Flexible EMI shielding fabrics by using conductive polymer

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Abstract

Nowadays, new development in electronics and electrical devices leads to a new type of electronic pollution, which is called electromagnetic interference. It affects the efficiency, life, and safety of the operation of electronic devices. Electromagnetic interference is the current major issue, and to overcome this issue, the EMI shield is used. For EMI shielding, metal oxide, magnetic materials, and metals are used, but they have some limitations like flexibility, heaviness and high costs. In this context, conductive polymers are widely studied and used to make conductive textile polymer composites due to their properties like electrical, high mechanical and optical properties, ease of synthesis, and environmental stability. The application of conductive polymers is done in many sectors, like industrial applications, and medical and scientific fields. Synthesis of these conductive polymers can be done by oxidative in situ chemical polymerization or by electrochemical polymerization. These conductive polymers can be applied over the fabric by using different application techniques like a jigger dyeing machine, electro-spinning techniques, and electrodeposition of conductive polymer on anode. This process involves the optimization of process parameters during the synthesis in terms of monomer concentration, reaction temperature, treatment duration and monomer: oxidant ratio. These ICP-coated fabrics can be then characterized in terms of surface resistivity (as ohms/square) and EMI Shielding effectiveness (dB).

Keywords

Conductive polymer, Conductive textile, Electromagnetic Interference, EMI shield, Polyaniline, Polypyrrole

Citation

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1.0 Introduction:

Electrical and electronic devices are used worldwide for different purposes; electromagnetic interference is a major issue because it distracts electronic devices. For example, in the case of any electronic device like a computer, it generates broadband electromagnetic energy. But due to its energy, it is picked up by other electronic devices like antennas or wireless devices or any other devices, which cause abnormal performance of the electronic gadget. Many researchers and electronic companies have been working on this issue to overcome it with some solutions.

To produce EMI shield material, different metal shit, metal tubes, and carbon nanotubes were used. But nowadays, textile products have caught more attention due to their properties like versatility and comfort, and ability to have different structures. Figure 1 shows the electromagnetic spectrum, the whole distribution of radiation according to radiation wavelength and its frequency. The rapid increase



Figure 1: Electromagnetic Spectrum

in the use of electrical products and electronic devices in commercial, scientific, and military systems has raised the issue of electromagnetic interference. In other words, it is called electromagnetic pollution [1]. Due to this problem,



Figure 2: EMI Shield Working(modified and redrawn from reference [1].)

EMI shielding nowadays increases interest. Previously for shielding techniques, metals, and their composites were generally used as shielding materials, but they have drawbacks such as heavy weight, corrosion, poor flexibility and efficiency of shielding. To overcome these problems, conductive polymer composites are mainly of interest.

EMI shield or control is succeeded by reducing the electromagnetic interference emission from the source, by changing the path of electromagnetic energy, and by improving the susceptor. EMI can be controlled by reduction, or conduction depending on the coupling path involved in it [2]. Figure 2 shows how EMI shielding can work. Electrically conductive fabrics can be produced by using metal particles, carbon particles by using different metal salts, or it can be produced by using metal copper wires in fabrics during the weaving of fabric. But the physical and mechanical properties of textile materials are affected by the use of metal wires in textile substrates. To overcome these problems, and because of some advantages of conductive polymer (such as lighter in weight, ease of synthesis, corrosion resistance, can be easily blended with any other material and low cost of the polymer,)currently, conductive textile is produced by using conductive polymers over metal particles or instead of metal wires used in weaving[3,4].

Conductive polymers are from a specific family of polymers made up of monomer units with conjugated bonds, under doping conditions. Widely conductive polymers are used to make conductive coatings, sensor production, microelectronic devices, antistatic materials, etc. Intrinsically conducting polymers are capable of transferring electricity due to their structure of alternate single, and double bonds of polymeric chains[5].

Textile material because of its high surface area used to make composite with intrinsic conducting polymers like polypyrrole, polyaniline, and polythiopene. Intrinsically conducting polymers are organic polymer which is subdivided into no heteroatom, nitrogen-containing, and sulphur-containing. Examples of conducting polymers are such as polyaniline, polypyrrole, polyparaphenylene, poly(3, 4-ethylenedioxythiophene), etc.[6].Conductive polymer is prepared by using monomers like aniline, pyrrole, thiophene, and its derivatives by electrochemical or chemical synthesis method[7].

Conductive composite fabrics are prepared with a thin layer of intrinsic conductive polymer. In situ, chemical polymerization techniques for organic monomers are used to create a conductive coating on textile substrates like nylon, cotton, polyester, silk, etc. Monomer adsorption on textile substrate depends on concentration, the temperature used for polymerization, time given for reaction, properties of textile substrate, etc. Conductive polymer processing can be increased by using dopants[8]. Intrinsic conductive polymers are conductive because of the presence of conjugated π electrons in their system. The intrinsic conductive polymer can go easily under the oxidation process in the presence of dopants, which are charge transferring agents, and by using them; conductive polymer can achieve the highest conductivity, like metals. Conductive textile or conductive polymer coated textile composites can be made by using different techniques; in situ polymerization technique of the conducting polymer, or grafting conductive polymer on a textile substrate during polymerization, and used coating techniques where conductive polymer is coated on a textile substrate by coating or by printing. Also, electro-spinning techniques are used to make conductive textiles[9].

2. Conductive Polymers

Several inherently conductive polymers have been studied, viz. polyacetylene, polyaniline, polypyrrole, polypropylene, PEDOT: PSSpoly(3-4 ethylene dioxythiophene): poly(styrene sulphonate), polyphenylene, polythiophene, etc. Among all conductive polymers polyaniline and polypyrrole have attracted the most attention nowadays due to their ease of synthesis, ease of processibility, monomer availability environmental stability, high conductivity and cost-effective nature. These conductive polymers can be coated over the fabrics to prepare a flexible conductive textile substrate which retains the comfort of the fabric as it is and does not deteriorate the mechanical and other textile properties of the textile substrate[10-12].

2.1 Polyaniline

Polyaniline is widely used to make conductive textiles due to its ease of synthesis & environmental stability. Polyaniline is made up of reduced and oxidised blocks. Polyaniline contains the chemical flexible -NH- group present in the backbones of polymers which takes part in protonation, and deprotonation and also contributes to π bond formation[13].Polyaniline is made up of aniline monomer in acidic conditions in the presence of oxidizing agents like ammonium peroxidisulphate, hydrogen peroxide, potassium dichromate, etc. The effective polymerization of aniline is effective under acidic conditions pH 1 to 2 where anilinium cation occurs. The stability and conductivity of polyaniline depend on the form of polymer. A conducting polyaniline polymer is prepared by electrochemically oxidative polymerization or by chemically oxidative polymerization. Chemical synthesis of polyaniline polymer requires three basic reactants; aniline monomer, acidic medium, and

oxidizing agent[14]. Polyaniline has different forms, which have different colours, conductivity, and stability. Figure 3 shows the oxidation stages of aniline. The leucoemeraldine form, which is a coloured substance that contains only amino groups and benzene, results in a non-conductive nature. When the leucoemeraldine form of polymer gets oxidised in acidic media, it converts to emeraldine salt which is conductive, showing a dark green colour to the polymer. Another form of polymer is pernigraniline, which is made up of quinonediimine, and amino benzene. Due to quinonediimine presence, it is unstable in' nucleophiles' presence, specifically water, pernigraniline, and its salts readily decompose in the air[15].



Leucoemeraldine state (yellow-pale yellow)



Figure 3: Oxidation stages of aniline

When polyaniline forms an emeraldine base, it is treated with acids where protons primarily react with imine atoms of nitrogen which results in polycations appearing. Because of the positive charge localised on the neighbouring nitrogen atom, it increases the total energy of the polymer. Polyaniline emeraldine salt is formed during the protonation of the emeraldine base with organic and inorganic acids. Polyaniline consists of both quinoid and benzenoid rings, different proportions and ratio differences cause the existence of three oxidised states; the fully reduced form of polyaniline is leucoemeraldine, which is in the quinoid state. The other form of polyaniline that is fully oxidised is pernigraniline, which is in a benzenoid state, and emeraldine, the salt form of polyaniline, has an equal ratio between both quinoid and benzenoid. The dopant, which is generally used during the synthesis of polyaniline does not change chemical properties or does not create bonds with the main change. It is present in the close vicinity of the polyaniline polymer chain. Different dopants were mainly used for polyaniline, like strong organic acid hydrochloric acid, organic base acids such as p-toluene sulphonic acid, Dodecylbenzene sulphonic acid, and some aliphatic acids like lauric acid.

The chemical oxidation process is a well-known method for synthesizing polyaniline. In this chemical oxidation method, the monomer of the precursor is mixed with an oxidizing agent in the presence of acids under suitable conditions for a polymer as a product. The color change of the reaction medium to green indicates the formation of polyaniline, which is conductive in nature.

2.2 Polypyrrole

The increasing demand for polypyrrole is due to its properties such as high conductivity and high stability. Initially, pyrrole was synthesized by using hydrogen peroxide to get black amorphous powder. In inorganic solvents, black pyrrole is insoluble and also shows conductivity in the range of 10⁻¹⁰ to 10⁻¹¹ s cm-1. Bulk polymer contains 15% crystallinity, and it is monoclinic, it acts as amorphous and not as crystalline. Polypyrrole is generally prepared by using oxidative in situ chemical polymerization of pyrrole using hydrogen peroxide, ammonium peroxide sulphate, potassium permanganate or ferric chloride as oxidizing agent. During this synthesis process, the addition of sulphonic acid-based dopants substantially increases the conductivity[16].Doped polypyrrole has been the most thoroughly investigated conductive polymer for different applications, because of its high electrical conductivity, ease of preparation, and ease of surface modification. Polypyrrole can be synthesised in bulk quantity at room temperature by using different common organic solvents and also water can be used[17]. In the case of Polypyrrolefactors affecting the synthesis process arenamelymonomer concentration, oxidant used, the ratio of precursor and oxidant, temperature and time of reaction. Conductive Polypyrrole, which is highly conductive, is synthesized by adding an oxidant and by controlling the oxidant potential of the solution when it is added. Polypyrrole is synthesized mostly by electrochemical synthesis method to obtain highly conductive polymer where the techniques and procedure use the same as other polymers. However due to small anode size; the yield of the product is limited[18].

2.3 Short review on adapting the various processes for coating conducting polymers on variable fabrics

Different techniques were developed to apply the conductive polymer to the substrate or prepare a composite of textile material and conductive polymer. A.J.Patil& S. C. Deogaonkar [2012] prepared a composite of cotton and polyaniline by using a jigger dyeing machine by two step in

situ chemical polymerisation. The concentration of monomer, oxidant to monomer ratio, concentration of protonic acid and duration of the polymerisation were studied. The minimum surface resistivity obtained resulted in 420 ohms/square. In this study, cotton fabric was first treated with monomer for a 1-hour duration by using a jigger dveing machine and after the monomer application on cotton fabric ammonium peroxidisulphate was introduced in the same bath with suitable sulphonic acid dopants in a controlled temperature of $4\pm 1^{\circ}$ C temperature[19]. YaphingZhaoet al. produced a composite of polyaniline and polyester fabric by two-stage in situ polymerisation techniques where for the preparation of the conductive composite they used beaker dipping techniques. Different variables like temperature time of the reaction and initial concentration of the monomer which enhanced the equilibrium of the adsorption of monomer on polyester fibers were observed and studied. To prepare polyesterpolyaniline composite fabric, the polyester fabric was soaked into the aniline and protonic acid solution for some duration and the polyester fabric dip the intooxidant solution to complete the polymerisation of the aniline monomer. To continue the polymerisation, fabric passed through the padder and was kept at a cooled condition of 273K for 2 hours[20]. The same techniques were used to produce a novel polyaniline bagasse fiber composite. Yang Zhang, et al discovered the bagasse fibre polyaniline composite. To prepare this polyaniline based fiberaniline monomer was added to protonic acid under ultrasonication conditions. After that oxidant was added to it to follow the polymerisation at a very low temperature. The conductivity achieved for this bagasse fiber polyaniline composite is 2.01±0.29 S cm⁻¹[21]. Zhou, Hone J. et al. Prepared ultrathin electro spun nanofibers using polyaniline in the presence of a doping agent and reported a bulk fiber conductivity of 10⁻² S/cm [22]. In addition to this conductive textiles can be prepared by knife-over coating techniques where conductive polymers can be blended with acrylate binder, thickener and pH regulator. Surface resistivity obtained from it was found to be in the range of 10⁸ to 10¹⁰ Ω /square[23]. Based on the surface resistivity obtained by the conductive fabrics, it can be used in a wide range of applications. However, in this paper, our focus is on the EMI Shielding application. The desired resistivity range for EMI shielding application is between 0.001 to 100 ohms/square. [1][24-25].

3. Electromagnetic Interference Shielding

Electromagnetic interference shielding (EMI Shield) is designed to isolate a device's energy so that it does not damage the environment and prevents external energy from attacking. All modern electronics release some electromagnetic radiation and have no EMI resistance. Along with grounding, filtering, and bonding procedures, EMI shielding is a way to attain EMC (electromagnetic compatibility). To change the route of the majority of unwanted electromagnetic waves entering or leaving the equipment, enclosures must be built using the proper material, structure, and form. Through conductive or magnetic substances, the electromagnetic wave is either absorbed or reflected, changing the course.

Electromagnetic interference shielding can be categorised into four types, depending on continuous or pulse and frequency range. The first type of EMI shielding is known as EMI power spectrum shielding, which is in the range of 1-100 KHz. The second type of electromagnetic interference is in the range of 100 KHz-1GHz and it is the radio frequency range. The third type of EMI is microwave and beyond frequency range and forth type is an electromagnetic pulse which has a broadband, with high-intensity duration bursts of electromagnetic energy, such as nuclear explosion and electric discharge[27].

Electromagnetic interference shielding can be expressed in terms of electromagnetic shielding effectiveness. The EMI shielding effectiveness is measured in terms of the ratio of the power of incoming, and outgoing waves, and it is expressed as follows[28].

SET (dB)= $10 \log (PT/PI) = 10 \log (HT/HI)$

Based on the physical properties of the substrate, these theoretical formulas are given. Because of this, electromagnetic shielding effectiveness is divided into three terms reflection phenomena, absorption phenomena, and multiple reflections. [29-30]

Where P_1 (E_1 and H_1) are the power of incident electromagnetic waves and P_T (E_T and H_T) is the power of transmitted electromagnetic waves [31]. The total shielding effectiveness can be further expressed and divided into three components,

 $SE_{T} = SE_{A} + SE_{R} + SE_{M}$

Where Shielding effectiveness due to SE_A absorption, SE_R reflection, and SE_M is multiple reflection. The S11 and S21 scattering parameters of the two port analyser networks can be related to the reflectance and transmittance, $T = IE_T / E_I I^2 = IS_{21}I^2 = IS_{12}I^2$ and $R = IE_R / E_I I^2 = IS_{12}I^2$

The absorbance can be mentioned as A= (1-R-T), where the absorbance coefficient is given with respect to the power of the incident EM wave. When SE_A absorbance is more than or equal to 10 dB, SE_M multiple reflection is negligible. Therefore, vanishes multiple reflections SE_M and SE_T can be expressed as SE_T=SE_R+SE_A[28].

The intensity of the incident electromagnetic waves inside the substance after reflections depends on the quantity of (1-R). Effective absorbance can be expressed as

A(eff) Effective absorbance=(1-R-T)/(1-R)

With respect to the power of the effectively incident electromagnetic wave inside the shielding material. Reflection and effective absorption losses are expressed in the form of $-10\log(1-R)$ and $-10\log(1-A_{eff})$, respectively.

It gives SE_R and SE_A as SE_R =-10 log (1-R) and SE_A =-10 log (1-A_{eff})

Dielectric conductivity σe is related to the dielectric loss $\check{e}r$ by the following expression,

 $\sigma e = GD \breve{e} = 2\pi f E0 Er''$

Absorption coefficient $A = \epsilon r'' f/nc$ suggests that microwave absorption increases as an increase in dielectric loss[31].

Different methods were introduced to measure the shielding effectiveness of the material. The basic principle to calculate shielding effectiveness is the same for all types of methods, only testing setups will differ from each other. By using all these methods we calculate the energy of electromagnetic waves which goes into the substrate and the energy of electromagnetic waves which is transmitted through the substrate to calculate the shielding effectiveness[32]. The effectiveness of the shielding is measured through transmission between two antennas with the enclosure's door open and closed. The shielding efficiency is a difference between these two values, in decibel (dB) units [33]. In some methods, we can calculate the amount of electromagnetic waves reflected from the material. Four techniques are commonly used to measure shielding effectiveness, which are the open field method, shielded room method, shielded box method and coaxial transmission method. Vector Network Analyser is generally and subsequently used to check the electromagnetic waves [34].

The open field method is known to be the most realistic method of measuring the EMI shielding effectiveness of a material or an enclosure as it simulates the conditions the shielding material would be subjected to during its usage[35]. The transmitting and receiving antennas are kept on either side of the shielding material in the shielded box approach, while the receiving antenna and necessary instruments are housed inside a sealed box. The shielded room approach, which in terms of function is comparable to the shielded box method, fixes some of the problems with the shielded box method. In the shielded room method, the specimen is exposed to EMW radiation from the transmitting antenna outside the room while the receiving antenna and equipment are retained in a sealed room[35]. The most commonly used method to measure shielding effectiveness is the coaxial transmission line method because of its repeatability and ability to use a wide range of frequencies. The technique uses a sample holder to hold the reference and load samples needed to measure the shielding effectiveness [32].

Well-known two standards have been developed on this technique, ASTM ES783 and ASTM D493510. [37] As per the first method, a torus-shaped sample is placed at the centre of the coaxial cell which is tapered at both ends to match 50Ω impedance. Figure 4 shows the ASTM D4935 coaxial transmission line fixture setup to check the EMI shielding behaviour of the substrate. The inner and outer diameters of the sample are matched with the diameters of the inner and output powers are measured using a network analyser and substituted to compute the shielding effectiveness of the substrate. Analytically, the calculation of SE of the sample is



Figure 4: ASTM D4935-10 Coaxial transmission line fixture setup (modify and redrawn using data available in Ref [36])

based on the fact that the TEM (Transverse Electromagnetic)wave propagating in the coaxial transmission line mimics the far-field incident plane wave while the sample acts as a load. The EMI SE of the sample is then computed using the following formula.[36].

 $SE=20 \log [1 + (Z_0/2Z_L)]$

Where, Z_0 and Z_L are the characteristic impedance of the coaxial transmission line and the impedance presented by the load, respectively. This expression is applicable when perfect contact between the transmission line walls and the sample is established. However, practically achieving perfect contact is extremely difficult. Such imperfections lead to the generation of a contact resistance ZCR in series with ZL, which participates in SE determination as follows,

 $SE=20 \log [1 + {Z0/2(ZL+ZCR)}]$

The technique to measure the SE of a material is very simple but lacks accuracy and is not repeatable as the ZCR may vary for different tests. Because of these reasons, the standards ASTM ES783 that was based on this technique were withdrawn in 1988. However, this technique is still very popular to make some crude lab estimations regarding the shielding material.

Each of these measurement techniques has specific measurement parameters such as the dimension of the sample and frequency of the electromagnetic waves.

D.C.Trivedi and S.K.Dhawan et al. produced electromagnetic interference shielding by using polyaniline textile composites using in-situ polymerization. Insitu polymerization of polyaniline is done over fabric in an aqueous condition at a low temperature of around 5-10°C in the presence of a dopant and an oxidizing agent. After grafting conductive polymer on a textile substrate, A.C. conductivity was measured at frequencies of 10 to 105 Hz at

amplitudes of 4 mV, and the coaxial transmission line method was used for measurement of EMI shielding effectiveness at frequencies of 1000 KHz to 1 GHz [38].

S. Geetha K.K. Satheesh Kumar, and D.C. Trivedi et al described a method for preparing and increasing the shielding effectiveness of polyaniline grafted e-glass fabric to control electromagnetic radiation. For the preparation of a composite of polyaniline and e-glass fabric para-toluene sulphonic acid, and camphor 10 sulphonic acid dopants were used. EMI shield effectiveness was checked by using the coaxial method with using frequency range of 0.1 to 1000 MHz. Different thickness samples give different EMI shield values, a 3mm thick sample of conductivity 0.8 S/cm of composite conductive e-glass SE of 39 dB at 0.1MHz and 54 dB at 1000 MHz.[39].

Overall ICP ICP-coated fabrics can lead to excellent EMI shielding property (i.e.>99.9%) by tuning the process parameters of synthesis of ICP-coated fabrics. However, the

washing and atmospheric durability of these developed fabricslimits its application commercially.

4. Conclusion

This review article aims to explore the application of conducting polymer and textile composite in electromagnetic interference shielding. The in situ polymerisation technique can be used to produce flexible conductive textile composite which can be used as EMI shielding. By using suitable dopants and conditions like concentration of monomer, temperature, and time of reaction, metallic conductivity can be achieved for textile conductive polymer substrate. EMI-shielded textiles can be characterised by surface resistivity, the conductivity of the fabric, and coaxial line transmission electromagnetic shielding effectiveness. Based on ease of synthesis and good flexibility, ICP-coated fabrics can be one of the best alternatives towards EMI shielding materials however its durability concerns to be considered for further commercial applications.

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