94] Vilcakova, J., Saha, P., Quadrat, O., *Eur. Polym. J.* 38, 2343 (2002).
- [95] Merhari, L., Springer, Berlin. 231 (2009).
- [96] Razafimahefa, L., Chlebicki, S., Vroman, I., Devaux, E., *Dyes Pigments* 66, 55 (2005).
- [97] Majumdar, D., Blanton, T. N., Schwark, D.W., *Appl. Clay Sci.* 23, 265 (2003).
- [98] Bhowmick, A.K. Bhattacharya, M., Mitra, S., Maji, P.K., Choudhury, A. George, J. J. Basak, G.C., Kumar, K.D., *Kautsch. Gummi Kunstst.* 62, 192 (2010).
- [99] Strawhecker, K. and Manias, E., *Chem. Mater.* 12, 2943 (2000).
- [100] Kojima, Y., Usuki, A., Kawasumi, M., Okada, A., Kurauchi, T., Kamigaito, O., *J. Polym. Sci. Polym. Chem.* 31, 983 (1993).
- [101] Ray, S. S., Okamoto, M., *Prog. Polym. Sci.* 28, 1539 (2003).
- [102] Nam, P.H., Maiti, P., Okamoto, M., Kotaka, T., Nakayama, T., Takada, M., *Polym. Eng. Sci.* 42, 1907 (2001).
- [103] Warren, L. F. and Anderson, D. P., *Electrochem. Soc.* 134(1), 101 (1987).
- [104] Armes, S. P., *Synth. Met.* 20, 365 (1987).
- [105] Bocchi, V., Gardini, G. P., *J. Chem. Soc. Chem. Commun.* 148 (1986).
- [106] Armes, S. P. and Vincent, B., *J. Chem. Soc., Chem. Commun.* 287 (1987).
- [107] Bocchi, V., Gardini, G. P., Rapi, S., *J. Mater. Sci. Lett.* 6, 1283 (1987).
- [108] Dhawan, S. K., Trivedi, D. C., *J. Bull. Mater. Sci.* 16 (5), 371 (1993).
- [109] Olio, A.D., Dascola, Y., Varacca, V., Bocchi, V., *C. R. C.* 267, 433 (1968).
- [110] Letheby, H., *J. Am. Chem. Soc.* 15, 161 (1862).
- [111] Armes, S. P. and Miller, J. F., *Synth. Met.* 22, 385 (1988).

- [112] Ali, M. A., Saion, E., Yahya, N., Kassim, A., Dahlan K. M., Hashim, S., J. Eng. Sci. and Technol. 2 (1), 111 (2007).
- [113] Bodugoz, H., Sevil U.A. Guven, O., *Macromol. Symp.* 169, 289 (1998).
- [114] Stejskal, J., Trchova, M., Ananieva, IA., Janca, J., Prokes, J., Fedorova, S., Sapurina, I., *Synth. Met.* 146, 29 (2004).
- [115] Fusalba, F., Belanger, D., *J. Phys. Chem. B*, 103, 9044 (1999).
- [116] Lim, VML. Kang, ET., Neoh, KG., Ma, ZH., Tan, KL., *Appl. Surf. Sci.* 181, 317 (2001).
- [117] Siphon, E. M., Gerald, F. M., David, E. M., Emmanuel, I. I., *J. Mater. Sci.* 45, 3325 (2010).
- [118] Lopatin, A.V., Kazantseva, N.E., Kazantsev, Y.N., D'Yakonova, O.A., Vilcakova, J., Saha, P., *J. Commun. Technol. Electron.* 53, 487 (2008).
- [119] Abbas, S.M., Chandra, M., Verma, A., Chatterjee, R., Goel, T.C., *Appl. Sci. Manuf.* 37, 2148 (2006).
- [120] Saib, A., Bednarz, L., Daussin, R., Bailly, C., Lou, X., Thomassin, J.M., *IEEE, Trans. Microw. Theory Tech.*, 54, 2745 (2006).
- [121] Stempien, Z., Rybicki, T., Rybicki, E., Kozanecki, M., Szykowska, M.I., *Synth. Met.* 202 49 (2015).
- [122] Hayashida, K., Matsuoka, Y., **Carbon**, **85**, 363 (2015).
- [123] Ahmad, M.S., Abdelazeez, M.K., Zihlif, A.M., *J. Mater. Sci.* 25, 5019 (1990).
- [124] Madani, M., Aly, R.A., *Mater. Des.* 31, 1444 (2010).
- [125] Huang, C.Y., Mo, W.W., *Surf. Coat. Technol.* 154, 55 (2002).
- [126] Vilcakova, J., Saha, P., Quadrat, O., *Eur. Polym. J.* 38, 2343 (2002).
- [127] Stejskal, J., Gilbert, R.G., *Pure Appl. Chem.* 74, 857 (2002).
- [128] Omastova, M., Trchova, M., Kovarova, J., Stejskal, J., *Synth Metal.* 138, 447 (2003).
- [129] Truong, V.T., Riddell, S.Z., Muscat, R.F., *J. Mater. Sci.* 33, 4971 (1998).
- [130] Abdi, M.M., Kassim, A., Mahmud, H., Yunus. W.M.M., Talib, Z.A., Sadrolhosseini, A.R., *J. Mater. Sci.* 44, 3682 (2009).
- [131] Soto-Oviedo, M.A., Araujo, O.A., Faez, R., Rezende, M.C., De Paoli, M.A. , *Synth. Met.* 156, 1249 (2006).
- [132] Paligova, M., Vilcakova, J., Saha, P., Kresalek, V., Stejskal, J., Quadrat, O., *Physica. A*335, 421 (2004).
- [133] Abron, K., Uzir, M., Wahit, B., Bahraeian, S., **Sci. Res. Essays**, 6(28), 5895 (2011).
- [134] Patoisa, T., Lakarda, B., Monneya, S., Roizardb, X., Fieveta, P., *Synth. Met.* 161, 2498 (2011).
- [135] Zhang, A.Q., Zhang, Y., Wang, L.Z., Li, X.F., *Polym. Compos.* 32, 1 (2011).
- [136] Yanılmaz, M., Karakaş, H., Saraç, A. S., Kalaoğlu, F., *Proceedings of the World Congress on Engineering*, 3, London, U.K. (2011).
- [137] Chakraborty, G., Gupta, K., Meikap, A.K., Babu, R., Blau, W.J., *Solid State Commun.* 152, 13 (2012).
- [138] Zhang, B., Xu, Y., Zheng, Y., Dai, L., Zhang, M., Yang, J., Chen, Y., Chen, X., Zhou, J., *Nanoscale Research Lett.*, 6, 431 (2011).
- [139] Leea, H., Kimb, H., Choa, M. S., Choib, J., Leea, Y., *Electrochim. Acta*, 56, 7460 (2011).
- [140] Pacheco-Catalán, D.E., Smit, M.A., Morales, E., *Int. J. Electrochem. Sci.* 6, 78 (2011).
- [141] Antar, Z., Feller, J.F., Noël, H., Glouannec, P., Elleuch, K., *Mate. Lett.* 67, 210 (2012).
- [142] Shao, Q.G., Chen, W.M., Wang, Z.H., Qie, L., Yuan, L.X., Zhang, W.X., Hu, X.L., Huang, Y.H., *Electrochem. Commun.* 13, 1431 (2011).
- [143] Qina, H., Kulkarnia, A., Zhang, H., Kim, H., Jiange, D., Kim, T., *Sens. and Actuat. B* 158, 223 (2011).
- [144] Tam, P. D. and Hieu, N. V., *Appl. Surface Scie.* 257, 9817 (2011).
- [145] Roy, C. J., Leprince, L., Boulard, A. D., Landoulsi, J., Callegari, V., Jonas, A. M. Champagne, S. D., *Electrochim. Acta*, 56, 3641 (2011).

- [146] Bootha, M. A., Harbison, S.A. Sejdic, J. T., Biosens. Bioelectron. 28, 362 (2011).
- [147] Liu, X., Yue, Z., Higgins, M. J., Wallace, G. G., **Biomater.** 32, 7309 (2011).
- [148] Shivakumar, G., Konda Kannan S. K., Subbian M., Muthana T. V., Trivedi, D.C., Compos. Sci. Technol. 70, 1017 (2010).
- [149] Li, C., Shi, G., Electrochim. Acta 56, 10737 (2011).
- [150] Wang, X., Yang, C., Wang, T., Liu, P., Electrochim. Acta 58, 193 (2011).
- [151] Mouc'ka, R., Mravč'akova, M., Vilc'akova, J., Omastova, M., Saha, P., Mater. Des. 32, 2006 (2011).
- [152] Zhang, A.Q., Cal, L.J., Sui, L., Qian, D.J., Chen, M., **Polym. Reviews** 53, 240 (2013)..
- [153] Rubeziene, V., Baltusnikaite, J., S Varnaite_Zuravliova, S., Sankauskaite, A., Abraitene, A., Matuzas, J., **J. Electrostat.** 75, 90 (2015).
- [154] Jamadade, S., Jadhav, S., Puri, V., Arch. Phys. Res. (1) 4, 205 (2010).
- [155] Melnykowycz, M., Koll, B., Scharf, D., Clemens, F., Sensors 14, 1278 (2014).
- [156] Kaur, A., Ishpal, Dhawan, S.K., Synth. Met. 162, 1471 (2012).
- [157] Shamsuddin, M. A., Daik. R. (2009) *Malaysia Poly Inter. Conference* (MPIC).
- [158] Hakansson, E., Amiet, A., Nahavandi, S., Kaynak, A. (2007) *Eur. Polym. J.*, 43, 205-213.
- [159] Liu, Z., Bai, G., Huang, Yi., Ma, Y., Du, F., Li, F., Guo, T., Chen, Y. (2007) *Carbon*, 45, 821.
- [160] Chung, D.D.L. (2001) *Carbon*, 39(2), 279-85.
- [161] Jamadade, S., Jadhav, S., Puri, V., (2010) *Arch. of Phys. Res.*, 1(4) 205-210.
- [162] Roy, M.K., Mahloniya, R.G., Bajpai, J., Bajpai, A. K., *Adv. Mat. Lett.*, 3(5), 426 (2012).

