CHAPTER V

Application of PANI-TiO$_2$ hybrid coated fabrics for electromagnetic interference (EMI) shielding in S band region

5.1. Literature Review

Flexible microwave absorbers and electromagnetic interference (EMI) shields are thought to be ingenious new generation materials and one of the needs of modern era. Conducting fabrics well suit this demand and it has got growing research interests. Metalized fabrics were prepared by various groups and studied for EMI shielding [1-8]. Conducting polymers have been coated on textile substrates for making flexible EMI shields [9]. For assessing the potential of materials as dielectric or EMI shields, the knowledge of its dielectric constant and dielectric loss becomes essential. The dielectric constant is the relative permittivity of a dielectric material and refers to the ability to store the charge under the applied electromagnetic field and then transmit the energy.

According to Balanis [10], in dielectric materials, the dominant charges of their atoms and molecules are positive and negative, which are kept in the same position by the atomic and molecular forces, and are not free to dislocate. However, upon applying an electric field to a dielectric material, the formation of several electric dipoles takes place, which align themselves according to the orientation of the applied electric field. The reciprocal influence on the electric field causes the storage of electric energy, which can be turned to heating by Joule effect. Such dielectric materials are used in microwave absorbers, EMI shields and heating elements.

Fibres and textile materials have been the subject of study in relation to electrical and dielectric behavior. Many authors have reported measurement methods of dielectric properties such as dielectric constant and loss factor of native textile materials. For the development of EMI shield and textile antenna, the knowledge of dielectric properties of these materials has become indispensable. There are some difficulties in observing the dielectric properties of
these fibre and fibrous materials. Because of the complexities involved in manipulating samples of textile materials in their original shape and the porous nature, exact values of the dielectric of the textile materials are still not found conclusively. Several models are proposed and these models and methods are reviewed by Bal and Kothari [11]. So far, no model has been able to successfully describe the behavior of textile materials as dielectrics.

Microwave properties of conductive polymers are also studied widely, because of their numerous applications in areas such as coating in reflector antennas, coating in electronic equipments, frequency selective surfaces, EMI materials, satellite communication links, microchip antennas, radar and microwave absorbing materials [12].

Non-biological materials exhibiting the dielectric properties of biological tissue at microwave frequencies have been used extensively to evaluate hyperthermia applicators, assess microwave imaging systems and determine electromagnetic absorption patterns. Conducting polymers composited with semiconductors result in unique properties. They generate a new field for the development of advanced materials in science and technology. Their properties are quite different from the constituent materials due to interfacial interactions between nano-structured semiconductors and polymers. The properties of these materials can easily be tuned to the desired application through the variation of particle size, shape and distribution of the nanoparticles.

The dielectric properties of PANI-TiO$_2$ are subjected to study by various research groups. Ultra-high dielectric constant was found in some cases and enhanced dielectrics in some others. Dey et al had reported high dielectric constant for PANI-TiO$_2$ and proposed possible mechanism [13]. They explained that interface and the nanosize of TiO$_2$ may play important roles to magnify the dielectric properties. The dielectric constant of PANI-TiO$_2$ was very large and almost independent of frequency. It decreased considerably with increase of PANI content. The presence of TiO$_2$ nanoparticles did not change the charge transport mechanism of PANI but enhanced the dielectric constant by about ten times that of pure PANI. Still the exact physical origins of the huge dielectric constant still remain unclear.
Permittivity and polarisation

The complex permittivity and permeability values with respect to applied frequency are important inputs for characterizing a sample for applications as dielectric or EMI shields. Permeability can be neglected in the case of non-magnetic substances. Complex permittivity is equal to \( \varepsilon' - j\varepsilon'' \), where \( \varepsilon' \) is the real part of permittivity and \( \varepsilon'' \) is the imaginary part proportional to loss index or dielectric loss.

The ability of the dielectric materials to store energy is attributed to the polarisation, i.e. electric field-induced separation and alignment of the electric charges, which can result in an increase in capacitance. When a dielectric material is exposed to an electromagnetic field, the electric field will influence the distribution of existing dipoles and induce the formation of new dipoles. This effect is called the polarisation. In principle, there are five types of polarisation mechanisms, which prevail at different time domains: (i) electronic polarisation (atomic polarisation), (ii) orientation polarisation (dipole polarisation), (iii) ionic polarisation, (iv) interface or surface polarisation (Maxwell-Wagner) and (v) hyperelectronic polarisation. In a dielectric material, at least one of these five types of polarisation mechanisms functions under static fields [14].

- **Electronic Polarisation:** The displacement of the charge center of electrons from the neutral nucleus will induce a dipole moment and produce an electronic polarisation. This polarisation is present in all materials, along with a wide frequency range. In non-polar solids, where there is no existence of permanent dipoles or ions in the solid such as silicon (Si), only electronic polarisation exists. For other solids, electronic polarisation may act simultaneously with other polarisation mechanisms including orientation polarisation and ionic polarisation. The induced dipole moment from the electronic polarisation is proportional to the applied electric field and has no dependence on the frequency. The time required to induce the electronic polarisation is \( \sim 10^{-15} \) s, therefore this polarisation mechanism is operative along the wide frequency range (up to \( 10^{15} \) Hz).

- **Orientation Polarisation:** Orientation polarisation usually occurs in polar liquids, gases or polymeric materials, where there are permanent dipoles with the freedom to rotate.
The external electric field will align the existing randomly oriented dipoles to some direction and produce a polarisation. It is operative up to the microwave frequency. The orientation polarisation is strongly dependent on the temperature, as thermal energy is needed to overcome the resistance from neighboring molecules for alignment. This temperature dependence is a characteristic of the orientation polarisation and helps to differentiate from electronic and ionic polarisations, as the latter two types of polarisation have no temperature dependence.

- **Ionic or atomic Polarisation**: Ionic polarisation exists where the electric field drags the charge center of positive ions away from that of negative ions yielding a net dipole in ionic solids. Ionic polarisation is operative up to infra-red frequency ($10^{12} - 10^{13}$ Hz), because the alignment involves the displacement of the entire ions in the lattice and the response to the electric field becomes slower. For the high dielectric constant material dominated by the ionic polarisation, the dielectric loss curve normally exhibits an abrupt loss peak and the conductivity is relatively large. One effective strategy to enhance the dielectric response in solids is through ion-doping. For example, by doping the polyaniline with iodine, the polyaniline is oxidized and the dielectric constant can be increased to more than 10 times higher than the undoped one.

- **Interface polarisation**: Interface polarisation is present in the surfaces, gain boundaries and inter-phase boundaries, where dipoles can orient to certain degree under electric field and contribute to the total polarisation of dielectric materials. The interface polarisation is operative up to $10^4$ Hz. The interface polarisation has been accounted for the high dielectric response in many heterogeneous systems, especially the ferroelectric polymers and ceramics. And the contribution of interface polarisation to the total polarisation of material is remarkable at low frequency range (Hz-KHz), that’s why a lot of dielectric materials have very high dielectric constant at lower frequencies. The interface polarisation mechanism has been widely used in inorganic/organic nanocomposites in order to enhance the dielectric response, and the degree of the polarisation depends on the size and morphology of the crystalline domain, the defects and number of boundaries, as well as the difference in
the conductivity between inorganic and organic materials. Maxwell-Wagner polarisation mechanism is generally used to explain the dielectric relaxation in polycrystalline materials. In addition, interface polarisation is a very complicated mechanism and no satisfactory models have been determined to calculate the interface polarisability yet. However, for amorphous solids, the term of hopping polarisation is used to describe this type of space charge polarisation. In an amorphous solid, the localized charge can hop from one site to another site; therefore form the dipole moment by the transition between two different potential wells. Depending on the width and height of the potential barrier between two sites, the localized charge can hop or even tunnel between neighboring sites.

- **Hyperelectronic polarisation:** In addition to the above basic polarisation mechanisms, another mechanism called hyperelectronic polarisation has been found in some long polymeric molecules with an extensive electronic orbital delocalization by Pohl et al [15-16]. The hyperelectronic polarisation is considered as the principle contributor to high dielectric constant in polyacene quinone radical (PAQR) polymers (e.g. 14000 at 100Hz for a PAQR polymer). Hyperelectronic polarisation may due to the pliant interaction of charge pairs of excitons, located on long, polarisable polymers under a low frequency external electric field. The long-range displacement of charge pairs along the giant macromolecule will result in a strong polarisation delocalized along the entire length or dimension of the macromolecule. The hyperelectronic polarisation shows a non-linear dependence on the electric field and its magnitude is several orders larger than that of the electronic polarisation, especially during the frequency range (KHz-MHz).
Dielectric loss of the dielectric material is resulted from distortional, dipolar, interfacial, and conduction loss. The distortional loss is related with electronic and ionic polarisation mechanisms. The interfacial loss originates from the excessive polarized interface induced by the fillers and specifically the movement or rotation of the atoms or molecules in an alternating electric field. The conduction loss is attributed to the dc electrical conductivity of the materials, representing the flow of actual charge through the dielectric materials.

**EMI shielding**

*Electromagnetic compatibility* (EMC) is the capability of electrical and electronic systems, equipment, and devices to operate in their intended electromagnetic environment within a defined margin of safety, and at design levels or performance without suffering or causing unacceptable degradation as a result of EMI. The term EMI is used to describe the unwanted radiations which generate or excite EM fields, intentionally or unintentionally, which can be received by other devices as propagated radiation. EMC can generally be achieved by suppressing EMI and immunizing susceptibility of the systems and devices. EMI can be transmitted from one electronic device to another via radiated or conducted paths or both. Suppression is the process of reducing or eliminating this EMI energy. It may include shielding and filtering.
Enormous usage of electronic gadgets multiplied the problems due to electromagnetic interference. The interest in Electromagnetic interference shielding materials increased due to their potential applications in wireless data communication, local area network, satellite television and heating systems [17-18]. The most common type of EMI occurs in the RF range of the EM spectrum, from $10^4$ to $10^{12}$ Hz. This energy can be radiated by computer circuits, radio transmitters, fluorescent lamps, electric motors, overhead power lines, lightning, and many other sources. The EMI problems include several electrical, economic, and biological adverse effects [19-25]. These unwanted radiations can interfere with simple household appliances and can generate disastrous results in large scale. The interference also leads to wastage of energy and there by economic loss. When a high frequency electromagnetic wave enters a human body, it vibrates molecules to give out heat. The network of veins within high-risk organs such as the eyes could be weakened because this heat cannot be easily dissipated. Moreover, it could increase the possibility of leukemia and other cancers. Biologists have reported that even a short-term exposure to low-density electromagnetic radiation could result in temporary sterility [26]. There is also increasing concern that EMI adversely affects the operation of biological devices such as pacemakers [27].

Myriad of investigations are being carried out for enhancing and exploring better EMI shields [28-34]. Materials to be used as electromagnetic field shield must meet the following conditions:

- have a suitably high coefficient of the shielding effectiveness (SE)
- be resistant to mechanical impact and easy to handle (rigidity, elasticity, gravity, way of installation, sealing),
- be resistant to harmful influence of external environment (oxidation, corrosion)
- durable
- homogenous
- easy to form the shield
- low cost of production.
Shields made as metal sheets or foil, and metal mesh are characterized by a good EM field shielding effectiveness coefficient. However they are characterized by low resistance to environmental impact. Their fundamental disadvantage is weight. They are primarily used in low frequency electromagnetic field shielding. Organic conducting polymers (OCPs) are chosen as suitable materials for EMI [35] because of their tunable conductivity, high strength to weight ratio, corrosion resistance and low cost. These materials have high conductivity (as compared with carbons), low density and corrosion resistance (as compared with metals) [36]. The shielding efficiency depends on many factors including intrinsic conductivity, dielectric constant and aspect ratio; hence can be tuned by tailoring these OCPs with dielectric materials like TiO$_2$, BaTiO$_3$. While designing composite shielding material, it is necessary to take into account the following factors that influence the efficiency of shielding [37]:

- volume fraction of inclusions,
- electrical and magnetic properties,
- shape and size of inclusions, and the way of their orientation,
- EM field frequency,
- Number and sequence of layers.

In EMI shielding, there are two regions, the near-field shielding region and far-field shielding region. When the distance between the radiation source and the shield is larger than $\lambda/2\pi$ (where $\lambda$ is the wavelength of the source), it is in the far-field shielding region. The electromagnetic plane wave theory is generally applied for EMI shielding in this region. When the distance is less than $\lambda/2\pi$, it is in the near-field shielding and the theory based on the contribution of electric and magnetic dipoles is used for EMI shielding.

Three mechanisms govern the amount of attenuation on EMI offered by a shield;

- The first is reflection (SER) of the wave from the shield. This occurs when the constituents of the shield work as an antenna and reflect the incident wave. This phenomenon is independent of the shield thickness and is a function of the material’s
conductivity, magnetic permeability, and frequency. When the wave impinges the surface of the object, it forces charges in the object to oscillate. This forced oscillating charge behaves as an antenna. The incident field is reflected in a pattern associated with a signal charge oscillating antenna, and hence the EMI is attenuated. Thus the shield prevents the wave from transmitting through it. This occurs only when there is a mismatch in impedance of the wave in free space and the shield. Hence, the mismatch may be higher or lower, shielding efficiency may be positive or negative. When an electromagnetic wave encounters a shield, if the wave’s impedance differs significantly from that of the shield, the wave is partially reflected back. Conversely, if the wave’s and the shield’s impedance are closely matched, the EMI energy will pass through the shield with minimal reflection. An electrically dominant wave (E-field) in the near field has high impedance (greater than 377 W). Higher conductive metals have low impedance and are successful at reflecting back electrically dominant waves because of the impedance mismatch. Reflection of EMI is the primary shielding mechanism for electrically dominant waves. Magnetically dominant waves (H-fields), on the other hand, have low impedance (less than 377 W). With these waves, reflection has no important role in shielding. Magnetic waves are more difficult to shield; however, their energy generally diminishes as the distance from the source increases. Over greater distances (far field), the electric field component dominates the wave, and it is this electrical component that must be dealt with through EMI shielding.

- The second phenomenon of EMI shielding is absorption (SEA) of the wave into the shield as it passes through the shield. Absorption in an EM shield transforms EM energy into thermal energy. EM shield made of EM absorbers attenuate undesirable EM waves and substantially solve EMI. The absorption loss does not depend on the wave impedance of the impinging field, and thus is not directly related to near-field or far-field conditions of the system. The shield’s effectiveness varies with frequency, shield geometry, positioning within the shield, type of field being attenuated, directions of incidence, and polarisation. In general, the materials used for absorbing EM waves can be classified into two groups: (1) materials with high dielectric constant, such as BaTiO₃, carbon particles, and (2) materials with high permeability, such as Fe₃O₄,
ferrite materials. Materials with high dielectric constant absorb the electric energy and convert it into thermal energy, while materials with high permeability convert the magnetic energy into thermal energy. EM absorbers could be applied in many fields besides EMI suppression i.e. radar camouflage and stealth technology, microwave noise control, microwave antenna patterning, microwave curing and heating, and finite resistance paths [38].

- The third is due to the re-reflections, i.e. the multiple reflections (SEm) of the waves at various surfaces or interfaces in the shield. This is neglected when the shielding due to absorption is higher than 15 dB. SE in decibel (dB) is a measure of the reduction of EMI at a specific frequency achieved by a shield, such as a coating.

Thus models must assume effective application of different mechanisms of shielding:

- Effectiveness of the reflection mechanism on interfacial surfaces, which among other things depends on their size. In the case of composite materials, this effect is obtained by implementing extenders with expanded specific surfaces.

- Losses caused by multiple reflections are negligibly small, when a distance between successive reflection surfaces (interfaces) is big in comparison to the depth of penetration, because of the skin effect. Hence effective use of whole cross section area of the elementary unit of extender, its size should be comparable or less than a depth of penetration.

- Effective absorption of radiation is obtained in material with a high permittivity and / or with a high magnetic permeability. The distribution of inner field is mainly determined by the orientation and the polarisation of the incident field. In order to achieve a relatively high and constant value of the shielding effectiveness, it is necessary to use anisotropic materials with certain number of layers displaying different orientation of fibres.

**EMI shielding efficiency measurements**

The techniques to measure the shielding effectiveness EMI shielding components include a variety of standard methods. A shielding effectiveness value can generally be
obtained using radiated measurement methods, transfer impedance testing methods, and other methods. Each measurement method is producing a performance value that is usually hard to correlate with the value obtained using another measurement method [21].

The complex S (scattering) parameters of materials measured by using a commercial vector network analyzer (VNA) in the radio and microwave frequency range provide complex permittivity and permeability, electromagnetic interference shielding efficiency characteristics. The S parameters represent the reflection and transmission coefficient of the materials, which are important for both scientific research and industrial applications. One can measure the EMI SE by using the ASTM D4935-99 method up to 1.5 GHz. However, for planar materials such as free standing film or thin film, this measurement technique has a major problem such that the results might be inaccurate and irreproducible due to contact resistance between the sample and sample holder [39-40]. The development of modern analyzers made the measurement easy and there is no paucity for data. But the transformation of S-parameter measurements from reference plane requires the knowledge of the position of the sample in the sample holder which is limited in many applications [41].

EMI shielding efficiency can also be derived from complex permeability and permittivity. The measurement of complex permittivity or permeability through cavity perturbation technique can provide more accurate data. The higher end radiowaves at S and X band can be measured using this technique [42].

The S band corresponds to frequencies of 2-4 GHz and X band corresponds to 4-10 GHz. In S band region, there will be a drastic change in polarisation mechanisms of materials as shown in the scheme. The Important applications of S band (2-4 GHz) is in satellite communication as it is used by NASA. It is used in wireless networking devices which comes under IEEE standards. For example, Wireless LANs and wireless-fidelity. Multimedia applications like mobile TV and satellite radio use S-band as their frequency range. Home based consumer electronics like microwave oven, cordless phones, wireless head phones, applications related to blue-tooth use S-band frequency.
Dielectric property measurements in microwave region

The methods of measuring the dielectric properties of the material in microwave frequencies can be divided into two main categories [43]: (1) non-resonant methods and (2) resonance methods. Non-resonant method mainly includes reflection methods and transmission/ reflection methods. Due to relative simplicity transmission/ reflection methods are used in broad-band measurements. A measurement in this method involves placing the sample in a section of waveguide or coaxial lines and measuring the two-port scattering parameters. Reflection methods utilize information on the reflection of electromagnetic (EM) wave from free space to the sample under test to extract the value of the dielectric constant of the sample. In transmission/ reflection methods, the dielectric properties are calculated on the basis of reflection from the sample and transmission through the sample.

Resonance methods are used to get accurate knowledge of dielectric properties at a single frequency or several discrete frequencies [44, 45]. These methods generally include the resonator method and the resonance perturbation method. The resonator method is based on the fact that the resonant frequency and quality factor of a dielectric resonator with given dimensions determined by its permittivity and permeability. The resonance perturbation method is based on resonance-perturbation theory. For a resonator with given EM boundaries, when some of the EM boundary conditions are changed by introducing a sample, its resonant frequency and quality factor will also be changed. From the changes of the resonant frequency and quality factor, the properties of the sample can be derived. The most common resonance techniques are those based on resonant cavities formed from a rectangular or circular waveguide. Shaw and Windle [46] reported a measurement technique for fabric samples at 3 GHz using cavity perturbation method, which can be counted as one of the best. When a cavity is excited to resonance at a frequency, in the fundamental or TM10 mode, the electric field in the cavity is directed parallel to the cylinder axis. The standing wave possesses a maximum at the axis and falls to zero at the cylinder walls. A piece of sample material placed therein affects the resonant frequency and quality factor of the cavity. The fundamental advantages of using a cavity resonator are narrow bandwidth (hence, it is perturbation sensitive) and high
fields (hence, it is able to achieve a substantial change in signal due to small change in permittivity).

**Composites of PANI for EMI shielding**

Microwave parameters such as complex permittivity, absorption, reflection and SE of bulk PANI, which was doped with two proprietary sulphonate dopants, were measured over a broadband of 4-18 GHz using coaxial line techniques [47]. The permittivity decreased monotonically with increase of frequency. The real part varied from 188 at 4 GHz to 32 at 10 GHz and 10 at 18 GHz; the imaginary part varied from about 35 at 4 GHz to ca. 2 at 8 GHz. The microwave SE of the PANI, calculated on the basis of the measured complex permittivity, was lower than -15 dB over the frequency range. Lower values as -50 dB was estimated for multilayer of PANI. The reflection loss and absorption loss were -5 to -1 dB and -5 dB over the range, respectively.

Free standing PANI films with different thicknesses, prepared by solution cast of EB in NMP and doped with HCl thereafter, were tested for EMI shielding in broadband ranges from 50 MHz to 13.5 GHz by both the ASTM sample holder and a new flanged coaxial line sample holder [40]. EMI SE measured using both holders agreed well in the range of 50MHz to 1.5GHz, as well as with the theoretical SE calculated based on conductivities. The thicker the films, the higher the SE values. In the higher frequencies (1.5-13.5 GHz), it was confirmed that the coaxial line method yielded reliable results.

Shacklette and coworkers were the first to report the EMI shielding with PANI composites [48]. An ultra-high dielectric constant composite of polyaniline, was synthesized using in-situ polymerisation of aniline in an aqueous dispersion of poly-acrylic acid in the presence of dodecylbenzene sulphonate [49]. At low frequency, PANI was reported to possess a dielectric constant larger than 104 in a partially crystalline system, for which an inhomogeneous disorder model was proposed. Still higher values around 1120 at 1 kHz and 433 at 10 kHz were reported for PANI / polyurethane composite [50]. In some cases doped PANI itself in insulating matrix gives high dielectric constant of $10^5$. The doped PANI is a
A typical system which consists of two types of charged species, one polaron/bipolaron system which is mobile and free to move along the chain, the others are bound charges (dipoles), which have only restricted mobility and account for strong polarisation in the system. However in S band region, the dielectric constant of PANI was lower as around 3 and it decreased with frequency [51]. PANI composited with PANI-TiO₂ composites are found to have increased dielectric than pristine PANI and EMI shielding of -31 dB at 10 GHz [52].

The exact conditions and reason for ultrahigh dielectric constant is not explained.

**Electrically conducting fabrics for EMI shields**

Electrically conducting fabrics developed by metal coating or metalwire weaving are used as EMI shields [1-7]. The Ni-Cu-P coating fabric was obtained by electroless plating. The surface morphology, crystal structure, composition, surface resistance and electromagnetic interference (EMI) shielding effectiveness of Ni-Cu-P plated PET fabric were investigated. The result showed that under the same amount of plating, the EMI shielding performance of the copper plated fabric is better than that of the copper-nickel plated fabric which is better than that of nickel plated fabric. After copper tinted, the nickel plated fabric shows obviously improved in its shielding performance [53].

Trivedi and Dhawan grafted PANI on surfaces of fabrics and measured their EMI SE using the coaxial transmission line method in the frequency range of 1000 kHz to 1 GHz. The results showed that at higher frequencies (0.1 MHz to 1 GHz), the SE is at 16–18 dB; while at lower frequencies it is more than 40 dB [54, 55]. Polyaniline and polypyrrole were grafted over cotton fabrics by in-situ polymerisation. The microwave absorption studies of the conducting fabrics in X-band (8.2-12.4 GHz) show absorption dominated total shielding effectiveness in the range 11.3 to 11.7 dB (>92% attenuation) and 9.2 to 9.6 dB (>88% attenuation) for fabrics grafted with PPYand PANI, respectively [56]. Polypyrrole coated fabrics was tried for microwave absorbtion and heating by Kaynak research group [57-59]. PEDOT coated fabrics also proved to be good EMI shields [60]. PANI coated fabrics were efficient in absorbing microwave frequencies in the range of 6-14 GHz [61]. But no studies are done with coated fabrics in the S band EMI shielding.
**Aim of the present study**

From the literature survey it is deduced that PANI-TiO$_2$ hybrids have enormous scope in EMI shielding. The fabric with EMI shielding property will of great advantage as it is flexible and durable in mechanical strength. According to the literature, there is limited study on the dielectric characteristics and EMI shielding properties of OCP coated fabrics in ‘S’ band region. Hence in the present study, electrically conductive fabrics were tested for EMI shielding in S band region. PANI-TiO$_2$ hybrid coated cotton, silk and PET were used for the study. The dielectric property of coated fabrics was studied. The frequency dispersion of complex permittivity was examined using cavity perturbation technique. This technique is non-destructive, simple and requires specimen of relatively small size.

**5.2 Experimental details**

PANI-TiO$_2$ coated fabrics of cotton, silk and polyester were prepared as per the procedure described in chapter III.

Cavity perturbation technique was used to measure the complex dielectric permittivity of materials in S band region. It was determined with the help of a vector network analyzer in the S (2–4GHz, Rohde &Schwarz-ZVB4). Rectangular cavity of dimensions 3.4 cm×7.2 cm×30.8 cm with a narrow line slot to insert the sample material into the cavity was fabricated. Calibration was performed by the method of through-open-short-match (TOSM) before carrying out the measurements. The microwave cavity was perturbed at different frequencies corresponding to different TE10n modes. The cavity perturbation technique is based on the change in the resonant frequency and quality factor of the cavity due to the insertion of a sample into it at the electric field maximum. The real part of the dielectric permittivity ($\varepsilon'$) is

$$\frac{\Delta f}{f_s} = 2v_s/v_c(\varepsilon' - 1)$$

$\Delta f$ = Shift in resonance frequency, $f_s$ is the frequency when sample is loaded. $v_c$ and $v_s$ are the volume of the cavity and that of sample respectively.
Imaginary part or dielectric loss ($\varepsilon''$) is given by

$$\frac{1}{2Q_c} - \frac{1}{2Q_s} = \frac{2v_s}{v_c} \varepsilon''$$

where $Q_s = f_s/\Delta f$ and $Q_c = f_c/\Delta f$

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

$$SE = 10 \ln \frac{P_{in}}{P_{out}} = 20 \ln \frac{E_{in}}{E_{out}} = SE_a + SE_r + SE_m$$

Here, $P_0(E_0)$ and $P_t(E_t)$ are the power (potential) of incoming and outgoing waves, respectively. $SE_a$, the shielding due to absorption, $SE_r$ is the shielding due to reflection and $SE_m$ is the shielding due to multiple reflection.

$$SE_a = 8.68 \alpha$$

$$SE_r = 20 \log \left(\frac{1+n}{4|n|}\right)$$

$$SE_m = 20 \log \left|1 - \frac{1-n}{1+n} \exp(2\gamma l) \tan^2 \delta\right|$$

$$\alpha = \left(\frac{2\pi}{\lambda_0}\right) \sqrt{\frac{(1+\sqrt{1+\tan^2 \delta})}{2}}$$

$$n = \sqrt{\frac{(1+\sqrt{1+\tan^2 \delta})}{2}} + i \sqrt{\frac{(1+\sqrt{1+\tan^2 \delta})}{2}}$$

$$\gamma = \left(\frac{2\pi}{\lambda_0}\right) \sqrt{\frac{(1+\sqrt{1+\tan^2 \delta})}{2}} + i \sqrt{\frac{(1+\sqrt{1+\tan^2 \delta})}{2}}$$

5.3 Results and Discussion

The dielectric property of native fabrics, pristine PANI coated fabrics and PANI-TiO$_2$ hybrid coated fabrics were studied and EMI shielding efficiency was calculated. The real and imaginary parts of permittivity $\varepsilon'$ and $\varepsilon''$ of native fabrics are given in fig 5.1 and fig 5.2. Cotton fabric had comparatively lower $\varepsilon'$ and $\varepsilon''$ and it decreased with increase in frequency.
In the case of silk and PET, there were abrupt ups and downs. The static electricity of native silk and PET may be the cause for higher values of $\varepsilon'$ and $\varepsilon''$.

The change in $\varepsilon'$ and $\varepsilon''$ of hybrid coated cotton fabrics with respect to TiO$_2$ content is given in fig.5.3 and fig.5.4 respectively. The real part of permittivity was consistent in frequency range studied, but decreased with TiO$_2$ content. This decrease may be due to reduction in ionic polarisation.

The factors which affect the polarisation of bound charges will affect $\varepsilon'$ and $\varepsilon''$. The greater the polarisability of the molecule, higher is the $\varepsilon'$ of the material. The polarisability depends on the dipole density and their orientation [23]. The Ti$^{4+}$ ions sit in the octahedral interstices formed by six O$^2-$ ions. At room temperature, there is a possible minimum energy position for the Ti$^{4+}$ ion, which is off-centered and gives rise to permanent electric dipoles formed with six O$^2$-. Similarly, the conducting polyaniline in its emeraldine base form, when protonated by sulphonic acid solutions, possesses permanent electric dipoles. Therefore, in both cases, orientation (dipolar) polarisation is the dominant polarisation and the associated relaxation phenomenon constitutes the loss mechanisms. But this polarisation will be feable in S band region. It can be assumed that dielectric property in the S band region is the result of dipolar (orientation) polarisation and ionic polarisation, in which latter is contributing the major part. In the presence of TiO$_2$, effective doping of PANI with CSA may not take place as discussed in chapter II. This will reduce the ionic polarisation.

At lower content of TiO$_2$, $\varepsilon''$ of coated cotton fabric was independent of frequency (fig.5.4). When TiO$_2$ content was increased, $\varepsilon''$ increased with frequency. This increase may be attributed to the increased relaxation loss. There was no semi-circular relationship between $\varepsilon'$ and $\varepsilon''$, which shows existence of some relaxation unlike Debye type relaxation. The decrease in $\varepsilon'$ and $\varepsilon''$ for hybrid coated cotton when compared to pristine PANI coated cotton may be due to the restriction imposed on the dipole orientation. The mobile electron carriers
can be trapped in TiO$_2$ sites and may be another reason for the lower dielectric of hybrid coated fabrics.

In the coated fabrics, there are two interfaces; one between fibre and hybrid, and other within the hybrid. Within the hybrid, contact between a semiconductor and another phase generally involves a redistribution of electric charges and the formation of a double layer. The transfer of mobile charge carriers between the semiconductor and the contact phase, or the trapping of charge carriers at surface states at the interface produces a space charge layer. A n-type semiconductor such as TiO$_2$ can have surface states available for electron trapping. The surface region will become negatively charged. To preserve electrical neutrality, a positive space charge layer develops just within the semiconductor causing a shift in electrostatic potential and a bending of bands upward toward the surface. Such interactions become prominent, where dielectric of substrate fabric is less. Here, this accounts for cotton than silk and PET. All coated cotton forms a lossy dielectric with small tan $\delta$ value. In pristine PANI coated fabrics, only one interface counts and results in increased dielectric in cotton and decreased dielectric in silk and PET.

The real part of complex permittivity for PANI coated silk fabrics was lower than the imaginary part (fig.5.5 and fig.5.6). This corresponds to high dielectric loss indicating random dipole rearrangements in silk, which may be due to loss of crystallinity. When coming to hybrid coated silk with high TiO$_2$, $\varepsilon'$ was randomly distributed over the range of frequency studied. The tan $\delta$ corresponding to dielectric loss was higher in hybrid coated silk than in PANI coated silk.

Coated PET fabrics have high dielectric loss as in the case of coated silk, which need not be conductive, but due to realignment of molecules within themselves. The real part of complex permittivity of coated PET fabrics is given in fig.5.7. It decreases with increase in frequency at low TiO$_2$ content. On varying the TiO$_2$ ratio, the dielectric constant varies abruptly. When the ratio of TiO$_2$ to PANI is 1:1, dielectric constant increases with frequency. This indicates that the polarisation mechanism contributing to the dielectric constant differs with respect to TiO$_2$ content. In pristine PANI coated fabrics, the polarisation mechanism may
be combination of orientation (minor part as it dies out in S band frequency) and ionic and hence decreases with increase in frequency. The polar nature of PANI and CSA may be the contributing factor for this polarisation. As the TiO$_2$ content increases, CSA incorporated decreases and hence this polarisation decreases. When TiO$_2$ content is equal to PANI, the ionic polarisation fades out and orientation polarization only prevails, which is not so strong. This orientation polarization increases on increasing the frequency as orientation can change by absorbing higher frequencies. The imaginary part of complex permittivity follows the opposite trend with respect to the real part (fig.5.8). The dielectric relaxation process may be high in pristine PANI and it decreases with TiO$_2$ content.

**EMI shielding efficiency**

Total EMI shielding efficiency is the sum of shielding due to reflection, absorption and multiple reflections. The effectiveness of shielding by each mechanism is calculated from the complex permittivity values. EMI shielding due to reflection for coated cotton fabrics is given in fig 5.9. It decreased with TiO$_2$ and was independent of frequency. It is in accordance to reported literature [35]. **Fig.5.10** shows shielding efficiency of coated cotton by absorption. It was very low showing that these coated fabrics could not be used as microwave absorbers in S band region. SEa decreased with frequency, showing that there exist some slow relaxation processes, which fail to respond at increased frequency. The shielding due to multiple reflections was also relevant as the SEa was low. This is given in fig.5.11.

SEr was above 20 dB for PANI coated silk and hybrid coated silk with low TiO$_2$ (fig.5.12). On increasing the TiO$_2$ content, SEr decreased dramatically and varied randomly with frequency. SEa for coated silk fabrics was greater than in coated cotton. It decreased with frequency (fig.5.13). SEm varied abruptly with frequency and TiO$_2$ content (fig.5.14). Non-uniformity of coating, interactions within the hybrid and between the fabric and hybrid may all contribute the shielding mechanisms that make a simple explanation difficult.
The SEr, SEa and SEm for coated PET fabrics are shown in fig. 5.15, fig. 5.16, and fig. 5.17 respectively. It showed ups and downs that may be due to the complex interactions. There is no regulating trend in increase or decrease of shielding with respect to frequency. SEa and SEm follows the similar trend.

The reflection shielding is more prominent in coated cotton, coated silk and coated PET fabrics. It is in accordance to the result reported in literature [52] explaining shielding effectiveness of PANI composites. Absorption shielding was very low in all coated fabrics. It may be due to the low values of tanδ (ε″/ε′). Hence, the fabrics will not be heated up on the radiation and can be used as capacitors. There were drastic changes in dielectric property and shielding effectiveness with respect to TiO₂ content. Several factors like uniformity in coating, interactions between fiber and hybrid etc may be contributing to it.

The total shielding effectiveness of coated cotton, silk and PET is given (fig. 5.18-fig. 5.20). As the target value of the EMI shielding effectiveness needed for commercial applications is around 20 dB, it is evident that all these fabrics can work as efficient shields for S band frequencies of electromagnetic spectrum.
Fig 5.1. Real part of permittivity $\varepsilon'$ of native fabrics
Fig 5.2 Imaginary part of permittivity $\varepsilon''$ of native fabrics.
Fig 5.3. Real part of permittivity $\varepsilon'$ of coated cotton fabric
Fig 5.4. Imaginary part of permittivity $\varepsilon''$ of coated cotton fabric
Fig 5.5. Real part of permittivity $\varepsilon'$ of coated silk fabric.
Fig 5.6. Imaginary part of permittivity $\varepsilon''$ of coated silk fabric
Fig 5.7. Real part of permittivity $\varepsilon'$ of coated PET fabrics
Fig 5.8. Imaginary part of permittivity $\varepsilon''$ of coated PET fabric
Fig 5.9. Shielding efficiency by reflection for coated cotton fabric
Fig 5.10. Shielding efficiency by absorption for coated cotton fabric

![Graph showing shielding efficiency](image-url)
Fig 5.11. Shielding efficiency by multiple reflection for coated cotton fabric
Fig 5.12. Shielding efficiency by reflection for coated silk fabric

![Graph showing shielding efficiency by reflection for coated silk fabric. The x-axis represents TiO$_2$ ratio with respect to PANI, and the y-axis represents $SE_r$ (dB). The graph includes lines for different frequencies: 3.6 GHz (blue), 3.2 GHz (green), 2.8 GHz (red), and 2.5 GHz (brown).]
Fig 5.13. Shielding efficiency by absorption for coated silk fabric
Fig 5.14. Shielding efficiency by multiple reflection for coated silk fabric
Fig 5.15. Shielding efficiency by reflection for coated PET fabric
Fig 5.16. Shielding efficiency by absorption for coated PET fabric
Fig 5.17. Shielding efficiency by multiple reflection for coated PET fabric

![Graph showing shielding efficiency vs TiO2 ratio with respect to PANI for different frequencies (3.6 GHz, 3.2 GHz, 2.8 GHz, 2.5 GHz). The graph plots SEM (dB) on the y-axis and TiO2 ratio with respect to PANI on the x-axis. There are four lines in different colors representing the different frequencies.](Image)
Fig 5.18. Total Shielding efficiency for coated cotton fabric
Fig 5.19. Total Shielding efficiency for coated silk fabric
Fig 5.20. Total Shielding efficiency for coated PET fabric
5.4. Summary

- The dielectric property and EMI shielding efficiencies of PANI-TiO$_2$ hybrid coated fabrics were studied.
- The real and imaginary part of complex permittivity obtained from cavity perturbation method was reliable data for calculating EMI-SE of fabrics.
- EMI shielding by reflection was prominent in all cases.
- The pristine PANI coated cotton fabric was more efficient in EMI shielding than hybrid coated cotton fabrics.
- The shielding was consistent in the range of frequency studied in the case of coated cotton fabric, while varied abruptly for coated silk and coated PET fabrics.
- The EMI shielding efficiency of hybrid coated silk and PET fabrics ($S_{0.1}$ and $P_{0.1}$) was higher than their corresponding pristine counterparts.
- In all cases studied, the total shielding efficiency was above the threshold limit of 20 dB required for commercial applications.
- Among the coated fabrics studied for EMI shielding, cotton behaved better than silk and PET.
References


