Development and Microwave characterization of selected Biocompatible materials and Conducting polymers

Thesis submitted to the Cochin University of Science and Technology
in partial fulfilment of the requirement for the degree of
***Doctor of Philosophy** under the Faculty of Technology*

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Declaration

I hereby declare that the work presented in this thesis entitled **"Development and microwave characterization of selected biocompatible materials and conducting polymers"** is a bona fide record of the research work done by me under the supervision of Dr. K. T. Mathew, Department of Electronics, Cochin University of Science and Technology, India and that no part thereof has been presented for the award of any other degree.

Cochin
14th June 2013

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Certificate

This is to certify that the thesis entitled **"Development and microwave characterization of selected biocompatible materials and conducting polymers"** is a bona fide record of the research work carried out by Mr. Ullas G. Kalappura under my supervision in the Department of Electronics, Cochin University of Science and Technology. The results presented in this thesis or part of it have not been presented for the award of any other degree.

Cochin
14th June 2013

Dr. K. T. Mathew
(Supervising Guide)

Abstract

The 20th century witnessed the extensive use of microwaves in industrial, scientific and medical fields. The major hindrance to many developments in the ISM field is the lack of knowledge about the effect of microwaves on materials used in various applications. The study of the interaction of microwaves with materials demanded the knowledge of the dielectric properties of these materials. However, the dielectric properties of many of these materials are still unknown or less studied. This thesis is an effort to shed light into the dielectric properties of some materials which are used in medical, scientific and industrial fields. Microwave phantoms are those materials used in microwave simulation applications. Effort has been taken to develop and characterize low cost, eco-friendly phantoms from Biomaterials and Bioceramics. The interaction of microwaves with living tissues paved way to the development of materials for electromagnetic shielding. Materials with good conductivity/absorption properties could be used for EMI shielding applications. Conducting polymer materials are developed and characterized in this context.

The materials which are developed and analyzed in this thesis are Biomaterials, Bioceramics and Conducting polymers. The use of materials of biological origin in scientific and medical applications provides an eco-friendly pathway. The microwave characterization of the materials were done using cavity material perturbation method. Low cost and eco-friendly biomaterial films were developed from Arrowroot and Chitosan. The developed films could be used in applications such as microwave phantom material, capsule material in pharmaceutical applications, trans-dermal patch material and eco-friendly Band-Aids. Bioceramics with better bioresorption and biocompatibility were synthesized. Bioceramics such as Hydroxyapatite, Beta tricalcium phosphate and Biphasic Calcium Phosphate were studied. The prepared bioceramics could be used as phantom material representing Collagen, Bone marrow, Human abdominal wall fat and Human chest fat. Conducting polymers- based on Polyaniline, are developed and characterized. The developed materials can be used in electromagnetic shielding applications such as in anechoic chambers, transmission cables etc.

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Without a lot of people this thesis would never have come to be. To name them all and not to forget anybody is the hardest task I had in writing this thesis.

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Chapter 1

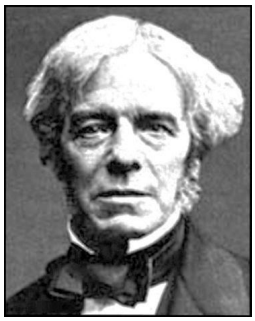
Introduction and Research Design

1.1 History of Electromagnetics

Electromagnetics may be defined as the branch of science which deals with the interaction and effects of forces that act between charged particles. The forces can be either magnetic or electric. They are characterized by electric or magnetic fields which they create. The force exerted by an electromagnetic wave, which is a combined effect of electric and magnetic forces, is one of the four fundamental interactions in nature. Except for the case of gravity, all other daily phenomena can be related to electromagnetism. The electromagnetic wave is propagated by the oscillation of the mutually perpendicular electric and magnetic fields which are in phase. Electromagnetic field is responsible for producing electromagnetic radiation. Electromagnetic radiation is a form of energy which exhibits wave like behaviour when it moves through space. In vacuum, electromagnetic radiation propagates at the speed of light (299792458 m/s). The electromagnetic field itself is formed by moving charges. A static charge can produce electric or magnetic field only. An electromagnetic radiation is formed due to the electromagnetic fields which are far away from the moving charges which produced it such that the absorption of the radiation doesn't affect the motion of the charges. Therefore it may be also considered as a far field, whereas charges and currents produce near field. The electric and magnetic fields are related intrinsically. A change in electric field can produce magnetic field and vice versa.

The application of electromagnetic waves has achieved tremendous progress in the last century. From radio transmissions, to mobile communications and satellite stations the applications of electromagnetic waves are countless. Each and each day several new discoveries are made. People cannot imagine a world without cellular communications today. The first observation on the effect of electric current on magnetic field was by Hans Christian Oersted on 1820 when he saw a magnetic needle got deflected when he turned on/off the current from the battery with a switch. This incident convinced him that electric and magnetic fields are mutually related.

Hans Christian Oersted



Michael Faraday

Andre Marie Ampere

His later publications proved that an electric current produced a magnetic field as it moved through a wire. His findings inspired many other talented scientists of the same era like Ampere, Faraday, Maxwell and Hertz. Ampere developed a single mathematical form to represent the magnetic forces between current-carrying conductors. Similarly, Michael Faraday, who is generally regarded as the best experimentalist in the history of science, discovered magnetic field, electromagnetic induction, diamagnetism and electrolysis. Faraday also established that magnetic fields could affect rays of light. These crucial discoveries even lead to understand the nature of light.

James Clerk Maxwell took the work of Faraday and others, and summarized it in a set of equations that is accepted as the basis of all modern theories of

electromagnetic phenomena. Maxwell's equations suggest that electricity, magnetism and light are all manifestations of electromagnetic field. He

James Clerk Maxwell

Heinrich Hertz

demonstrated that electric and magnetic fields travel through space in the form of waves and at the constant speed of light. His unified model of electromagnetism is regarded as one of the greatest advances in physics.

Heinrich Hertz experimentally proved the existence of electromagnetic waves. He engineered instruments which could transmit and receive radio pulses. The scientific unit of frequency was named "hertz" (Hz) in his honor by the International Electro-technical Commission. In 1894 J.C. Bose publicly demonstrated radio control of a bell using millimeter wavelengths, and conducted research into propagation of microwaves. Marches Guglielmo Marconi, achieved signal transmission by means of radio waves over 10m in 1895 and over the Atlantic Ocean in 1901.

1.1.1 Electromagnetic spectrum

The electromagnetic spectrum covers a wide range of frequencies ranging from the low frequency RF signals used for radio communication to the extremely high frequency cosmic rays. The wave length covered extends from thousands of kilometers down to the size of an atom. Radio waves, microwaves, x-rays, gamma

rays etc. are all electromagnetic radiation. Each of them has a different interaction mechanism with living matter. Low frequency RF waves and Microwaves are non-ionizing radiations. But high frequency waves like X-rays are ionizing. Prolonged exposure to such radiation can even cause genetic mutation. The visible light, which is also an electromagnetic wave, is blocked by living tissue. Body tissues are opaque to visible light. Figure 1.1 shows the electromagnetic spectrum.

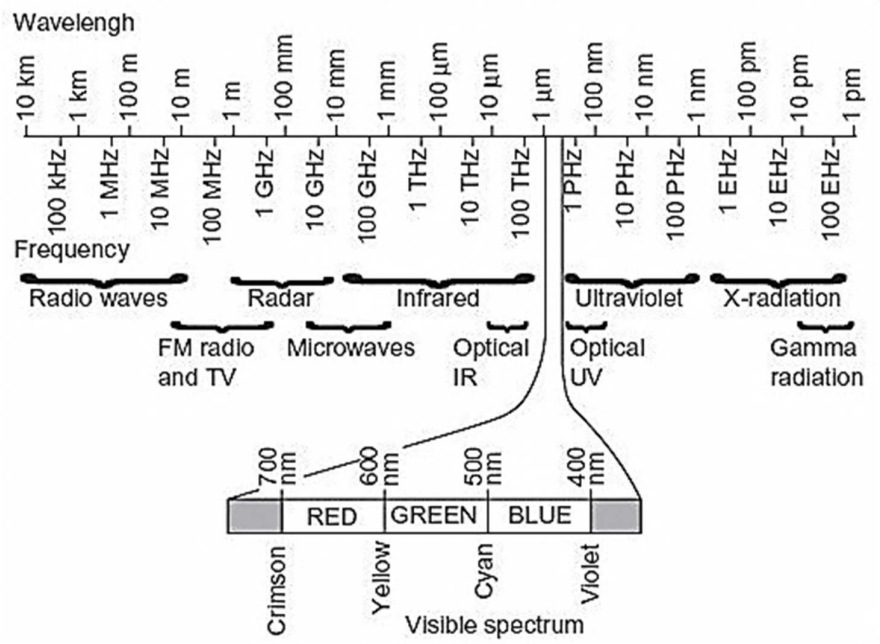


Figure 1.1 Electromagnetic Spectrum

1.1.2 Radio & Microwaves

RF/Microwave frequencies are characterized by their ability to radiate. If the wavelength of the signal is smaller than the structure, then it can efficiently radiate. A structure which is smaller than the wavelength poorly radiates. RF energy has been used for treatment in medical field. The Magnetic resonance imaging (MRI) technique uses radio frequency waves to image human body. The RF frequency spectrum covers the medium frequency (MF), high frequency (HF),

Table 1.1 Microwave frequency bands

Frequency	Microwave Band designation	
	New	**Old**
500-1000MHz	VHF	C
1-2 GHz	L	D
2-3 GHz	S	E
3-4 GHz	S	F
4-6 GHz	C	G
6-8 GHz	C	H
8-10 GHz	X	I
10-12.4 GHz	X	J
12.4-18 GHz	Ku	J
18-20 GHz	K	J
20-26.5 GHz	K	K
26.5-40 GHz	Ka	K

and very high frequency (VHF) bands. Frequencies, from RF as low as 400kHz through microwave frequencies as high as 10GHz, are presently being investigated for therapeutic applications in areas such as cardiology, urology, surgery, ophthalmology, cancer therapy, and others and for diagnostic applications in cancer detection, organ imaging etc. The boundary between RF and Microwave spectrum is not well defined. It continuously changes with the advances in technology and devices. In general, microwave frequencies are considered to be ranging from 300MHz -300GHz of the electromagnetic spectrum. The low frequency RF circuits systems are much smaller than the wavelength of the signals they use. But at microwave frequencies, the size of the electronics components is often comparable to the wavelength of the signal. Microwave frequency bands in old and new designations are shown in Table 1.1

1.1.3 Maxwell's equations

James Clerk Maxwell did the unification of laws of electromagnetics. Faraday's law, Ampere's law and Gauss law were unified by Maxwell. This unification of laws concerning electromagnetism have been called the "second great unification in physics", after the first one realized by Isaac Newton. Maxwell also introduced the concept of displacement current to overcome the inconsistency of Ampere's law. The Ampere's law was unsuccessful in explaining time varying equation of continuity. This inconsistency was circumvented when Maxwell introduced the concept of displacement current. The displacement current is responsible for the propagation of electromagnetic waves inside a hollow wave guide. Maxwell demonstrated that electric and magnetic fields travel through space in the form of waves and at the constant speed of light. The Maxwell's equations can be summarized as below.

Differential form	**Integral form**
$\nabla \times H = J + \dot{D}$	$\oint H \cdot ds = \int (J + \dot{D}) \cdot da$
$\nabla \times E = -\dot{B}$	$\oint E \cdot ds = -\int \dot{B} \cdot da$
$\nabla \bullet D = \rho$	$\oint D \cdot da = \int \rho \, dv$
$\nabla \bullet B = 0$	$\oint B \cdot da = 0$

And the equation of continuity for time varying fields,

$$\nabla \bullet J = -\dot{\rho} \qquad \oint J \cdot da = -\int \dot{\rho} \, dv$$

Here $\dot{D}$ is known as the displacement current and is found as $\dot{D} = \frac{\partial D}{\partial t}$

1.1.4 Wireless applications

Heinrich Hertz was the first one who demonstrated the existence of electromagnetic waves. After several decades, the wireless field prospers with

numerous applications in day to day life. Applications like RADAR, Cellular communications, Satellite communications, Imaging applications, WLAN, GPS etc. are most common among them. Another RF and microwave wireless communications system is the personal communications system (PCS). A commonplace example of a PCS is the pager. A pager is similar to a miniature cellular telephone. The pager uses a one-way path; a message is transmitted to the pager, where it is displayed for the user to act on [1]. WLAN is another significant application of wireless network. WLAN is very useful in campuses, hospitals, airports, work places etc. Quick installation, mobility of equipment and increased coverage are the main advantages. Another standard that is widely used is Bluetooth. Bluetooth operates at a frequency of 2.4 GHz, which has been set aside by international agreement for use in industrial, scientific, and medical areas. It provides an approach which enables various devices to communicate with each other within basically a 10 m range. Bluetooth is designed to provide a universal short-range wireless network that is available worldwide for unlicensed low-power use.

Another wireless application is Radio Frequency Identification (RFID) [2]. RFID is a generic term for any combination of circuitry that uses RF or microwave energy to provide a means of identification. RF tags can be active, passive, or semi-passive. Global positioning system (GPS) is also an application for navigational purposes [3]. The system consists of 24 satellites in orbit 20,000 to 26,000 nautical miles above the earth. GPS can show the exact location anywhere on Earth (global), any time, and in any weather. With the proper GPS receiver the signals transmitted from the satellites can be detected and displayed to tell the location. The most familiar application of wireless is perhaps, the RADAR. Measurement and tracking radars lock on to a target and track it for a certain distance or for a certain time period. Military applications of radar systems are for gun control and missile guidance. A special type of RADAR called Doppler RADAR is used by the police to find the speed of moving vehicles. Microwave imaging also uses wireless signals for detection of malicious tissues in a body. The

applications of wireless are playing an important role in the development and advancement of science and humanity.

1.1.5 Microwave Antennas

Antennas are transducers which are used for communication applications. They can send and receive electromagnetic signals. It is usually made of metal, but other materials may also be used. An antenna acts as an impedance transformer between the guiding device and free space. The radiation from an antenna is possible only if the charges are accelerated/ time varying. A static field/uniform varying current carrying element cannot radiate. The charges in the antenna structure, accelerated by an external source sets up a charge flow. These charges reaching the discontinuity or transition in the structure get decelerated and their energy is radiated. The most commonly used antenna types are Monopole, Dipole Antennas, Loop Antennas, Aperture Antennas, Reflector Antennas, Waveguide Horn, Reflector Printed antennas, Array Antennas, Multiple Element Dipole Antennas, Yagi Antennas, Flat Panel antennas, Parabolic Dish antennas, Helix, Slotted Antennas, Microstrip Antennas (MSAs), Phased array antenna and Dielectric resonator antennas.

1.1.6 ISM applications of Microwaves

The ISM band is the portions of RF spectrum which are reserved for the use of RF energy in Industrial, Scientific and Medical applications other than communication purposes. Some most common applications are microwave oven, industrial microwave dryers, fruit dryers, medical diathermy, microwave imaging etc. These machines operate at the ISM band of frequencies. The devices operating at ISM band doesn't require license from FCC [1]. If the emissions from these devices are powerful enough, they can result in electromagnetic interference and affect the devices which are using the same band for communication purposes. In general, communications equipment operating in these bands must tolerate any interference generated by ISM equipment, and users have no regulatory protection

from ISM device operation. In recent years, the ISM band is used for low power communication applications such as Bluetooth, Cordless phone and NFC devices. The ISM bands defined by ITU-R are shown in Table 1.2

Table 1.2 ISM Bands defined by ITU-R

Operating frequency range		Band width	Center frequency
6.765 MHz	6.795 MHz	30 KHz	6.780 MHz
13.553 MHz	13.567 MHz	14 KHz	13.560 MHz
26.957 MHz	27.283 MHz	326 KHz	27.120 MHz
40.660 MHz	40.700 MHz	40 KHz	40.680 MHz
433.050 MHz	434.790 MHz	1.84 MHz	433.920 MHz
902.000 MHz	928.000 MHz	26 MHz	915.000 MHz
2.400 GHz	2.500 GHz	100 MHz	2.450 GHz
5.725 GHz	5.875 GHz	50 MHz	5.800 GHz
24.000 GHz	24.250 GHz	250 MHz	24.125 GHz
61.000 GHz	61.500 GHz	500 MHz	61.250 GHz
122.000 GHz	123.000 GHz	1 GHz	122.500 GHz
244.000 GHz	246.000 GHz	2 GHz	245.000 GHz

The most common device operating at ISM band is the microwave oven. Its operating frequency is 2.45 GHz. The same band is also shared with Wireless sensor networks which operate at 915 MHz and 2.450 GHz bands. It is also shared with Wireless LANs and cordless phones in the 915 MHz, 2.450 GHz, and 5.800 GHz bands. Wireless LAN devices use wavebands as follows:

Bluetooth 2450 MHz band

HIPERLAN 5800 MHz band

IEEE 802.11/WiFi 2450 MHz and 5800 MHz bands

IEEE 802.15.4, ZigBee and other personal area networks may use the 915 MHz and 2450 MHz ISM bands. Also several brands of radio control equipment use the 2.4 GHz band range for low power remote control of toys, from gas powered cars to miniature aircraft.

The microwaves are used in industry mainly for heating and drying purposes. It is either performed at a frequency close to 900MHz or at 2.45GHz. Most of the materials heated at RF can also be heated at microwave frequencies together with some other which are difficult with RF because of their low loss factor [4]. Because microwave heating takes place at a much higher frequency than RF, the chance of arcing is less in Microwave heating. The higher power density enables the plant to be smaller. However, shorter penetration depth may affect the uniformity of heating when compared to RF. The overall efficiency of a microwave system is much higher because of the highly efficient magnetrons (85% at 900MHz and 80% at 2.45GHz) used in the heating system.

Figure 1.2. Front end view of Microwave sludge dryer

Thermotherapy was a popular treatment method from the ancient times itself. Rheumatism and joint/muscle diseases were cured by this method of treatment. EM waves, ultrasonic sound, IR radiation, warm water, oil were the heat sources used. These sorts of therapy utilizing EM waves at wavelengths from several hundred to several tens of meters have been called diathermy. Microwave diathermy and ultrasonic diathermy were popular in medical field. Among these thermotherapies, a hyperthermic method for the malignant tumor has been called hyperthermia. In medical field, radiators using an EM wave or an ultrasound wave are called applicators. The applicators using microwave technology are classified into dielectric heating applicator and inductive heating applicator. Microwaves are also used in medical field for imaging applications. Microwaves are non-ionizing radiation. Hence unlike X-rays, they could be used more frequently for imaging purposes. Prolonged exposure to ionizing radiations can result in cancer and other genetic mutations. Although Microwaves are non-ionizing, effects of prolonged exposure to such radiation have not yet been fully understood. It is still a controversial subject in scientific discussions. The effect of radiation could not be studied unless it is simulated in a material which could mimic living tissues as if in a biological system. For these simulation applications, phantom materials which have dielectric properties similar to human tissues/body parts are used. Low cost, stable phantoms are necessary for such simulation studies involving dosimetry and SAR.

1.2 Microwaves in biology

Biological materials are prone to electromagnetic field. Several applications in medical field involve interaction of living tissue and electromagnetic field. Also humans are living in an electromagnetic layer created by cellular and radio communication signals. The effects of electromagnetic field inside a biological material are determined by several factors and effects. The behavior of such a field depends greatly on the dielectric properties of the material.

1.2.1 Skin effect

When a conducting material is exposed to an electromagnetic field, a current flows through it whose density is limited by collision of electrons moving in a positive ion network. In good conductors the amount of free charges is negligible so that the electron current is free to move without any resistance. In good conductors, the displacement current is negligible with respect to conduction current. The Maxwell's equations which define wave propagation are reduced to a diffusion equation in such materials. And the solution of the diffusion equation gives the parameter Skin depth (δ), which is the decay parameter of the field inside the material. The amplitude of the field is decayed exponentially inside the material.

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \tag{1}$$

For most biological materials the displacement current is of the order of the conduction current over a wide frequency range. In such cases a more general form of the equation may be used to determine Skin depth.

$$\delta = \left(\frac{1}{\omega}\right)\left\{\left(\frac{\mu\varepsilon}{2}\right)\left[\sqrt{1+p^2}-1\right]\right\}^{1/2} \tag{2}$$

Here P is the ratio of the amplitudes of the conduction current to displacement current.

$$P = \frac{\sigma}{\omega\varepsilon}$$

When P is large, Eqn. 2 reduces to Eqn. 1. The skin depth decreases when the frequency, the permeability, and the conductivity of the material increase. Due to Skin effect, at a depth of 3δ, the field amplitude is only 5% of its amplitude at the interface, and the corresponding power is only 0.25%; at a depth of 5δ, the field amplitude reduces to 1% and the corresponding power to 10^{-4}, which is an isolation of 40dB.

1.2.2 Dielectric polarization and relaxation

Polar materials are those materials with permanent dipole moments. Their molecular structure lack center of symmetry (Hydrogen Chloride, Water).

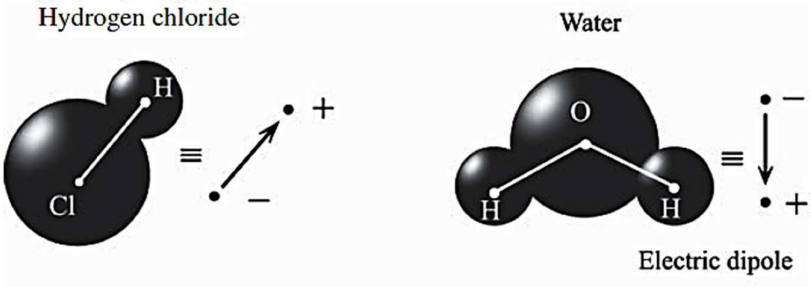


Figure 1.3 Permanent dipole of Polar materials

When an external electric field is applied to a polar material, the dipole orientation is modified; it essentially rotates. For a polar material, the relationship between polarization and applied field is found to be nonlinear. If an electrostatic field is applied to water, then the permanent dipole begins to move in the electric field direction. But this movement is interrupted by an intermolecular binding force and is submitted to resistance from the thermal motion. Therefore there is a time delay for the permanent dipole to align to the direction of the applied field and thereby achieve uniform polarization. If the applied field is suddenly turned off soon after achieving uniform polarization, the dipole returns to the initial state (polarization returns to zero) only after a time delay. The time used by the polarization to decrease to 1/e of its steady-state value is called the relaxation time (τ). The phenomenon is called dielectric relaxation.

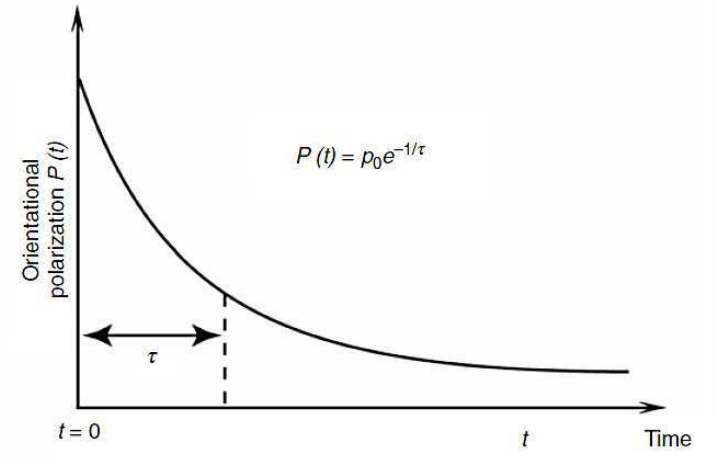


Figure 1.4 Polarization returns to zero when Electric field is cut at t=0

The applied electric field and the polarization p (C/m^2) are related by the relation [5]

$$p = \varepsilon_0 E(\varepsilon_s - 1) \tag{3}$$

When an alternating electric field $E = E_0 e^{jwt}$ is applied to dielectric material exhibition relaxation, the polarization P has a phase delay with respect to the applied electric field. Therefore, complex permittivity has been introduced as the way for expressing the delay of this polarization. Therefore, the dielectric constant is expressed as a complex permittivity. The complex permittivity

($\dot{\varepsilon}_s = \varepsilon_s^{'} - j\varepsilon_s^{"}$) when introduced to Eqn. 3, the expression changes as

$$\dot{p}(t) = \varepsilon_0(\dot{\varepsilon}_s - 1)E_0 e^{j\omega t} \tag{4}$$

Relaxation time is different for different materials. It depends on the dielectric constant of the material. The relaxation time of some materials is shown in Table 1.3.

Table 1.3 Relaxation time of some common materials

Material	Relaxation time τ
Copper	1.51^{-19} s
Silver	1.31^{-19} s
Sea Water	2.01^{-10} s
Distilled Water	10^{-6} days
Quartz	10 days

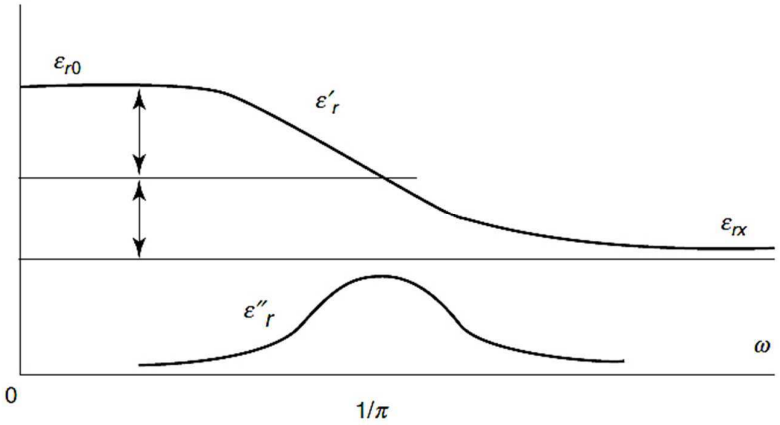


Figure 1.5 Variation of Real and Imaginary part of permittivity due to relaxation effect

Figure 1.5 shows the general behavior of permittivity and loss factor variation with frequency. It can be seen that the imaginary part is nonzero only when the real part varies as a function of frequency. At all other times the loss factor is zero. The real part and the imaginary part can be found from one another by following the variation of the other over the whole frequency range.

1.2.3 Resonance Absorption

Dielectric relaxation occurs due to the ordering of permanent dipoles under the influence of an external field. But matter can take up energy from a system

even without the presence of permanent dipoles if the field perturbs oscillations. An individual atom or molecule consists of positive and negative charges. It can be considered as a harmonic oscillator. The distance between the centers of gravity of this positive and negative charges are altered if the restoring force is overcome. The oscillator takes energy from an electric field, at a resonant frequency, determined by the restoring force. This phenomenon is called resonance absorption. Individual molecules have discrete energy states and they absorb energy from an alternating field of frequency f, so that

$$hf=\Delta W \quad J \tag{5}$$

where ΔW is the energy difference between two quantum levels and h is Planck's constant. The molecule can take up or radiate energy only at the appropriate frequencies and in the appropriate amounts determined by Eqn. 5

1.2.4 RF measurements

The measurement of the dielectric properties of a material is very significant for its use in a scientific or industrial application. It is usually made possible by making the material a part of an electrical circuit and by measuring the variation in the voltages or power levels of the circuit due to the introduction of the material. The specimen is usually introduced into a capacitor, a wave guide or a cavity which is a part of an electrical circuit. Above 1 MHz, the sources generally use CW for operation.

Common discrete circuit elements can be used at very low frequencies of operation. But for frequencies above a few Mega Hz, the use of discrete elements is of no meaning. The inductances and capacitances cannot be realized using discrete elements. They are considered distributed over the circuit. For frequencies up to 1 GHz, resonant circuits can be used. The measurement is usually done with an LCR meter. The energy absorption exhibits a resonant peak and the width of this peak $2\Delta w$ is measured, where Δw is the difference between the frequency where the

energy loss is a maximum and the frequency where it is reduced to half the maximum. The Quality factor (Q-factor) [6] of a series LCR circuit is defined as,

$$Q = \frac{\omega_0}{2\Delta\omega} = \frac{\omega_0 L}{R} = \frac{1}{\omega_0 CR} \qquad (6)$$

As the capacitor is the only lossy component, Q is inversely proportional to tan δ of the dielectric at ω_0.

1.2.5 Microwave measurements

At microwave frequencies, the size of the components in the circuit becomes comparable to the wavelength of the signals used for measurement. Above 300MHz, the shape and size of the measuring assembly becomes important in relation to the wavelength. Earlier microwave measurements used slotted line for material dielectric property characterization. In this technique, the amplitude and phase of an impedance at a given frequency as a function of the position on the line was measured. The propagation term is the product of the propagation constant and the position on the line. Hence, operating at constant frequency as a function of the position on the line yields the same type of results as operating at a given point on the line as a function of frequency. The use of slotted line is limited to one single frequency at a time which makes it less popular in present day measurement setups. Still it is one of the most accurate measurement techniques.

Vector Network Analyzers are used to obtain the amplitude and phase of an impedance at a specific point of a line as a function of frequency. They cover a wide range of frequencies. A Network Analyzer needs to be calibrated properly for measurements. The calibration is done for mismatches, losses, defects, imperfections etc. Calibration compensates all these, so that the actual measurements are not degraded. Short circuit, Open circuit, Matched load and transmission lines with different lengths are used for calibration purposes. Also in certain measurements including comparison, the measurement setup is calibrated with a material with known dielectric properties to find the dielectric properties of

the unknown material [7]. The scattering parameters are used usually for estimating errors. When measuring the electric properties of a dielectric, the container in which the specimen is placed is considered as an electrical two-port. In measurements above 20GHz, the connectors used for the measurement have to be chosen properly as it can result in measurement inaccuracy.

1.3 Electromagnetic compatibility

Electromagnetic compatibility (EMC) deals with the unintentional generation, propagation and reception of electromagnetic energy with reference to the unwanted effects (Electromagnetic interference, or EMI) that such energy may induce. EMC ensures that equipment items or systems will not interfere with or prevent each other's correct operation through spurious emission and absorption of EMI. EMC is sometimes referred to as EMI Control, and in practice EMC and EMI are frequently referred to as a combined term "EMC/EMI". While electromagnetic interference is a phenomenon - the radiation emitted and its effects - electromagnetic compatibility is an equipment characteristic or property - to not behave unacceptably in the EMI environment.

1.3.1 Microwave absorbers

Microwave absorbers are mostly used in military applications. They are also used in applications which demand shielding from EMI signals. The EM wave absorber has been defined as an object that can absorb incident EM waves and convert these into a Joule heat or which can cancel the phase of the incident wave. The level of absorbing ability of the absorber is measured quantitatively using the return loss or reflection coefficient in decibels (dB). A level of -20dB is usually taken as a standard for a wave absorber. A -20 dB value corresponds to a 0.1 value of the reflection coefficient of the electric field and a 0.01 value of the reflection coefficient of electric power. It means that 99% of the total EM wave energy emitted to the wave absorber is absorbed.

1.3.2 Type of microwave absorbers

Electromagnetic wave absorbers are classified based on constituent material, structural shape, frequency characteristics, and application, respectively.

i) Classification by constituent material

Microwave absorbers can be classified according to the constituent material used as resistive type absorbers, dielectric type absorbers and magnetic type absorbers. Resistive type absorbers use resistive materials such as carbon black, graphite nichrome, and chromium as a basic material. They are used either in plate form or in film form. The HF energy which is incident on the surface of a resistive absorber is converted to heat energy (Joule's heat).The dielectric type absorbers use polymer/rubber based materials to absorb microwaves. To the polymer or rubber base, carbon black and other conventional microwave absorbers are added as filler materials. Urethane, styrene and rubber are the materials commonly used. The matching characteristic depends on the frequency dispersion characteristic of the complex relative permittivity of the absorber. Magnetic type absorber is essentially formed of ferrite. The ferrite materials depend on the frequency dispersion characteristics of the complex relative permeability to achieve absorption. Sintering ferrite, rubber ferrite, plastic ferrite etc. are commonly used.

ii) Classification by structural shape

Electromagnetic wave absorbers are also classified on the basis of two structural shapes: one based on number of layers constituting the wave absorber and the other based on appearance.

1. Based on number of layers

EM wave absorbers can be single layer, two layer and multilayer type absorbers. The absorber that is composed of only a single layer or single material is called a single-layer absorber. A conductive plate is attached to the back of this absorber. A typical example of this type is the ferrite wave absorber. The two layer wave absorber is composed of two different absorptive materials. This arrangement

is chosen to obtain broadband absorption characteristics and to improve them. The microwave absorber with more than three layers is usually called a multilayer wave absorber. In this case, the different layers are composed of absorbers with different material constants. The multilayer design ensures broad band operation of the absorber.

2. *Based on appearance*

The microwave absorbers are classified according to their appearance as Plane type wave absorber, Sawtooth type wave absorber and Pyramidal type wave absorber. The plane-type wave absorber has the shape of a plane surface in the incident plane of the EM wave. A ferrite absorber is usually used for this. A sawtooth wave absorber has the shape of a sawtooth in the incident plane of the EM wave. Broad band absorbers can be realized using sawtooth wave absorbers.

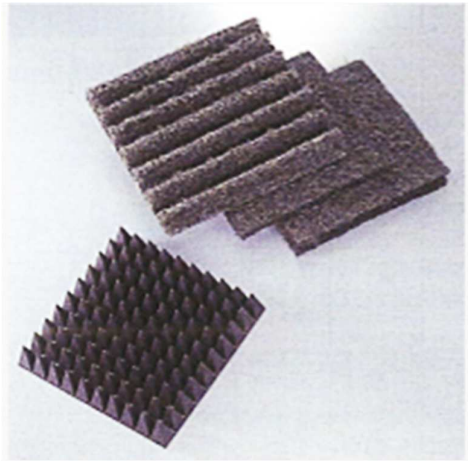


Figure 1.6 Wave absorbers based on shape

A pyramidal type absorber has a broadband frequency characteristic because the absorber has the structure of pyramidal taper in the incident plane of the EM wave. A typical absorber of this kind consists of foam polyurethane rubber containing carbon powder.

1.3.3 Absorption, Reflection and Transmission coefficients

The Reflection coefficient (R) is defined as the ratio of the reflected voltage or current to the respective incident voltage or current.

$$\Gamma = \frac{V_{ref}}{V_{inc}} = \frac{-I_{ref}}{I_{inc}}$$

The Transmission coefficient can be similarly represented as the ratio of the transmitted voltage or current to the respective incident voltage or current.

$$T = \frac{V_{tr}}{V_{inc}} = \frac{-I_{tr}}{I_{inc}}$$

When a wave is incident on a material, part of the wave is reflected back, part is transmitted and the rest is absorbed in the material. It can be represented as,

$$P_I = P_R + P_T + P_A$$

It can be shown that

$$A = 1 - (R + T) \qquad (7)$$

Where,

A is the absorption coefficient $A = P_A/P_I$,

R, the reflection coefficient $R=P_R/P_I$ and

T, the transmission coefficient $T= P_T/P_I$

The magnitude of Γ should never be greater than unity, $|\Gamma| \leq 1$. The microwave absorption is proportional to the thickness of the material. It increases with the increase in thickness of the absorbing material.

1.3.4 Shielding Efficiency

Shielding is defined as the ratio of the electromagnetic field intensity measured before and after the shielding material is installed. The purpose of shielding is to confine radiated energy to the bounds of a specific region, or to

prevent radiated energy from entering a specific region [8]. Shields can be of many forms. Partitions, boxes, cable and connector shields etc. The main characteristic of a shield is its shielding efficiency which is a measure of the decibels by which the shield reduces the field strength. Shielding efficiency depends mainly on the type of material used and the thickness of the material. It also depends on the frequency used, the distance from source to shield and the quantity and shape of shield discontinuities. The design of a shield involves the following steps - finding the field level at a particular point without shielding and finding the tolerable field level. When both these levels are obtained, the difference between them gives the desired shielding effectiveness of the shield.

Shielding can be achieved in three ways,

By reflection – In this mechanism, the incident energy is reflected back by the shield surface. When the wave enters the shield surface, it encounters an impedance discontinuity at the air-metal boundary. Larger the discontinuity, greater the reflection. Here, material thickness is not much significant. This type of shielding depends mainly on the wavelength of the wave and the skin depth of the metal which is used as shield.

By absorption- Here an absorbing material is used as shield. The field gets attenuated as it passes through the shielding material. In these types of materials, the thickness of the shielding material is an important factor which determines shielding effectiveness. The absorption of the energy can result in heating of the shield material.

By internal reflection- This technique uses the combination of absorption and reflection. Here an impedance discontinuity is offered at the other end of the shield. When the energy passes through the shield, it gets attenuated. And when it reaches the other end, it encounters another air-metal boundary. Thus some of the energy again gets reflected back into the shield.

The attenuation through the shield is designated as A,

Absorption loss, $A=1.314\sqrt{f\mu_r\sigma_r}\ d$ dB (8)

Where d = shield thickness in cm

σ_r = conductivity relative to that of copper, σ_c ($\sigma_c = 5.8 \times 10^7\ S/m$)

The reflection loss (R) depends not only upon the surface impedance of the shield, but also on wave impedance and the distance from source to shield (D). For plane waves, the impedance of the wave is a constant 377 ohms. So D doesn't appear in the formula for R for plane waves.

For low impedance (magnetic) source,

$$R = 20\log_{10}\{[1.173\sqrt{\mu_r / f\sigma_r}\,/D] + 0.0535\ D\sqrt{f\sigma_r/\mu_r} + 0.354\}\ \text{dB} \quad (9)$$

For a plane wave source,

$$R = 168 - 10\log_{10}(f\mu_r/\sigma_r) \quad \text{dB} \quad (10)$$

For a high impedance (electric field) source,

$$R = 362 - 20\log_{10}[\sqrt{\mu_r f^3/\sigma_r}\ D] \quad \text{dB} \quad (11)$$

The first reflection of the wave results in a "single reflection loss". Subsequent reflections result in a "multiple reflection correction term" designated as B. B is significant only if $A \le 15$ dB. For $A > 15$ dB, the effect of these internal reflections can be ignored. The correction term B is defined as,

$$B = 20\log_{10}|1 - w^{-A/10}(\cos 0.23A - j\sin 0.23A)| \quad (12)$$

$$w = 4\frac{(1-m^2)^2 - 2m^2 - j2^{(3/2)}m(1-m^2)}{[1+(1+\sqrt{2}m)^2]^2}$$

$$m = 0.3015\ D\sqrt{f\sigma_r/\mu_r}$$

The parameter $w \cong 1$ except for low audio frequency shielding against low impedance fields. The Shielding effectiveness S is defined as the sum of the sum of the absorption loss, reflection loss and the multiple reflection correction term. This method can be used to find shielding efficiency when we know the parameters of the shielding material.

$$SE = A + R + B \quad \text{dB} \tag{13}$$

The Shielding efficiency can also be calculated from the electric and magnetic field components with and without the shield. The Shielding Efficiency can be defined as [9],

$$\begin{aligned} SE[dB] &= 10\log_{10}(P_1 / P_2) \\ SE[dB] &= 20\log_{10}(E_1 / E_2) \\ SE[dB] &= 20\log_{10}(H_1 / H_2) \end{aligned} \tag{14}$$

The values of power P_1, Electric and magnetic components E_1 and H_1 are measured without the shield, whilst the values P_2, E_2 and H_2 are measured with the shield in place. Shielding effectiveness in the near field will differ for the magnetic field H and the electrical field E.

From Eqn 14,

$$SE[dB] = 10\log_{10}(P_I / P_T) \tag{15}$$

P_T=output transmitted power through the shield,
P_I=incident power on the shield

The ratio $\frac{P_T}{P_I}$ is the transmission coefficient, T

ie, $T = \frac{P_T}{P_I} = |S_{21}|^2$ (16)

From Eqns 15 &16,

$$SE[dB] = 10\log_{10}(1/T)$$

Or

$$SE[dB] = -20\log_{10}(S_{21}) \tag{17}$$

Here S_{21} is in linear scale.

1.4 Motivation for present work

The existence of radio waves was predicted by James Clerk Maxwell in 1864 from his equations. In 1888, Heinrich Hertz was the first to demonstrate the existence of radio waves by building a spark gap radio transmitter that produced 450 MHz microwaves, in the UHF region. From that time onwards the field of microwaves has flourished and its applications began to spread in many diverse fields of human life. Today we cannot imagine any communication technology without microwaves. Microwaves are used in food processing, medical field, satellite communication, cellular communication etc. They are widely used in industrial, scientific and medical (ISM) applications.

The major hindrance to many developments in the ISM field is the lack of knowledge about the effect of microwaves on the materials used in those applications. Each material has a different response to a microwave signal. At low frequencies one is able to predict the behavior of a material in response to a voltage or current. Here the material properties such as resistance, capacitance, inductance etc. tell a lot about the response of the field. The response can be predicted up to a close value without much error if good computation facilities/equipment are used. But as the frequency increases we are no more dependent in lumped capacitances and inductances. The impedance of such a network will be distributed. It will be fatal if we follow conventional laws to evaluate response to a microwave field.

Materials with high polarizability are known as dielectrics. When a microwave field is applied to a dielectric material, its molecules will align to the field. Hence it forms a dipole. The properties of a dipole are collectively named as dielectric properties. It includes complex permittivity, conductivity, skin depth, heating coefficient, attenuation constant etc. The ISM band of 2.45 GHz is where most of the common applications of microwaves are concentrated on. Radio-frequency process heating, microwave ovens, medical diathermy machines, Cordless phones, Bluetooth devices, NFC devices, and wireless computer networks all use the ISM bands. The microwave response to a system is predictable only if

we know the dielectric properties of the material which is exposed to microwaves. Even after a century since the discovery of microwaves, we know very little about the dielectric properties of many common materials used at microwave frequencies. We are supposed to be living in a microwave mesh which is created by numerous cellular towers and other communication equipment. This situation has motivated the present work on the development and characterization of materials which are used at microwave frequencies. The materials developed can find important applications in medical, scientific and industrial fields as their dielectric properties have been found.

1.4.1 Significance of the work

The research work carried out is on the class of materials which have significant uses in present day life. The first part of the work is based on biomaterials. Biomaterials are those materials of synthetic as well as of natural origin. They are usually used in contact with living tissue, blood and other body fluids. They are used for therapeutic applications as well. They are often used and/or adapted for a medical application, and thus comprise whole or part of a living structure or biomedical device which performs, augments, or replaces a natural function. Many of these type materials used today are not eco-friendly. Some of them interact with the body and the results are unpredictable. The material may become a clinical success, but it may have some adverse effects on some other part of the body. For example, if a clinically successful hip replacement material has a very low dielectric heating coefficient, when the body is exposed to a microwave field, the material will undergo dielectric heating and it will affect the operation of the whole body. The results can be fatal if the same thing happens with a pacemaker replacement material. So the studies of the dielectric properties of these materials are very important. Another significant application of the biomaterial is as phantoms. The possibility of the use of biomaterials as phantoms which can simulate body parts in an electromagnetic simulation environment has also been explored. The biomaterials used in the study are Arrowroot (starch) and

Chitosan (biopolymer). We were successful in developing transparent plastic-like films with Arrowroot. This work might be one of the pioneer works on development and microwave characterization of Arrowroot film. The second part of the study is on bioceramic materials which are used for medical implantation applications. Bioceramic materials studied are calcium/phosphate based materials. They are widely used as successful implantation materials. But their dielectric properties are less studied. So an attempt has been made to study the dielectric properties of common bioceramic materials. Materials such as Calcium Hydroxyapatite, Beta Tricalcium Phosphate and Biphasic Calcium Phosphate bioceramic have been studied. The study on the use of materials in clinical applications without ignoring its relevance in microwave environment is done.

The microwaves used in scientific and medical applications directly/indirectly interact with living tissues. The biological effects of microwaves are not as much harmful as the exposure to ionizing radiations like x-ray. But still, the effects on prolonged exposure to microwaves have not yet fully understood. All the microwave devices used in close proximity with the body can stimulate biological effects. This is because more than 80% of body is made up of water which is a highly polar material. Microwaves don't require a medium to propagate. If there is a medium, then power dissipation occurs. The body cannot be protected from such radiations unless the radiation source is perfectly shielded. A shield does the job of keeping unwanted radiations away from the body or confined to a transmission line. Thus materials are to be developed for shielding purposes. Conventional shielding was done using metallic braid or meshes. Metallic shielding cannot be easily implemented on all surfaces and is not economical. Thus it paved way to the use of conducting polymers for shielding applications. Conducting polymers are a class of polymers with π conjugated chain structure. Because of this structure, they are able to achieve conductivities even close to metallic ranges. As the conductivity of the material increases, the shielding due to reflection increases. Shielding can also be achieved by absorption of power. But it results in heating of the material which is used as the shield. Several class of

conducting polymers are already discovered. The conducting polymers can be used in their pure form or as blends/composites with other materials. Electromagnetic compatibility studies on Polyaniline based composites have been performed. The common materials used in composites are carbon black, graphite, carbon nano tubes, ferric oxide, graphene, fly ash etc. The properties of the composite vary depending on the material used as the filler. The newly developed materials can be used in electromagnetic shielding applications such as in anechoic chambers, transmission cables etc.

1.4.2 Objectives of the work

The objectives of the work can be summarized as follows,

- To develop cost- effective biomaterial based phantoms
- To perform dielectric characterization of biomaterial phantoms for ISM applications
- To improve the mechanical strength of the biomaterial film
- To develop and characterize cost effective bioceramic materials for microwave phantom applications
- To reduce the interaction of microwaves with living tissues by developing materials for shielding applications
- To perform dielectric characterization of conducting polymers for shielding applications
- To enhance the accuracy in the dielectric characterization of conducting polymers using modified cavity perturbation measurement

1.5 Experimental setup and methodologies

Dielectric characterization is the basic step in finding the suitability of a material to work in a microwave environment. The behavior of a material to high frequency can be predictable only with the knowledge about its dielectric

properties. The mechanical characterization is required to find the strength of the materials in film form. Properties like stress, strain, young's modulus and compressive strength are often evaluated for materials. Similarly morphological studies are done to find texture of film surfaces and to understand about the particle size of materials. The XRD and FTIR techniques help in finding the crystal structure and components in a material.

1.5.1 Perturbation methods

The term perturbation means a secondary influence on a system that causes it to deviate slightly or the act of causing disorder. Resonant perturbation is a method which uses a resonator into which the sample is inserted so that the dielectric parameters of the sample can be evaluated from the change in resonant frequency and quality factor of the cavity [7]. There are also other methods like non resonant perturbation [10,11], open ended probe [12,13], transmission/ reflection line method[14], planar circuit method[15] etc. Cavity perturbation [16-20] is popular because of the simplicity and the high accuracy in method. There is also another resonant method called dielectric resonator method. In dielectric resonator method, the sample under test resonates in the circuit. From the resonant frequency and the quality factor, the parameters of the sample can be found. These methods are commonly used for low loss materials, materials of irregular shape, powders etc.

There are three types of cavity perturbations: cavity shape perturbation, wall impedance perturbation, and material perturbation. The cavity shape perturbation is a technique which involves either pushing in or pushing out part of the cavity wall. This changes the resonant frequency and hence the energy stored in the cavity, but the energy dissipated remains the same. In wall impedance perturbation, part of the cavity wall is replaced. Here cavity shape is not changed. The cavity shape perturbation is used to retune the resonant frequency of the cavity whereas wall-impedance perturbation is used to measure surface impedance of

conductors. We use material perturbation for evaluating the dielectric properties of the sample material which is inserted into the resonant cavity.

Cavity material perturbation

The cavity perturbation method for small objects requires that the electric field outside the sample does not change. A material with permittivity ε and permeability μ is introduced into the resonant cavity. The sample occupies a small portion of the cavity. The electromagnetic properties of the space except the sample do not change. The resonant frequency of the cavity is changed due to the perturbation of the field within the cavity by the introduction of the sample material. The cavity perturbation works well for the measurement of the dielectric parameters of low-loss and medium-loss materials. If the quality factor of an empty cavity before the perturbation is not high, the power dissipation of the empty cavity may be much larger than the loss due to the introduction of the sample to be measured, and so the introduction of the sample hardly affects the quality factor of the cavity.

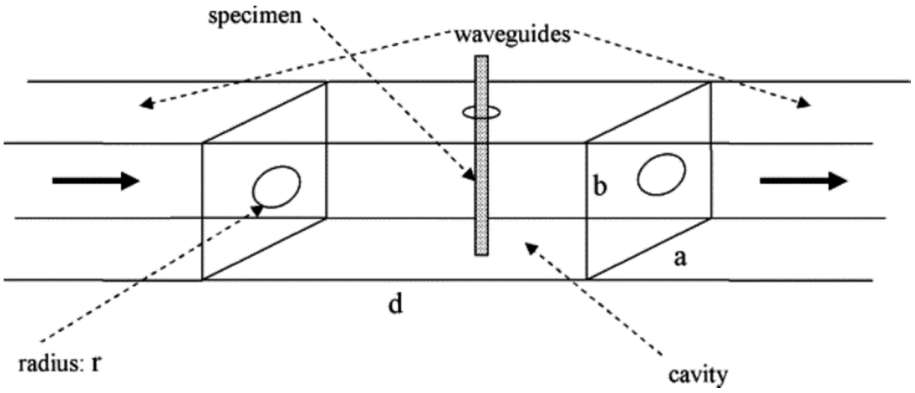


Figure 1.7 Cavity Perturbation setup

The conventional cavity-perturbation method could not correctly give the value of the imaginary part of the permittivity. The quality factor of the cavity may even increase after introducing an extremely low-loss sample, so that the

conventional cavity-perturbation formulae will give a negative value for the imaginary part of permittivity [7]. The main reason for this error is that the conventional cavity-perturbation formulae for permittivity measurements incorporate many approximations and assumptions.

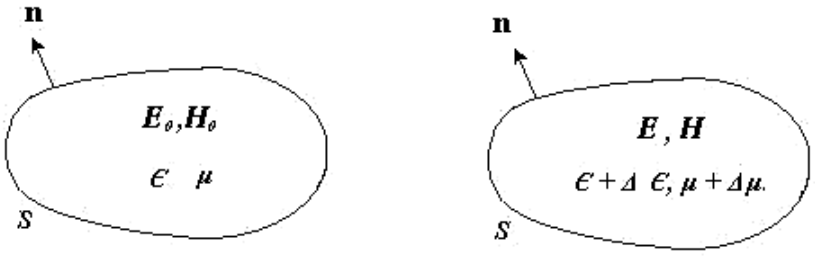


Figure 1.8 The variation of parameters of unperturbed and perturbed cavity

Figure 1.8 shows the variation of parameters before and after the perturbation of the cavity. μ and ϵ are the permeability and permittivity of the medium of the original cavity. In the perturbed cavity the parameters of the medium are changed to μ+Δμ and ϵ+Δϵ. The field equations in the two cases are,

$$-\nabla \times E_0 = j\omega_0 \mu H_0 \qquad -\nabla \times E = j\omega(\mu + \Delta\mu)H$$

$$\nabla \times H_0 = j\omega_0 \epsilon E_0 \qquad \nabla \times H = j\omega(\epsilon + \Delta\epsilon)E \tag{18}$$

Take the conjugate of the first equation and multiply it scalarly by *H*, and the last equation scalarly by E_0^*. Add these resulting equations to give

$$\nabla \cdot (H \times E_0^*) = j\omega(\varepsilon + \Delta\varepsilon)E \cdot E_0^* - j\omega_0 \mu H_0^* \cdot H$$

Similarly we get

$$\nabla \cdot (H_0^* \times E) = j\omega(\mu + \Delta\mu)H \cdot H_0^* - j\omega_0 \varepsilon E_0^* \cdot E$$

Add the above two equations and integrate throughout the cavity to get

$$\iiint_\tau [\nabla \cdot (H \times E_0^*) + \nabla \cdot (H_0^* \times E)] d\tau$$

$$= \iiint_{\tau} j\{[\omega\ (\varepsilon + \Delta\varepsilon) - \omega_0 \varepsilon]E.E_0^* + [\omega(\mu + \Delta\mu) - \omega_0 \mu]H \cdot H_0^*\} d\tau \quad (19)$$

$n \times E$ and $n \times E_0$ on *S,* both equal to zero.

Apply the divergence theorem to the left hand side, and it vanishes to zero as

$$0 = \iiint_{\tau} \{[\omega\ (\varepsilon + \Delta\varepsilon) - \omega_0 \varepsilon]E.E_0^* + [\omega(\mu + \Delta\mu) - \omega_0 \mu]H \cdot H_0^*\} d\tau$$

$$0 = (\omega - \omega_0) \iiint_{\tau} [\varepsilon E \cdot E_0^* + \mu H \cdot H_0^*] d\tau + \omega \iiint_{\tau} [\Delta\varepsilon E \cdot E_0^* + \Delta\mu H \cdot H_0^*] d\tau$$

$$\frac{\omega - \omega_0}{\omega} = -\frac{\iiint_{\tau} (\Delta\varepsilon E \cdot E_0^* + \Delta\mu H \cdot H_0^*) d\tau}{\iiint_{\tau} (\varepsilon E \cdot E_0^* + \mu H \cdot H_0^*) d\tau} \quad (20)$$

In the limit, as $\Delta\varepsilon \to 0$ and $\Delta\mu \to 0$, we can approximate *E, H,* ω by E_0, H_0, ω_0 and we obtain

$$\frac{\omega - \omega_0}{\omega_0} \approx -\frac{\iiint (\Delta\varepsilon |E_0|^2 + \Delta\mu |H_0|^2) d\tau}{\iiint (\varepsilon |E_0|^2 + \mu |H_0|^2) d\tau} \quad (21)$$

This equation states that a small increase in ε and /or μ decreases the resonant frequency. In terms of energy stored in the fields the above perturbation equation becomes

$$\frac{\omega - \omega_0}{\omega_0} \approx -\frac{1}{W} \iiint \left(\frac{\Delta\varepsilon}{\varepsilon} \overline{w}_e + \frac{\Delta\mu}{\mu} \overline{w}_m\right) d\tau$$

Where $\overline{w}$ the energy density and W is the total energy stored in the original cavity.

By taking $\Delta\varepsilon = \varepsilon - \varepsilon_0$ and $\Delta\mu = \mu - \mu_0$,

$$\frac{\omega - \omega_0}{\omega} = -\frac{\iiint_{\tau} [(\varepsilon - \varepsilon_0) E \cdot E_0^* + (\mu - \mu_0) H \cdot H_0^*] d\tau}{\iiint_{\tau} (\varepsilon_0 E \cdot E_0^* + \mu_0 H \cdot H_0^*) d\tau}$$

$$= -\frac{\iiint_{\tau}[(\varepsilon-\varepsilon_0)E\cdot E_0^* + (\mu-\mu_0)H\cdot H_0^*]d\tau}{2\iiint_{\tau}\varepsilon_0 \quad E\cdot E_0^* d\tau} \tag{22}$$

If the element is introduced into a region of *E* field

$$\frac{\omega - \omega_0}{\omega} = -\frac{\iiint_{\tau}[(\varepsilon-\varepsilon_0)E\cdot E_0^* d\tau}{2\iiint_{\tau}\varepsilon_0 \quad E\cdot E_0^* d\tau} \tag{23}$$

Consider a rectangular cavity to which the sample is inserted. Electromagnetic energy is coupled to the cavity through coupling irises at the ends of the cavity. A non-radiating slot is provided at the broad wall of the cavity for the introduction of the sample. On exciting the cavity resonator in the TE_{10p} mode, a typical resonant frequency spectrum is obtained. The cavity resonates at different frequencies depending on its dimensions. The basic principle involved in the technique is that the field within the cavity resonator is perturbed by the introduction of the dielectric sample through the non-radiating slot. The resonant frequency and the quality factor of the cavity get shifted due to perturbation. Assuming that the medium inside the cavity is a vacuum: $\mu_1 = \mu_2 = \mu_0$, and $\varepsilon_1 = \varepsilon_0$, the relative complex frequency shift of the resonator is given as

$$\frac{d\Omega}{\omega_0} \approx -\left(\frac{\overline{\varepsilon_r} - 1}{2}\right)\frac{\int_{Vs} E.E_0^{*}{}_{\max}\, dV}{\int_{Vc} |E_0|^2\, dV} \tag{24}$$

where ε_r is the relative permittivity given by $\varepsilon_r\varepsilon_0 = \varepsilon$ and $d\Omega$ is the complex frequency shift. V_s and V_c are the volumes of the sample and the cavity resonator respectively.

Let $\omega = \omega_r + j\omega_i$

$\omega_r = 2\pi f$

$$Q = \frac{\omega_r}{2\omega_i}$$

If we assume that, $\omega_{r1} \approx \omega_{r2}$ *and* $\omega_i >> \omega_r$

$$\frac{d\Omega}{\omega_0} = \frac{\omega_2 - \omega_1}{\omega_2}$$

$$= \frac{(\omega_{r2} - \omega_{r1}) + j(\omega_{i2} - \omega_{i1})}{\omega_{r2}(1 + j\frac{\omega_{i2}}{\omega_{r2}})}$$

$$\approx \left(\frac{f_c - f_s}{f_s}\right) + \frac{j}{2}\left(\frac{1}{Q_S} - \frac{1}{Q_C}\right) \qquad (25)$$

Q_s and Q_c are the quality factors of cavity resonator with and without the sample.

Therefore from equations 24 & 25,

$$\left(\frac{f_c - f_s}{f_s}\right) + \frac{j}{2}\left(\frac{1}{Q_S} - \frac{1}{Q_C}\right) = -\left(\frac{\overline{\varepsilon_r} - 1}{2}\right)\frac{\int_{Vs} E.E_0^{*}{}_{\max}\, dV}{\int_{Vc} |E_0|^2\, dV} \qquad (26)$$

For dominant TE_{10p} mode in rectangular wave guide,

$$E_0 = E_{0\max} Sin\frac{\pi x}{a} Sin\frac{p\pi z}{d}, \qquad p = 1, 2, 3..... \qquad (27)$$

From equations 26 and 27, we get

$$\varepsilon_r' - 1 = \frac{f_c - f_s}{2f_s}\left(\frac{V_c}{V_s}\right) \qquad (28)$$

$$\varepsilon_r'' = \frac{V_c}{4V_s}\left(\frac{Q_c - Q_s}{Q_c Q_s}\right) \qquad (29)$$

The real part, ε_r' of the complex permittivity is usually known as dielectric constant. The imaginary part, $\varepsilon_r''$of the complex permittivity is associated with dielectric loss of the material. The effective conductivity, σ_e is given as

$$\sigma_e = \omega\varepsilon'' = 2\pi f \varepsilon_0 \varepsilon_r'' \tag{30}$$

The dielectric loss of a material will be usually expressed by a term loss tangent or tanδ as

$$\tan\delta = \frac{\varepsilon_r''}{\varepsilon_r'} \tag{31}$$

The Skin depth gives a measure of the depth of penetration of electromagnetic wave inside the material. It is found from the basic relation

$$\delta = \frac{1}{\sqrt{\pi f_s \mu \sigma}} \tag{32}$$

The microwave heating coefficient (J) and attenuation constant (α) are found using the formulae [21]

$$J = \frac{1}{\varepsilon_r' \tan(\delta)} \tag{33}$$

$$\alpha = \frac{\varepsilon_r'' f_s}{\sqrt{(\varepsilon_r' + \varepsilon_r'')} * C} \tag{34}$$

1.5.2 Open ended probe method

The open ended probe method is a popular method for dielectric properties of materials owing to its simplicity, broad-band response, and capacity for noninvasive measurements [22]. Although the method is simple, it does have some drawbacks. The main drawbacks are the inconsistency in measurements due to the effect of air gap between the probe and the sample and poor accuracy at high frequencies. Enhanced calibration has to be done at high frequencies. It is used for evaluating dielectric properties of liquids [23]. At low frequencies, the radial

electric field distribution at the aperture region of the open ended probe is inversely proportional to the radius. The formulae are modified for high frequencies by including the effect of higher order modes excited at the aperture. Some open ended probes are used with infinite ground plane flanges. The use of flanged probes increases the accuracy in measurement [7]. Several theoretical models are used for analyzing open ended probes. They include capacitance model, radiation model, virtual line model and rational function model.

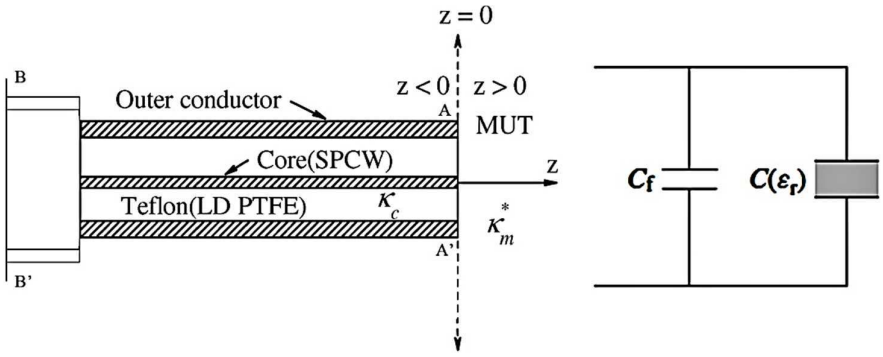


Figure 1.9 Open ended probe with equivalent circuit

Figure 1.9 shows the coaxial probe which is terminated by a semi-infinite sample and its capacitive equivalent circuit at the plane A-A'. Here the equivalent circuit consists of two capacitances connected in parallel. $C_{(\varepsilon_r)}$ is the capacitance depending on the dielectric properties of the material under test and C_f is the capacitance independent of the dielectric properties of the material.

The complex reflection coefficient at the tip of the open ended probe can be defined as,

$$\Gamma^* = \Gamma e^{j\phi}$$

$$= \left(\frac{Z_L - Z_0}{Z_L + Z_0} \right) e^{j\phi}$$

$$= \left(\frac{1 - j\omega Z_0 \cdot [C(\varepsilon_r) + C_f]}{1 + j\omega Z_0 \cdot [C(\varepsilon_r) + C_f]} \right) \tag{35}$$

Where, $C(\varepsilon_r) = \varepsilon_r C_0$

C_0 is the capacitance of the capacitor which is filled with air and Z_0 is the characteristic impedance of the coaxial line connected to the open-ended probe. Solving for ε_r from Eqn.32, we get

$$\varepsilon_r = \frac{1 - \Gamma^*}{j\omega Z_0 C_0 (1 + \Gamma^*)} - \frac{C_f}{C_0} \tag{36}$$

The parameters C_f and C_0 are obtained by calibrating the open ended probe with a standard sample with known dielectric properties [24].

$$C_0 = \frac{(1 - |\Gamma^*_{diel}|^2)}{\omega Z_0 \varepsilon''_{diel} (1 + 2|\Gamma^*_{diel}| \cos(\phi_{diel}) + |\Gamma^*_{diel}|^2)} \tag{37}$$

$$C_f = \frac{-2|\Gamma^*_{diel}| \sin(\phi_{diel})}{\omega Z_0 (1 + 2|\Gamma^*_{diel}| \cos(\phi_{diel}) + |\Gamma^*_{diel}|^2)} - \varepsilon'_{diel} C_0 \tag{38}$$

where ε'_{diel} and ε''_{diel} are the real and imaginary parts of the complex permittivity of the standard sample. Similarly $|\Gamma^*_{diel}|$ and ϕ_{diel} are the magnitude and phase of the complex reflection coefficient Γ^*_{diel}. The reflection coefficient should be measured at the plane A-A'.

If the reference plane is defined at plane B-B', then the phase difference between the planes A-A' and B-B' are to be included in calculation.

$$\theta = \frac{\phi_{A-A'} - \phi_{B-B'}}{2}$$

Where $\phi_{A-A'}$ and $\phi_{B-B'}$ are the reflection phase angles of A-A' and B-B' planes respectively.

$$\Gamma^*_{A-A'} = \Gamma^*_{B-B'} e^{j2\theta} \quad (39)$$

1.5.3 Low frequency measurements

The low frequency response of a material depends on the dielectric relaxation of the material. Up to about 1GHz, the materials respond to relaxation phenomena. The alignment of the molecule dipolar moment due of an applied field is called dipolar polarization. The dipole usually possesses a field of its own. So they are influenced by an external field as well as by mutual influence. The relaxation process involves the equilibrium of a system which is initially not in thermodynamic equilibrium. Hence the process is irreversible [5]. Relaxation occurs when the free energy stored in the system is degraded into heat, or in other words, if entropy is created irreversibly. For materials with many relaxation times, the polarizable elements are divided into groups of given relaxation times; then a principle of superposition is used to obtain an analytical expression for the complex permittivity.

The exposure to low frequency radiation depends mainly on the dielectric properties of the living tissues. Before finding the effect of electromagnetic radiation in humans, its effect on animals is to be demonstrated. Hence a process of exposure (dosimetry) in animals and prediction (scaling) of the equivalent exposure in humans is employed [25]. The low frequency dielectric properties of a material are obtained from the measurement of variation of parameters such as capacitance, resistance and inductance in response to a given field. At low frequencies, the measurement of these properties is usually performed using an LCR meter (Impedance Analyzer). For highly conducting material samples, techniques like four probe method [26] are used for improved accuracy in measurement.

1.5.4 Impedance Analyzer

The dielectric properties of the materials at low frequencies were studied using Agilent E4980A Impedance Analyzer along with the aid of Agilent 16451B dielectric material test fixture. The E4980A is used for evaluating LCR

components, materials, and semiconductor devices over a wide range of frequencies (20 Hz to 2 MHz) and test signal levels (0.1 mVrms to 2 Vrms, 50 µA to 20 mArms). With Option 001, the E4980A's test signal level range spans 0.1 mV to 20 Vrms, and 50 µA to 200 mArms. The E4980A with Option 001 enables up to ±40-Vrms DC bias measurements (without Option 001, up to ± 2 Vrms), DCR measurements, and DC source measurements using the internal voltage source.

Figure 1.10 Agilent E4980A Impedance Analyzer

The E4980A offers C-D measurement with a basic accuracy of ±0.05% (C), ±0.0005 (D) at all frequencies with seven-digit resolution (the dissipation factor resolution is 1 ppm) in every range. With its built-in comparator, the E4980A can output comparison/decision results for sorting components into a maximum of ten bins. Furthermore, by using the handler interface and scanner interface options, the E4980A can be easily combined with a component handler, a scanner, and a system controller to fully automate component testing, sorting, and quality-control data processing. The E4980A's list sweep function permits entry of up to 201 frequencies, test signal levels, or bias level points to be automatically measured.

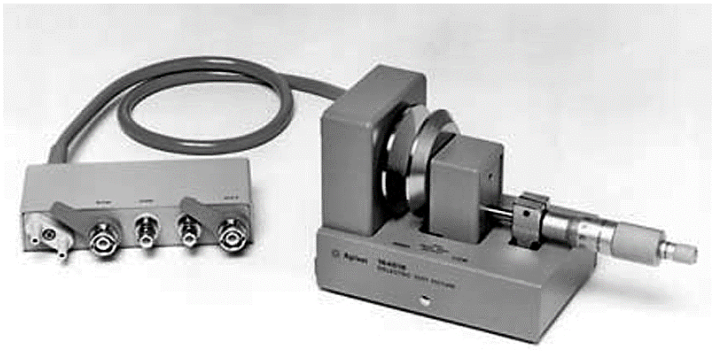


Figure 1.11 Agilent 16451B dielectric material test fixture

The 16451B is a Dielectric Test Fixture used with LCR meters and impedance analyzers for accurate measurement of insulating and dielectric materials. It can be used with LCR meters and impedance analyzers which use the 4-terminal pair measurement configuration. The 16451B is used to evaluate the dielectric constant of solid dielectric materials accurately, and complies with ASTM D150. The 16451B employs the parallel plate method, which sandwiches the material between two electrodes to form a capacitor [27]. LCR meter or an Impedance Analyzer is then used to measure the capacitance created from the fixture. The permittivity and loss factors can be defined as,

$$\varepsilon_r' = \frac{C * t}{\varepsilon_0 A} \tag{40}$$

$$\varepsilon_r'' = D * \varepsilon_r' \tag{41}$$

Where C = Measured capacitance, t = Thickness of the sample, A = Area of sample,

D = Dissipation factor (Loss tangent). Eqns. 30-34 can be used to find out the other properties once permittivity and loss factor are found.

1.5.5 Vector Network Analyzers

Network analyzers are often used to characterize two-port networks such as amplifiers and filters, but they can be used on networks with an arbitrary number of ports. The two main types of network analyzers are

Scalar Network Analyzer (SNA) — measures amplitude properties only

Vector Network Analyzer (VNA) — measures both amplitude and phase properties

Two network analyzers were used in this work for the dielectric characterization of materials at microwave frequencies. They are Agilent (HP) 8714ET and Rhode & Schwarz ZVB-20. The Agilent Technologies 8714ET is an RF network analyzer (300MHz-3GHz) optimized for production measurements of reflection and transmission parameters [28]. The source features 1 Hz resolution, 40 ms (or faster) sweep time, and up to +16 dBm output power. The three-channel, dual mode receivers provide dynamic range of greater than 100 dB in narrowband-detection measurement mode. For measurements of frequency-translating devices, the network analyzer features broadband internal detectors and external detector inputs.

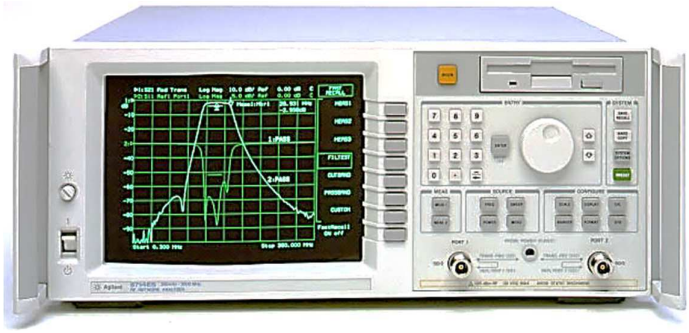


Figure 1.11 Agilent 8714ET Vector Network Analyzer

The Rhode & Schwarz ZVB20 (10MHz - 20GHz) is the other VNA used for measurements. It has four ports for measurements. The maximum output power of

over +10 dBm is available at each of the four test ports irrespective of the direction of measurement. With a maximum dynamic range between the test ports of > 120 dB, the ZVB20 features very fast measurement times - even for applications requiring a high dynamic range [29]. The optional direct generator/receiver access increases sensitivity and dynamic range by typically 10 dB. High-speed parallel measurements can be achieved because the generator signal can

Figure 1.12 Rhode & Schwarz ZVB20 Vector Network Analyzer

be output to multiple test ports simultaneously. Also the data can be captured at multiple ports simultaneously and all displayed at the same time. Data processing in the instrument, from RF and IF to digitization and display, is also carried out in parallel. Moreover, data transfer can be performed simultaneously with measurement. The entire execution time for measurements with repeated data transfer via IEC/IEEE bus or LAN is therefore determined solely by the measurement time. For measurements on active DUTs, power is supplied by a DC bias applied via the inner conductor of each test port.

1.5.6 Evaluation of mechanical properties

The mechanical properties such as stress and strain are evaluated with the aid of Shimadzu AG-1 Universal Testing Machine. It has a load cell capacity of

10KN and cross head speed 50mm/min. The film samples are cut into strips of 10 cm length and 1 cm width for measurement purpose. The gauge length is taken to be 40 mm.

The properties Stress and Strain define the mechanical strength of a film. They are evaluated by the formulas,

$$\text{Stress} = \text{load} / (\text{width} \times \text{thickness}) \quad (42)$$

$$\text{Strain in \%} = (\text{Stroke} / \text{Gauge length}) \times 100 \quad (43)$$

The slope of the Stress/Strain plot gives Young's Modulus or modulus of elasticity. The area under Stress/Strain curve up to a value of Strain gives the Strain energy consumed by the material in straining to that value.

Figure 1.13 Shimadzu AG-1 Universal Testing Machine

1.5.7 Morphological studies

The structural and morphological properties of the prepared samples were analyzed using Scanning Electron Microscope (SEM) measurement. The surface irregularities as well as porosity of films can be found using SEM study. Similarly grain size can be found for powder/mixture type materials. The electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. Biological films cannot be scanned with high power electron beam as it may possibly burn out the samples. So those type samples were imaged using low power electron beams (5kV). For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Nonconductive specimens tend to charge when scanned by the electron beam, and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts. They are therefore usually coated with an ultrathin coating of electrically conducting material, deposited on the sample either by low-vacuum sputter coating or by high-vacuum evaporation. Non-conducting specimens may be imaged uncoated using Environmental SEM (ESEM) or low voltage mode of SEM operation. Magnification in a SEM can be controlled over a range of up to 6 orders of magnitude from about 10 to 500,000 times.

1.5.8 X-ray Diffractometry (XRD)

Diffraction occurs as waves interact with a regular structure whose repeat distance is about the same as the wavelength. Electrons do not penetrate as deeply into matter as X-rays, hence electron diffraction reveals structure near the surface. X-ray diffractometry is a technique in which X-rays are used to structurally characterize a material. A diffractometer can be used to make a diffraction pattern of any crystalline solid. With a diffraction pattern an investigator can identify an unknown mineral, or characterize the atomic-scale structure of an already

identified mineral. A diffraction pattern records the X-ray intensity I, as a function of 2-theta angle. Every crystalline substance gives a pattern. Even if the crystalline substances are mixed, each ingredient gives its pattern independent of the other patterns. The powder diffraction method is therefore suited for characterization and identification of polycrystalline phases. The main use of powder diffraction is to identify components in a sample by a search/match procedure. Also, the areas under the peak are related to the amount of each phase present in the sample.

An X-ray striking an electron produces secondary spherical waves emanating from the electron. A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg's law[30]:

$$n\lambda=2d\sin\theta \quad (44)$$

Here d is the spacing between diffracting planes, θ is the incident angle, n is any integer, and λ is the wavelength of the beam. X-rays are used to produce the diffraction pattern because their wavelength λ is typically the same order of magnitude (1-100 angstroms) as the spacing d between planes in the crystal. In powder or polycrystalline diffraction it is desired to have a sample with a smooth plane surface. The ideal sample is homogeneous and the crystallites are randomly distributed. If we have a truly random sample, each possible reflection from a given set of h, k, l planes will have an equal number of crystallites contributing to it. It is sometimes necessary to rotate the sample orientation to eliminate the effects of texturing and achieve true randomness. We have to rock the sample through the glancing angle θ in order to produce all possible reflections.

1.5.9 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas [31]. The term Fourier transform infrared

spectroscopy originates from the fact that a Fourier transform is required to convert the raw data into the actual spectrum. In "dispersive spectroscopy" technique, a monochromatic light beam is passed through the sample. The amount of absorbed light is noted and the experiment is repeated for other wavelengths. In FTIR, rather than shining a monochromatic beam of light at the sample, a beam containing many frequencies of light is shine at once. The atoms of the material absorb the light and vibrate faster. The absorption occurs only when the radiation interacts with a molecule undergoing dipole change. Also the incoming IR photon should have sufficient energy to put the atom to the next vibrational energy state. The amount of energy absorbed by the sample is measured. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is repeated many times. Afterwards, a computer takes all these data and works backwards to infer what the absorption is at each wavelength.

1.5.10 Shielding measurements

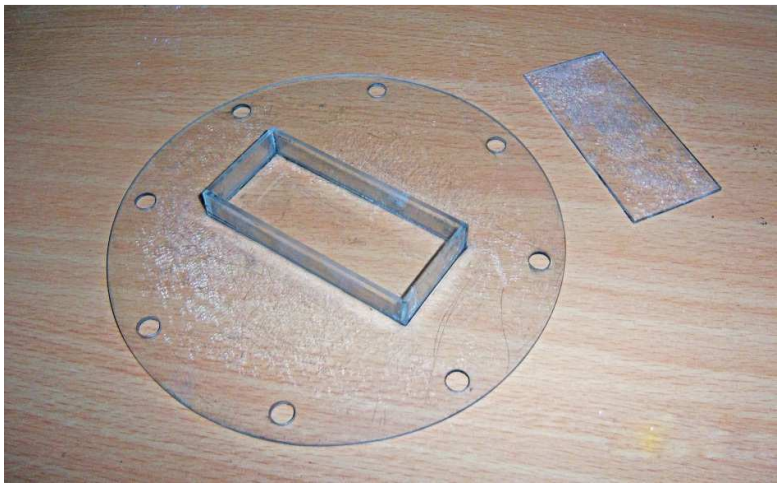


Figure 1.14 Perspex holder used for shielding measurement

The EMI shielding properties are studied by sandwiching the sample in between two wave guide adapters. One wave guide adapter is connected to the

reflection port of the VNA and the other to the transmission port of VNA. The microwave signal which emerges from the reflection port travels through the sample and reaches the transmission port.

The parameters such as reflection coefficient and transmission coefficient are measured from the analyzer data. From these values, absorption coefficient can be found. Also shielding effectiveness is calculated from the transmission coefficient. If the sample is in powder form, then sample holders made of Perspex and having various holder thicknesses (2.5mm, 5mm, 7.5mm) are used in between the wave guide adapters. Perspex has low microwave absorption characteristics. Hence, its use won't affect the measurement. Furthermore, the measurement setup is calibrated with the holder in place prior to taking measurements with sample.

1.5.11 Pelletizer for solid samples

The cavity perturbation method demands use of thin samples (<3mm thickness) for dielectric property measurements. The sample in powder form is pelletized using a die and hydraulic press. Pressures varying from 1.5 ton-2.5 ton/m^3 are applied on the sample to compress it. The amount of pressure applied is a function of the mechanical properties of the material. Rectangular and cylindrical dies were made. The dies are made up of high chromium die steel and are hard chromium coated for corrosion prevention. The rectangular die produces pellets of 5mm length, 3mm thickness and of varying height depending on the need. The

Figure 1.15 Rectangular and cylindrical dies designed for pelletizing samples

Figure 1.16 Hydraulic press

The cavity perturbation method demands use of thin samples (<3mm thickness) for dielectric property measurements. The sample in powder form is pelletized using a die and hydraulic press. Pressures varying from 1.5 ton-2.5 ton/m^3 are applied on the sample to compress it. The amount of pressure applied is a function of the mechanical properties of the material. Rectangular and cylindrical dies were made. The dies are made up of high chromium die steel and are hard chromium coated for corrosion prevention. The rectangular die produces pellets of 5mm length, 3mm thickness and of varying height depending on the need. The cylindrical dies are of diameters 24mm and 13mm. The Hydraulic press used is shown in figure 1.16. It can apply a maximum pressure of 280Kg/cm^2. Usually 50-75Kg/cm^2 pressure is applied for ceramic materials. The amount of pressure that can be applied depends on the sample amount and thickness.

1.5.12 Muffle Furnace

Figure 1.17 Programmable Muffle furnace

The ceramic materials require high temperature sintering during final stage of development. The pelletized samples also sometimes require sintering or high temperature calcination. A temperature of 1000-1200° C is usually used for sintering ceramics. 600-700°C is used for calcination of powder and solid samples. For high temperature sintering applications, a muffle furnace from Hasthas Scientific Instruments was used. The programmable furnace can go up to 1200°C temperature. The heater current can also be adjusted in this model. The furnace has an accuracy of +/- 50C at full temperature of setting.

1.6 Electromagnetic simulation tools

Electromagnetic simulation tools enable testing and analysis of experimental setups and their validation. Popular electromagnetic simulation tools include Ansoft HFSS (FEM), CST Microwave studio, Zeland IE3D (MoM based), Agilent ADS, Comsol Multiphysics, Flomerics MicroStripes (TLM) etc. Ansoft

HFSS is the tool used in our simulations. HFSS™ is the industry-standard software for S-parameter, Full-Wave SPICE™ extraction, and 3D electromagnetic field simulation of high-frequency and high-speed components [32]. It uses mathematical method FEM for its solver. It integrates simulation, visualization, solid modeling, and automation. HFSS calculates the S, Y and Z-parameters, resonant frequency, Q-factors, near/far fields, smith chart, specific absorption rate (SAR), electric and magnetic fields in vector/magnitude forms and lot other parameters and displays them in high quality 2-D/3-D/animated plots. HFSS uses an interactive simulation system whose basic mesh element is a tetrahedron. HFSS uses technologies like Tangential vector finite elements, Adaptive meshing and Adaptive Lanczos-pade sweep for FEM analysis. HFSS within established EDA design flows to evaluate signal quality, including transmission path losses, reflection loss due to impedance mismatches, parasitic coupling and radiation.

Summary

Microwaves and RF waves have become an integral part of modern life. The microwaves are mainly used at the ISM band of frequencies whereas the RF waves are used mainly for communication applications. The materials which are used in these frequencies are tested for their suitability through various dielectric characterization techniques. Bioceramics are those materials which are interacting very closely with human body. Likewise, conducting polymers represent the group of polymers which are used for shielding from harmful electromagnetic radiations. Various measurement techniques and the instruments used to perform those measurements are summarized in this chapter.

Equation parameters

ω = angular frequency	Γ= reflection coefficient	
σ = conductivity	P_I= incident power	C= velocity of light
μ = permeability	V_c= volume of cavity	V_s=volume of sample

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Chapter 2

Review of Literature

2.1 Introduction

Material science has found tremendous progress in the last century. Several new materials were developed for use in the Industrial, Scientific and Medical fields. These materials pave way to new branches in material science. The past few decades also witnessed the systematic classification of literature data which were scattered around in journals and magazines. As the work scrutinizes the development and application of materials for use in ISM band of microwave frequencies, care has been given to include the literature data based on their use/application in various fields. The chapter begins with the literature data on

Biomaterials - those used in medical field,

Bioceramics - those used in medical and industrial fields

Conducting polymers - a new branch of materials and the study of their use in Scientific and Industrial applications.

And then proceeds to the microwave applications in which these materials are used. The literature on important applications such as microwave phantoms for confocal and tomography imaging applications, the interaction of microwaves with biological tissues, application of conducting polymers in electromagnetic compatibility etc. are reviewed.

2.2 Biomaterials

Biomaterials can be defined as those biocompatible materials which are in constant contact with body tissues/ blood and other body fluids [7]. They

shouldn't produce adverse effects on the body parts where they are being used. They can be of natural or synthetic nature. The development of biomaterials, as a science, is about fifty years old. Biomaterials science comprehends elements of medicine, biology, chemistry, tissue engineering and materials science. Biomaterials are used as,

- Joint replacements
- Bone plates
- Bone cement
- Artificial ligaments and tendons
- Dental implants for tooth fixation
- Blood vessel prostheses
- Heart valves
- Skin repair devices (artificial tissue)
- Cochlear replacements
- Contact lenses
- Breast implants
- Surgical Sutures
- Catheters

Biomaterials which are used within human body are to be subjected to biocompatibility studies [24, 85]. These studies can reveal whether the host body can response appropriately to the implanted material. The host responses like resistance to blood coating (e.g. Haemodialysis membrane), resistance to bacterial colonization (e.g. Urinary catheter) and normal, uncomplicated healing (e.g. Tissue engineering applications) are the most important things which are considered while examining biocompatibility [73].

The successful implant of a biomaterial inside a body requires not only the biocompatible features of the material, but it also depends on external factors such as the health of the patient, the environment in which the surgery is done, the competency of the surgeon as well as the quality of monitoring equipment used.

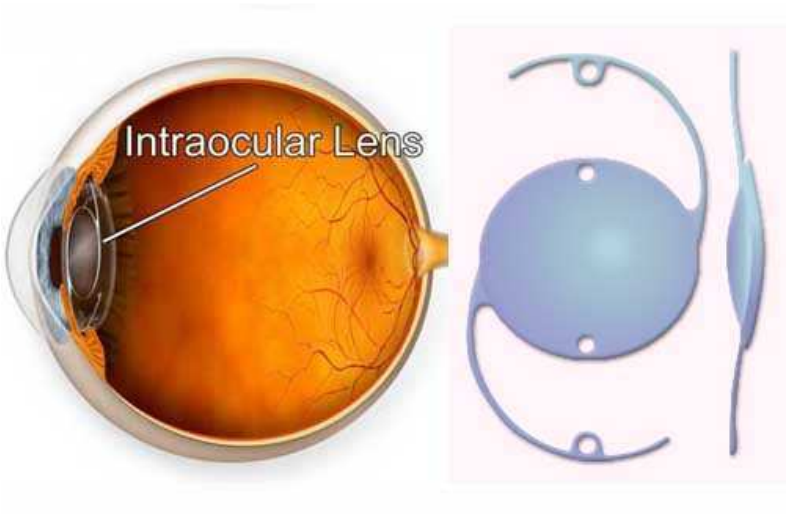

Figure 2.1* Typical Application of a Biomaterial

The first Consensus Conference of the European Society for Biomaterials (ESB) in 1976 defined biomaterial as 'a nonviable material used in a medical device, intended to interact with biological systems'; however, the ESB's current definition for a biomaterial is a 'material intended to interface with biological systems to evaluate, treat, augment or replace any tissue, organ or function of the body' [94]. The change in the definition implies that the use of biomaterials have been evolved from merely interacting with the body to influencing biological processes. The major use of a biomaterial is as a scaffold or a platform over which the tissues can grow. The scaffold eventually becomes a part of the system and is degraded biologically. Ceramics, natural polymers and synthetic polymers are commonly used as scaffold materials. The biomaterials also include biopolymers (also called renewable polymers) such as Chitosan, Polylactic acid, Cellulose etc. Biopolymers are produced from biomass for use in the packaging industry. Biomass comes from crops such as sugar beet, potatoes or wheat: when used to produce biopolymers, these are classified as non-food crops. These can be converted in the following pathways:

*http://katouganka.com/wp-content/uploads/2012/12/cataract_1.jpg, http://img.tradeindia.com/fp/1/346/510.jpg

Sugar beet > Glyconic acid > Polyglonic acid
Starch > (fermentation) > Lactic acid > Polylactic acid (PLA)
Biomass > (fermentation) > Bioethanol > Ethene > Polyethylene

Some biopolymers such as polylactic acid (PLA), naturally occurring zein, and poly-3-hydroxybutyrate can be used as plastics, replacing the need for polystyrene or polyethylene based plastics.

Biomaterials are also useful as phantom materials which possess the essential dielectric properties that mimic a tissue or body part. They are used in microwave imaging applications and for studies which involve microwave interaction with biological tissues like SAR studies. Mariya Lazebnik *et. al.* [62] reported the use of oil-in-gelatin dispersions that approximate the dispersive dielectric properties of a variety of human soft tissues over the microwave frequency range from 500 MHz to 20 GHz. The study involved mimicking of various biological tissues by varying the oil concentration. It has been reported that the materials can be used to construct heterogeneous phantoms, including anthropomorphic types, for narrowband and ultra wideband microwave technologies, such as breast cancer detection and imaging systems.

On another work, simulated bio-tissues were developed by Cheung and Coopman [5] for use in dosimetry studies at X and S bands of microwave frequencies. The specific heat of the developed phantoms matched with the tissues for which they were used. Bindu *et. al.* [66] developed Polyvinyl acetate based phantoms which represent low water content tissues. They were developed for microwave tomographic imaging applications.

2.2.1 Chitosan

Chitosan (poly[β-1–4]) D-glucosamine) comes from chitin a natural biopolymer originating from crustacean shells [54,74]. Chitin is the second most abundant natural polymer in nature after cellulose. Chitin and Chitosan are highly basic polysaccharides. Chitin is similar to cellulose in morphology; a bountiful

natural polysaccharide that contains amino sugars. It is structurally identical to cellulose, but it has acetamide groups (−NHCOCH3) at the C-2 positions [59]. Chitin is a white, hard, inelastic, nitrogenous polysaccharide found in the exoskeleton as well as in the internal structure of invertebrates. The production of chitosan from crustacean shells obtained as a food industry waste is economically feasible, especially if it includes the recovery of carotenoids. The shells contain a carotenoid named astaxanthin which has not yet been synthesized and has good commercial value.

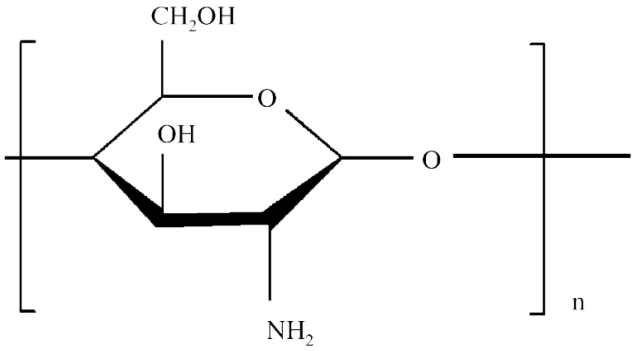

Figure 2.2 Chemical structure of Chitosan

Chitosan has a low value of pKa (Acid dissociation constant). In contrast to chitin, the presence of free amine groups along the chitosan chain allows this macromolecule to dissolve in diluted aqueous acidic solvents due to the protonation of these groups, rendering the corresponding chitosan salt in solution. Chitin and chitosan are naturally abundant and they are renewable polymers. They have excellent properties such as, biodegradability, bio-compatibility, non-toxicity, good ability for guided tissue regeneration, bioabsorbability and nonantigenic nature. They exhibit properties such as solubility in various media, solution, viscosity, polyelectrolyte behaviour, polyoxysalt formation, ability to form films, metal chelations, optical, and structural characteristics [40]. Chitosan is used in

drug delivery applications. It is biocompatible and can increase membrane permeability both *in vitro* and *in vivo* [32,28].

2.2.2 Arrowroot (starch)

Arrowroot is obtained from the rhizomes of Marantha arundinacea, a tropical and perennial tuberous plant belonging to the family Maranthaceae [55]. Arrowroot is basically starch. More than 85% (on dry basis) of this tuberous root is starch. It is a chief ingredient of baby food, talcum powder etc. It has been reported to have used in food industry as chief ingredient in various products [41]. Arrowroot is a traditional medicine for wound healing. It has also been used in therapeutic applications [21] and for treatment of diarrhoea in irritable bowel syndrome patients [42]. Arrowroot powder could be gelatinized when heated in aqueous solution. Arrowroot thickens at a lower temperature than flour or corn starch, is not weakened by acidic ingredients, has a more neutral taste, and is not affected by freezing. Overheating tends to break down Arrowroot's thickening property. The gelatinization properties of starch with various temperature and mechanical methods were studied by Perez *et. al* [35]. Figure 2.3 shows the chemical structure of simple starch.

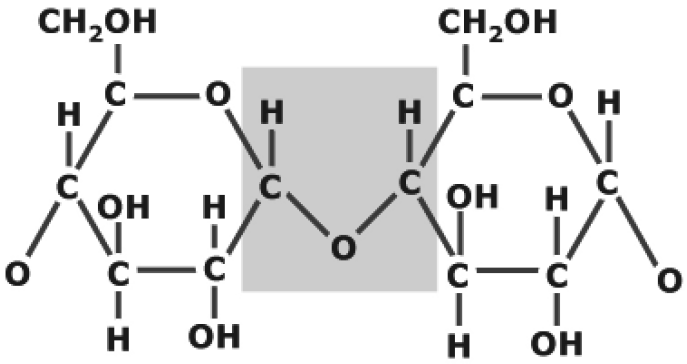

Figure 2.3 Chemical structure of starch

Arrowroot was also used to make photographic papers back in 1850s. Starch papers became very popular and almost completely displaced plain salted papers for matte-surfaced prints [8]. Arrowroot is very light on the stomach and in Victorian times used to be concocted into a drink and given to convalescing patients, or as a jelly to babies being weaned. The calorie content of Arrowroot is found to be very low. Due to this fact, nowadays arrowroot enjoys great popularity among calorie-conscious dieters.

2.2.3 Cellulose

Cellulose is the most abundant natural polymer in nature [92]. It is an organic compound with the formula $(C_6H_{10}O_5)n$. Cellulose is a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units [1,9]. The acetal linkage is beta which makes it different from starch. Here all the beta acetal links connect C # 1 of one glucose to C # 4 of the next glucose. This peculiar difference in acetal linkages results in a major difference in digestibility in humans.

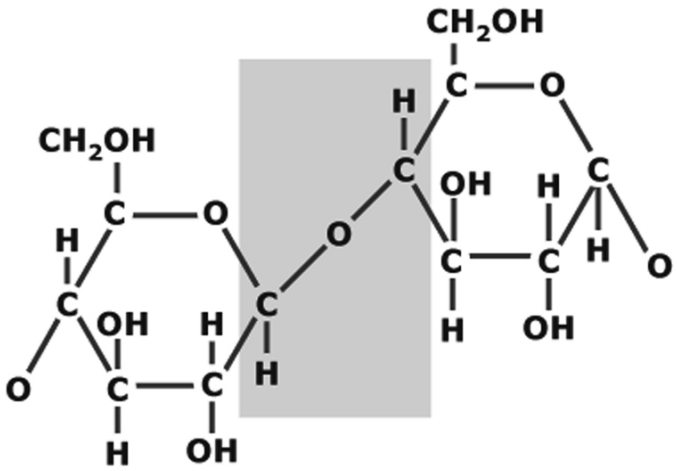

Figure 2.4 Chemical structure of Cellulose

The undigested Cellulose helps in the smooth operation down the intestinal tract. Cellulose was reported for making 3D phantoms using 3D printing technology [75]. In this method, three dimensional objects were created by solidifying layers of deposited powder using a liquid binder. Cellulose finds many uses such as wood for building, paper products, cotton, linen, and rayon for clothes; nitrocellulose for explosives, cellulose acetate for films etc.

2.2.4 Collagen

Collagen is a group of naturally occurring proteins found in animals, especially in the flesh and connective tissues of mammals [56]. It connects and supports other bodily tissues, such as skin, bone, tendons, muscles, and cartilage. Collagen does not exist as isolated molecules in the extracellular space in the body. Instead, Collagen molecules aggregate into fibrils. Depending on the tissue and age, a Collagen fibril varies from 50nm-300nm in diameter [76]. There are more than 25 types of Collagens that naturally occur in the body. About 25 percent of the total amount of proteins in the body is Collagen. Collagen works along with elastin in supporting the body's tissues. It gives body tissues form and provides firmness and strength. Elastin gives the same body tissues flexibility. Collagen has been widely used in cosmetic surgery, as a healing aid for burn patients for reconstruction of bone and a wide variety of dental, orthopedic and surgical purposes. Both human and bovine collagen is widely used as dermal fillers for treatment of wrinkles and skin aging. Collagen is also used a medium for drug delivery [26].

2.3 Bioceramics

Bioceramics are a subset of biomaterials. These materials find application mainly as alternative for bones, heart valves, dental implants etc. They are used in powder, paste and solid forms depending on the application. They are characterized by high melting point, high to medium mechanical strength, very low elasticity,

hard brittle surface and low conductivity of heat and electricity [77]. Bioceramics range in biocompatibility from the ceramic oxides, which are inert in the body, to the other extreme of resorbable materials, which are eventually replaced by the materials which they were used to repair. Bioceramics are also used in many types of medical procedures. Bioceramics can be classified according to their reactivity with living tissue as bioactive or bioinert [86]. Those ceramics designed to induce tissue reactions for bonding or those used to deliver drugs are usually bioreactive (eg. Calcium phosphates and glass ceramics).

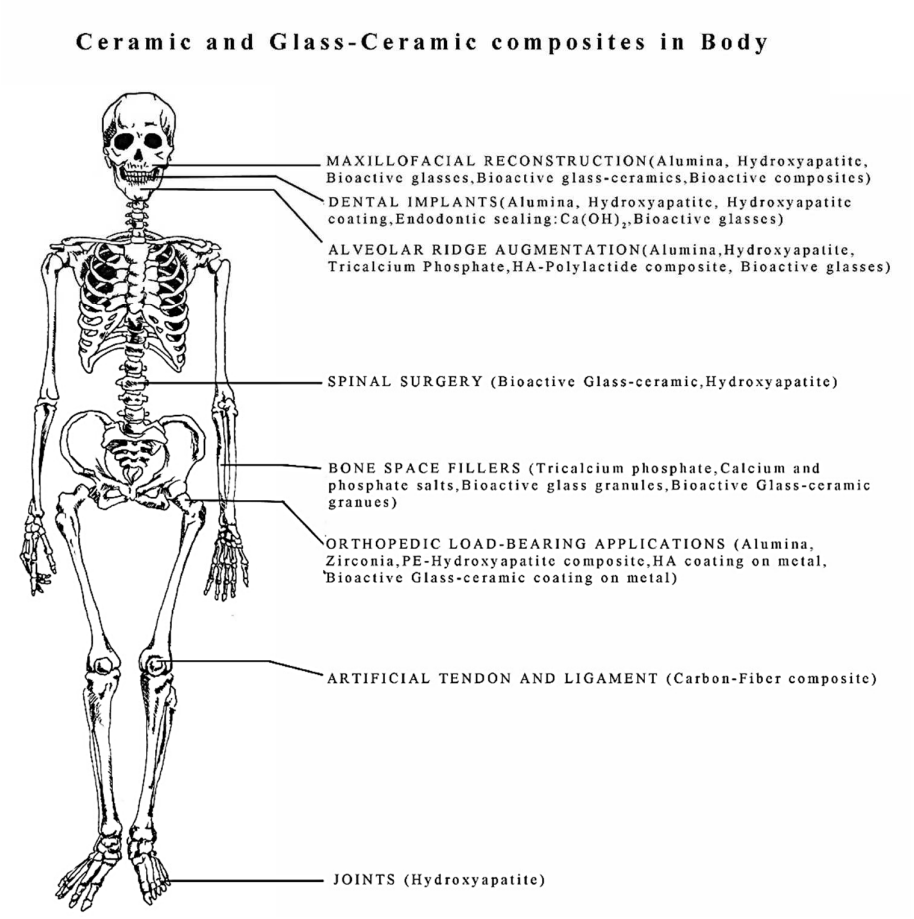

Figure 2.5 Use of Bioceramics and Bio Glass composites in human body

Bioceramics are relatively inert to body fluids, have high compressive strength and aesthetically pleasing appearance. These properties make them important in dental applications. Unlike metals and polymers which can shear plastically, ceramic materials cannot shear. This is due to the (ionic) nature of bonding and minimum number of slip systems. These features make the ceramic non-ductile and are responsible for almost zero creep at room temperature [19]. The porosity of the bioceramics is a critical factor for growth and integration of tissue into an implant. It becomes more significant if the bioceramics implant is inert. Bioceramic materials can be made porous by many techniques. Starch consolidation [36,51] and drip casting [29] are the commonly used methods.

Figure 2.5 shows various applications of Bioceramics and Bioactive glasses within human body. It can be observed that bioceramics can be of great help in repairing and maintaining many parts of human endoskeleton.

2.3.1 Composition of Bone

Bone provides support and protects various organs of a vertebrate. The bone comes in different shapes and is different in both internal and external structure. However the physiochemical structure of the bone is similar regardless of the variation in size and shape. The bone can be defined as a special blend of organic matrix and inorganic elements. The organic matrix constitutes 30% whereas the inorganic materials constitute the rest 70% [78]. The organic material is largely collagen and the inorganic matter is Calcium phosphate compounds which are similar to Hydroxyapatite ceramic. Living cells called Osteocytes and Osteoblasts are present in bone which builds bone. It also has cells called Osteoclasts which resorb old bone during bone remodelling. With these three living cells in action, the bone constantly rebuilds and renews throughout the lifetime of a person [60].

2.3.2 Osteoconduction and Osteoinduction

Osteoconduction and Osteoinduction are two important properties of bone. The meaning of Osteoconduction is different in many fields. For clinical use,

osteoconduction means bone formation towards implant from host bone bed. Hydroxyapatite ceramics have found to be osteoconductive in many studies [10, 12]. Any biomaterial can be osteoconductive due to the regeneration ability of bone itself. Osteoconduction in biomaterials science means guided bone formation on material surfaces resulting in bone bonding. This property is also known by the names "bioactivity", "osteocoalesce" and "osteointegration". Osteoconductive biomaterials ensure the structural and mechanical continuity of the repaired bone [15,18]. Osteoconductive materials are good bone grafting materials.

The guided bone formation in osteoconductive biomaterials is limited by distance. They cannot stimulate bone formation in large bone defects. For large bone defects, the bone should be formed far from host bone bed by osteoinduction. Osteoinduction is a kind of bone formation that doesn't start directly from osteogenic cells. The process of Osteoinduction involves two steps. In first step, cell differentiation from non osteogenic cells to osteogenic cell occurs. In second step, bone morphogenesis occurs. If a biomaterial causes bone formation after implantation in a non-osseous site, the biomaterial is defined as an osteoinductive biomaterial [60].

2.3.3 Hydroxyapatite, Beta Tricalcium Phosphate and Biphasic Calcium Phosphate

The more often-used calcium phosphate ceramics are hydroxyapatite ceramic (HAp), Tricalcium phosphate ceramic (β-TCP) and the mixture of those two, Biphasic Calcium Phosphate ceramics (BCP with both HAp and β-TCP at different ratio). All calcium phosphate ceramics are biocompatible, osteoconductive, non-toxic, antigenically inactive and non-carcinogenic. The Calcium phosphate materials also differ in their dissolution behaviour. The HAp is almost non resorbable whereas β-TCP is highly resorbable. The resorbability of BCP depends on the ratio between HAp and β-TCP.

Hydroxyapatite has the chemical formula $Ca_{10}(PO_4)_6(OH)_2$ and is the most commonly used bioceramics material. It is stable in body fluid and in dry or moist

air up to 1200°C and does not decompose. The HAp of bone is about (1.5-3.5 nm) × (5.0-10.0) × (40.0-50.0) in size with a platelet shape [22]. Pure hydroxyapatite powder is white. Naturally occurring apatites can, however, also have brown, yellow, or green colorations. The Ca/P ratio in HAp is 1.67 and it possesses a hexagonal structure. Various manufacturing methods of HAp are shown in Table 2.1. HAp is used as dense blocks, Cements, as plasma coating and in composite form. Synthetic HAp varies in morphology, size, chemical composition and crystallinity. Hydroxyapatite ceramic was implanted subcutaneously in dogs and got good results [17]. Techniques like micro-arc oxidation were used for coating of porous HAp on commercially pure titanium [79].

Table 2.1 Preparation techniques of Hydroxyapatite

Techniques	Starting materials	Synthetic conditions	Comments
Solid-state reaction	$Ca_3(PO_4)_2 + CaCO_3$ $Ca_2P_2O_7 + CaCO_3$	900~1,300°C, usually with water vapor flowing	Ca/P = 1.67, large grain size, irregular forms, inhomogeneous
Wet chemical method	$Ca(NO_3)_2 + (NH_4)_2HPO_4$ $Ca(OH)_2 + H_3PO_4$	R.T. ~ 100°C pH: 7~12	Ca/P < 1.67, fine irregular crystals with low crystallinity, inhomogeneous
Hydrothermal method	Wet chemically prepared HA, other calcium phosphates, seeding	100~200°C (1~2 MPa) 300~600°C (1~2 kbar)	Ca/P = 1.67, homogeneous, fine single crystals or large crystals
Gel growth method	Gel + Ca^{2+} + PO_4^{3-}	R.T. ~ 60°C pH: 7~10	Large monetite, brushite, OCP, but small Hap
Melt growth method	$Ca_3(PO_4)^{2-}$ PO_4^{3-} CaF_2, $CaCl_2$	1650°C	Large crystals with lattice strain
Flux growth method	CaF_2, $CaCl_2$ as flux $Ca(OH)_2$ as flux	1325°C (FAp, ClAp) HA	Large crystals with little lattice strain

Hydroxyapatite can be found in teeth and bones within the human body. Thus, it is commonly used as a filler to replace amputated bone or as a coating to promote bone ingrowth into prosthetic implants. HAp ceramics cannot be used for heavy load bearing applications, but common uses include bone graft substitution and coatings on metallic implants.

β-TCP has better bioresorption properties than Hydroxyapatite ceramics. They are most commonly used as bone fillers. Porous β-TCP could be gradually degraded and finally replaced by new bone when it was buried in the bone defect. β-TCP has been used as a bone substitute in maxillofacial, orthopedic and neurosurgical operations for several years. Hisaya Orii *et. al.* performed studies on the use of β-TCP for posterolateral spine fusion [63]. Beta tricalcium phosphate (β-TCP) is represented by the chemical formula $Ca_3(PO_4)_2$, the Ca/P ratio being 1.5. β-TCP shows an X-ray pattern consistent with a pure hexagonal crystal structure but the related α-TCP is monoclinic. β-TCP turns into α-TCP around 1200°C; the latter phase is considered to be stable in the range 700 to 1200°C. β-TCP is highly soluble in body fluid. HAP is formed on exposed surfaces of TCP by the following reaction.

$$4Ca_3(PO_4)_{2(s)} + 2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_{2(surface)} + Ca^{2+} + 2HPO_4^{2-}$$

Due to the rapid degradation and weak mechanical properties of β-TCP, present day research works are concentrated on mixed calcium phosphates (mixtures of β-TCP and HAp or β-TCP and polymer)

Biphasic Calcium Phosphate is obtained by mixing β-TCP and HAp and calcinating the mixture at 650-700ºC for 3-4 hours [57]. The bioresorbability of BCP depends highly on the β-TCP/HAp ratio. BCP ceramic has a higher osteoinductive potential than HAp. Calcium phosphate materials were used to study osteoinduction in animals. Both HAp and BCP ceramics induce bone formation in muscles of dogs, but only BCP that has a higher osteoinductive potential than HAp induced bone formation in soft tissues of rabbits and mice [46].

2.4 Conducting polymers

Conducting polymer field has never stayed out of focus of the science community since the accidental discovery of highly conducting Polyacetylene film by Shirakawa *et al.* in 1967 [80]. The efforts made by Alan J. Heeger, Hideki Shirakawa, and Alan G. MacDiarmid were honored by the Nobel prize in 2000 [95].

There are two main classes of electron-conducting polymers based on the mode of electron transport: redox polymers and electronically conducting polymers. Redox polymers contain electrostatically and spatially localized redox

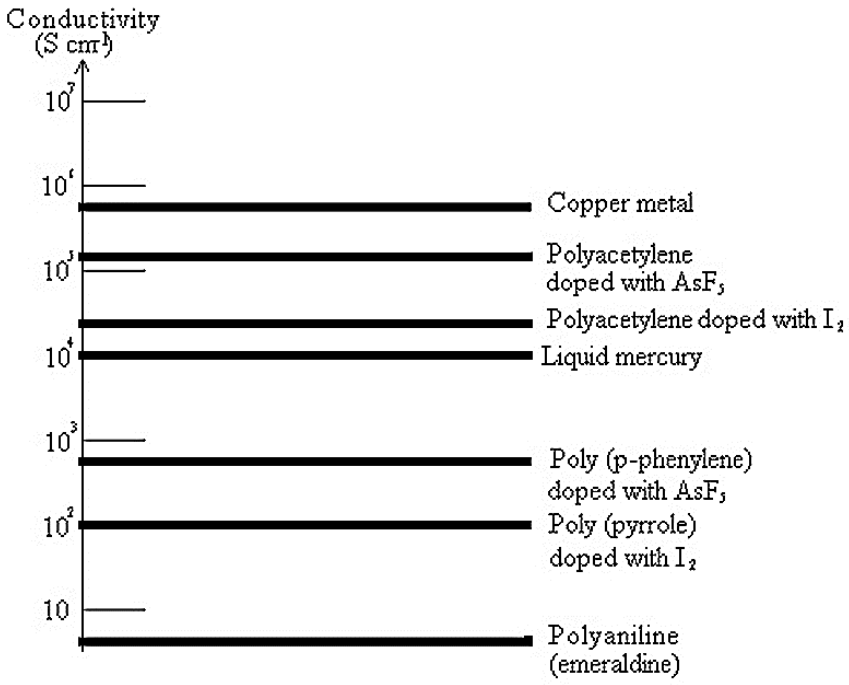

Figure 2.6 Comparison of conductivity of some conducting polymers and metals

sites which can be oxidized or reduced, and the electrons are transported by an electron exchange reaction (electron hopping) between neighbouring redox sites. Conductive polymers or, more precisely, intrinsically conducting polymers (ICPs)

are organic polymers that conduct electricity [87]. They are polymeric materials whose conductivities vary from that of a semiconductor to a metallic conductor. Their Conductivity, unlike metals, is not due to the valance band electrons but by the presence of π conjugated pairs of monomer units in the polymer chain [47, 48]. The conjugated chain indicates the presence of alternate single and double bonds in the polymer chain. The electric conduction occurs when the delocalized charges in the ICP chain shifts their place [16]. However, the electron hopping mechanism is likely to be operative, especially between chains (inter-chain conduction) and defects. Several polymers such as PEDOT, poly pyrrole, poly urethane, polysulfur nitride are good conductors of electricity. Some have even attained conductivities of the order of 10^3 S/cm and above, nearing to the conductivity of copper (~10^5 S/cm) [80]. Figure 2.6 shows the logarithmic conductivity ladder of some common conducting polymers and metals.

Many studies have been performed on the electrical and microwave properties [11,20] of conducting polymers. S. V. Jadhav and Vijay Puri [88] performed a work based on overlay technique for finding the permittivity and microwave absorption of Polyaniline. The effect of drying conditions on dielectric behavior of Polyaniline was studied by Honey *et al* [52]. The conducting polymer is subjected through a process called doping which involves treatment with acid. The acid protonates the polymer and result in production of delocalized charges which enhances the conductivity of the material. In a similar way, a conducting polymer can be de-doped by treatment with alkali. By varying the pH of the solution used for treatment, we can control the conductivity of the material to the desired value. The acids commonly used are Nitric acid, Perchloric acid, Hydrochloric acid, Sulphuric acid, Phosphoric acid and organic acids like Camphor sulphonic acid, Dodecyl Benzene Sulphonic acid, Toluene Sulphonic acid etc. The electrical properties of conducting polymers vary with the amount of oxidation. Table 2.2 shows the variation of the qualitiative properties of conducting polymers in their oxidized and conducting states.

*PEDOT-Poly(3,4-ethylenedioxythiophene)

Table 2.2 Qualitative properties of conducting polymers as a function of their charge state

Properties/Charge state Reduced Oxidized	*Properties/Charge state Reduced Oxidized*	*Properties/Charge state Reduced Oxidized*
Stoichiometry	Without anions (or with cations)	With anions (or without cations)
Content of solvent	Smaller	Higher
Volume	Smaller	Higher
Colour	Transparent or bright	Dark
Electronic conductivity	Insulating, semiconducting	Semiconducting, metallic
Ionic conductivity	Smaller	High
Diffusion of molecules	Dependent on structure	Dependent on structure
Surface tension	Hydrophobic	Hydrophilic

Conducting polymers find significant applications such as antistatic coatings, microwave absorption, microelectronics, electroluminescent and electrochromic devices, membranes and ion exchanger, corrosion protection, sensors, as materials for energy technologies, artificial muscles, electrocatalysis etc. Conducting polymers offer a unique combination of properties that make them attractive alternatives for certain materials currently used in microelectronics. Conducting polymers are effective discharge layers as well as conducting resists in electron beam lithography, find applications in metallization (electrolytic and electroless) of plated through-holes for printed circuit board technology.

Polyaniline

Conductive polyaniline (Pani) has been studied extensively because of its ease of synthesis in aqueous media, its environmental stability and special electrical and other properties [82]. Polyaniline exists in a variety of forms (pernigraniline, emeraldine, leucoemeraldine) that differ in chemical and physical properties. The most common green protonated emeraldine has conductivity on a semiconductor level of the order of 100 S cm–1, many orders of magnitude higher

than that of common polymers (<10–9 S cm–1) but lower than that of typical metals (>104 S cm–1).

Pani is prepared by mixing aqueous solutions of aniline hydrochloride and ammonium peroxydisulfate (APS) at room temperature, followed by the separation of Pani hydrochloride precipitate by filtration and drying. The efficient polymerization of aniline is achieved only in an acidic medium, where aniline exists as an anilinium cation. Peroxydisulfate is the most commonly used oxidant. The resulting Pani, protonated with various acids, differs in solubility, conductivity, and stability [33]. The oxidation of aniline is exothermic so the temperature of the reaction mixture can be used to monitor the progress of reaction.

Figure 2.7 shows the oxidation reaction of Aniline hydrochloride with Ammonium peroxydisulphate yielding Polyaniline (Emeraldine) hydrochloride.

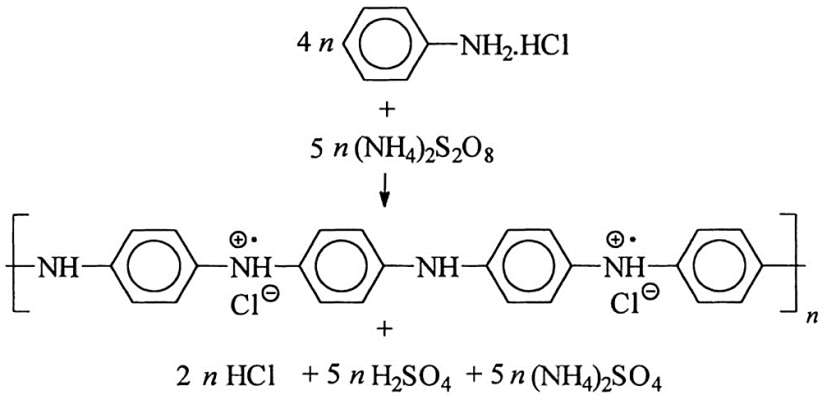

Figure 2.7 Preparation of Polyaniline by oxidation of Aniline hydrochloride with APS

To minimize the presence of residual aniline and to obtain the best yield of PANI, the stoichiometric peroxydisulfate/aniline ratio 1.25 is recommended [13]. The conductivity of Pani shows variation during storage. The conductivity of Pani bases is many orders of magnitude lower compared to that of Pani salts. Even after

a long-term storage, the conductivity remains more than 10^8-times higher than the conductivity of Pani base and, in this sense, the conductivity change during storage may be considered as being negligible [67]. The powder form of Pani is more prone to changes than pellet form.

Polyaniline composites have been used as microwave absorber [81, 93]. In a study which involved PVC loading of Pani, it was found that the conductivity and absorption coefficient of the composites increased with the increase in PVC loading. To explain the microwave behaviour of a conducting polymer, its dielectric properties have to be investigated. Several researchers have determined the dielectric properties of Pani and its blends/composites at various frequencies using various techniques [58,68,83,89].

2.5 Microwave interaction with biological tissues

The effects of the interaction of RF and microwave radiation with biological tissues can be considered as the result of three phenomena [69]

1. The penetration of EM waves into the living system and their propagation into it.
2. The primary interaction of the waves with biological tissues.
3. The possible secondary effects induced by the primary interaction.

The interaction of the electromagnetic wave implies that the end result depends on two things, the penetration of the wave into the living tissue as well as the reaction produced in the living tissue. It may either result in physiological compensation or in pathological compensation. Physiological compensation means that the strain given by the wave is fully compensated and the organism is able to perform normally. Pathological compensation means that the strain leads to visible functional disturbances of the organism or structural alterations. Pathological

*PVC-Polyvinyl Chloride

compensation can lead to undesired results and the line of separation between these two effects is quite narrow and almost undetermined.

2.5.1 Electromagnetic Radiation

When an electromagnetic wave interacts with a body, the scope and mode of interaction depends mainly on the dielectric properties of the tissue which is exposed to the radiation. The radiation mechanism involves a source which emits electromagnetic energy. When a biological system is exposed to such a radiation, part of the incident energy is reflected back, part of it gets absorbed in the tissues/body fluids and the rest is transmitted through the body. A person's body contains a large amount of water which absorbs the microwave frequency radiation. The physical laws of EM field theory, reflection, diffraction, dispersion, interference, optics, and quantum effects, must be applied to investigate and explain the observed phenomena. When the wavelength of a signal is significantly larger than the cross-section of the human body being penetrated there is very little effect on the signal. These wavelengths occur at frequencies below 4 MHz. Above 4 MHz, the absorption of RF energy increases and the human body may be considered to be essentially opaque. Above roughly 1 GHz the dielectric properties of the human body begin to introduce a scattering effect on the RF signal.

2.5.2 Ionizing and Non Ionizing radiation

Radio frequencies and microwaves are nonionizing radiation. High frequency radiations like x-rays are ionizing. Ionization can occur not only due to absorption of the radiation, but also due to the collision with foreign/injected particles as well as collision with its own atoms [69]. The ionization caused by external causes outside the living system may permanently alter or destroy the functioning of the living system. If the incident energy quantum has sufficient magnitude, it can pull an electron away from one of the constituent atoms. The “Ionization potential” is the energy required to remove one electron from the highest energy orbit. Typical ionization potentials are of the order of 10eV. The

chemical binding forces are electrostatic. Hence when a material is ionized, it essentially brings about chemical changes. At RF/Microwaves, and even at millimetre waves, the quantum energies are well below the ionization potential of any known substance.

Exposure to non-ionizing radiation (NIR) may cause different biological effects. Biological effects may be without any known adverse or beneficial consequences, other effects may result in pathological conditions (diseases) [53]. Annoyance or discomfort may not be pathological as such but, if substantiated, can affect the physical and mental well-being of a person and the resultant effect should be considered as a potential health hazard. Some adverse effects and the relevant mechanism of interaction of non-ionizing radiation are shown in table 2.3.

Table 2.3 Adverse effects and mode of interaction of Non-ionizing radiation

Part of NIR spectrum	*Relevant mechanism of interaction*	*Adverse effect*
Static electric fields.	Surface electric charges.	Annoyance of surface effects, shock
Static magnetic fields.	Induction of electric fields in moving fluids and tissues.	Effects on the cardiovascular and central nervous system
Time-varying electric fields (up to 10 MHz).	Surface electric charges. Induction of electric fields and currents.	Annoyance of surface effects, electric shock and burn. Stimulation of nerve and muscle cells; effects on nervous system functions.
Time-varying magnetic fields (up to 10 MHz).	Induction of electric fields and currents.	Stimulation of nerve and muscle cells; effects on nervous system functions.

Electromagnetic fields (100 kHz to 300 GHz).	Induction of electric fields and currents; absorption of energy within the body. > 10 GHz: Surface absorption of energy. Pulses < 30 ps, 300 MHz to 6 GHz, thermo-acoustic wave propagation.	Excessive heating, electric shock and burn. Excessive surface heating. Annoyance from microwave hearing effect.

2.5.3 Microwave Syndrome

Humans exposed to very low power densities (often in between a few microwatts per square centimeter and a few milliwatts per square centimeter) may develop the so called microwave syndrome or microwave sickness. The microwave syndrome may involve headache, perspiration, emotional instability, irritability, tiredness, somnolence, sexual problems, loss of memory, concentration and decision difficulties, insomnia, and depressive hypochondriac tendencies. However, these complaints are very subjective and their evaluation is difficult in the absence of well-established dosimetric data. These effects may well be due to environmental factors unrelated to microwaves, but a possible nonthermal mechanism cannot be completely ignored [37].

Mechanisms and effects in alarm and resistance phase characterise the microwave syndrome. In alarm phase, the brain which is subjected to a short stimulation of artificial EMF radiation of microwave type triggers specific reactions from the organism involving neuronal, neuro-endocrinal, metabolic and behavioural responses. This includes response from the organism via the tonsils and the hippocampus that acts on the hypothalamus and on the cerebral trunk reticulated formation in order to activate the Vegetative nervous system and the Adrenal gland. After the alarm phase, if the stress element persists even at low dosage or becomes chronic, the result is that the hypothalamus, etc. are going to

assess this constant stress and activate the secretion of various hormones. This phase is called resistance phase.

2.5.4 Low level pulsed exposure

Low level pulsed microwave exposure is reported to have an impact on brain neurochemistry [25]. The low level exposure is supposed to be a cause for mild stress. The long-term biological consequences of repeated microwave exposure also depend on the exposure parameters. At present, there is no convincing evidence that repeated exposure to low-level microwaves could lead to irreversible neurological effects.

2.5.5 Microwave absorption

When a body is exposed to microwave radiation, some of the incident microwave power is reflected back, some is transmitted and the rest is absorbed by the body. This can be represented as

$P_I = P_R + P_T + P_A$

The biological effects of microwaves do not depend solely on the external power density; they depend on the dielectric field inside the tissue or the body. The body fluids mainly constitute towards the dielectric properties of the body. Hence the amount of absorbed power depends chiefly on the amount of water present in the particular body part. As a result, the fatty areas do not absorb much microwave, but reflects it. Bones which compose of Calcium and Phosphorous compounds absorb less microwave power. They transmit microwaves rather than reflect. Different energy absorption rates can result in thermal gradients causing biological effects that may be generated locally and are difficult to anticipate. Dosimetric studies quantify the interactions of RF fields with biological tissues and bodies. A biological body is an inhomogeneous lossy dielectric material. The intensity of the internal fields depends on a number of parameters such as frequency, intensity, and polarization of the external field; size, shape, and dielectric properties of the body; spatial configuration between the exposure source and the exposed body; and the

presence of other objects in the vicinity [69]. So the computational complexity increases with increase in model size. The incident microwave energy can be converted to other forms of energy and cause interference with the functioning of the living system. Most of this energy is converted into heat: This is absorption. The waves do not necessarily penetrate the entire body. Penetration is limited by the skin effect, characterized by skin depth. In general, at a given frequency, the lower the water content of the tissue, the deeper a wave can penetrate. Also, at the frequencies of interest, the lower the frequency, the deeper is the depth of penetration into tissues with given water content.

2.5.6 Specific Absorption rate (SAR)

The SAR information of RF equipment is one of the most speculated information as far as exposure to electromagnetic radiation is concerned. It is a measure of the rate at which energy is absorbed by the body when subjected to electromagnetic radiation. It is defined as the power absorbed per mass of tissue and has units of watts per kilogram (W/kg).

1. All SAR limits are to be averaged over any six-minute period.
2. Localized SAR averaging mass is any 10 g of contiguous tissues; the maximum SAR so obtained should be the value used for the estimation of exposure.

When a body is exposed to radiation, localized heating occurs. The human body counters this local heating by thermoregulation (blood flow through the affected organs). The eyes and male testes are particularly susceptible to RF heating because these organs have no direct blood supply and, hence, no way of dissipating heat. With the invention and popular use of cell phones, safety concerns have been focussed on RF absorption by head. Many studies have been performed on RF exposure [96,97]. Exposure to time-varying EMF results in internal body currents and energy absorption in tissues that depend on the coupling mechanisms and the frequency involved. The amount of RF exposure is linked with the exposure time. Maximum exposure is normally averaged over 6 minute periods

during the 24 hour day. The most widely accepted SAR standards are those developed by the ICNIRP and the American National Standards Institute/Institute of Electrical and Electronics Engineers (ANSI/IEEE). These limits are shown in tables 2.4 and 2.5.

Table 2.4 SAR limits recommended by ICNIRP

Exposure characteristics	Frequency range	Whole body average SAR (W/kg)	Localized SAR (head and trunk) (W/kg)	Localized SAR (limbs) (W/kg)
Occupational exposure	100KHz-10GHz	0.4	10	20
General public exposure	100KHz-10GHz	0.08	2	4

Table 2.5 SAR Limits Recommended by ANSI/IEEE

Exposure characteristics	Frequency range	Whole body (W/kg)	Partial body (W/kg)	Hands, wrists, feet and ankles (W/kg)
Occupational exposure	100KHz-6GHz	0.4	8	20
General public exposure	100KHz-6GHz	0.08	1.6	4

1. For occupational exposure, the SAR limits are averaged over any six-minute interval.
2. For general public exposure, the averaging time for SAR limits varies from six minutes to 30 minutes.
3. Whole-body SAR is averaged over the entire body, partial-body SAR is averaged over any 1 g of tissue defined as a tissue volume in the shape of a

cube. SAR for hands, wrists, feet and ankles is averaged over any 10 g of tissue defined as a tissue volume in the shape of a cube.

Exposure to low-frequency electric and magnetic fields normally results in negligible energy absorption and no measurable temperature rise in the body. However, exposure to electromagnetic fields at frequencies above about 100 kHz can lead to significant absorption of energy and temperature increases [38]. In tissue, SAR is proportional to the square of the internal electric field strength. When the long axis of the human body is parallel to the electric field vector and under plane-wave exposure conditions (far-field exposure), whole-body SAR reaches maximal values. The amount of energy absorbed depends on a number of factors, including the size of the exposed body. The SAR values depend mainly on factors such as frequency, intensity, polarization, near/far field of the incident wave, the size and internal/external geometry of the exposed body, the dielectric properties of the tissues and the presence of other objects in the vicinity of field near the exposed body.

2.6 Dielectric characterization of body tissues

The dielectric characterization of body tissues have been reported by many authors [14,30,65]. These studies were mostly done on dead tissue as the measurement process involves the contact of the measuring device with the tissue. Non-destructive evaluation is possible, but is prone to measurement errors as several factors like blood pressure, other body fluids, skin condition (dry/wet), and multiple reflection form different layers etc. tend to influence the measurement accuracy.

From an electrical point of view, the skin can be regarded as a two-layered structure, namely the poorly conducting stratum corneum and the more conductive epidermis. Valerica Raicu *et. al* [43] used coaxial open ended probe to determine the dielectric properties of human tissues in vivo, either dry or moistened with physiological saline. Their study suggested that the coaxial probe reports on the

properties of the superficial layer, the stratum corneum, when the skin surface is dry, whilst the signal from deeper skin layers becomes dominant after wetting the skin with conductive physiological saline. The use of coaxial probe is limited by factors such as probe size, skin condition and the separation between the probe and skin. Typical variation of dielectric properties of hum skin (back of neck, young male) is shown in figure 2.8.

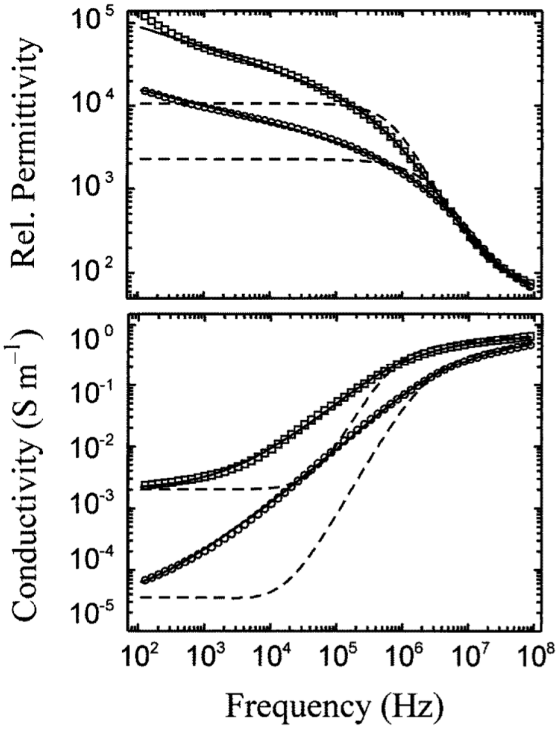

Figure 2.8 Dispersion spectra of relative permittivity and conductivity of human skin *in vivo*

O ,dry and □ , moistened with physiological saline.

Water is the major constituent in most tissues, and in several respects the dielectric properties of tissues reflect those of water. At RF frequencies, the conductivity of tissue is essentially that of its intracellular and extracellular fluids. At microwave frequencies the dielectric dispersion arises from the dipolar relaxation of the bulk tissue water. Water associated with protein surfaces has a

lower relaxation frequency than that of the bulk liquid, and this water fraction contributes noticeably to the dielectric dispersion at frequencies near 1GHz. The dielectric properties of various body tissues at 2.4GHz is shown in Table 2.6 [98].

Table 2.6 Dielectric properties of body tissues at 2.4GHz

Tissue name	Conductivity [S/m]	Relative permittivity	Loss tangent	Wavelength [m]	Penetration depth [m]
Air	0	1	0	0.12491	N/A
Aorta	1.4041	42.593	0.2469	0.018998	0.02486
Bladder	0.67265	18.026	0.27948	0.029143	0.033828
Blood	2.5024	58.347	0.32123	0.016151	0.016407
Blood Vessel	1.4041	42.593	0.2469	0.018998	0.02486
Body Fluid	2.4392	68.24	0.26771	0.01499	0.018137
Bone Cancellous	0.78761	18.606	0.31705	0.02861	0.029428
Bone Cortical	0.38459	11.41	0.25244	0.036693	0.046992
Bone Marrow	0.092834	5.3024	0.13113	0.054131	0.13196
Brain Grey Matter	1.773	48.994	0.27104	0.017687	0.021147
Brain White Matter	1.1899	36.226	0.24602	0.020601	0.027051
Breast Fat	0.13344	5.1563	0.19382	0.054755	0.090761
Cartilage	1.7172	38.878	0.33081	0.019772	0.019531
Cerebellum	2.069	44.893	0.34518	0.018379	0.017439
Cerebro Spinal Fluid	3.4122	66.319	0.38536	0.015071	0.012895
Cervix	1.6933	47.673	0.26604	0.017936	0.021834
Colon	1.9997	53.969	0.27753	0.016845	0.019686
Cornea	2.2588	51.697	0.32725	0.017151	0.017118
Duodenum	2.1671	62.239	0.26079	0.015703	0.019487
Dura	1.6394	42.099	0.29167	0.019054	0.021228
Eye Sclera	1.9967	52.698	0.28378	0.01704	0.01949
Fat	0.10235	5.2853	0.14503	0.054193	0.11956
GallBladder	2.023	57.68	0.26269	0.01631	0.020098
GallBladder Bile	2.7575	68.417	0.30187	0.014936	0.016101
Gland	1.9283	57.272	0.25217	0.016378	0.020998
Heart	2.2159	54.918	0.30221	0.016671	0.017951
Kidney	2.3901	52.856	0.33868	0.016947	0.016372
Lens	1.4738	44.681	0.24705	0.018549	0.024258

Liver	1.6534	43.118	0.2872	0.018834	0.021296
Lung Deflated	1.6486	48.454	0.25484	0.017803	0.022593
Lung Inflated	0.79022	20.51	0.28857	0.027305	0.030733
Lymph	1.9283	57.272	0.25217	0.016378	0.020998
Mucous Membrane	1.5618	42.923	0.27253	0.018895	0.022471
Muscle	1.705	52.791	0.24191	0.017069	0.022785
Nail	0.38459	11.41	0.25244	0.036693	0.046992
Nerve	1.0681	30.196	0.26494	0.022538	0.027546
Oesophagus	2.1671	62.239	0.26079	0.015703	0.019487
Ovary	2.2277	44.817	0.3723	0.018354	0.016218
Pancreas	1.9283	57.272	0.25217	0.016378	0.020998
Prostate	2.1273	57.629	0.27648	0.016302	0.019121
Retina	1.9967	52.698	0.28378	0.01704	0.01949
Skin Dry	1.4407	38.063	0.2835	0.02005	0.022956
Skin Wet	1.5618	42.923	0.27253	0.018895	0.022471
Small Intestine	3.1335	54.527	0.43042	0.016553	0.012785
Spinal Chord	1.0681	30.196	0.26494	0.022538	0.027546
Spleen	2.2	52.546	0.31358	0.017029	0.017701
Stomach	2.1671	62.239	0.26079	0.015703	0.019487
Tendon	1.644	43.21	0.28496	0.018817	0.021437
Thymus	1.9283	57.272	0.25217	0.016378	0.020998
Thyroid	1.9283	57.272	0.25217	0.016378	0.020998
Tongue	1.7662	52.698	0.25102	0.017075	0.021989
Tooth	0.38459	11.41	0.25244	0.036693	0.046992
Trachea	1.4206	39.79	0.2674	0.019631	0.023779
Uterus	2.2058	57.897	0.28535	0.016255	0.018494
Vacuum	0	1	0	0.12491	N/A
Vitreous Humor	2.4392	68.24	0.26771	0.01499	0.018137

It can be seen that the dielectric properties highly depend on the water content of the tissues. High water content tissues have permittivity values above 60 (Body fluid, Cerebro Spinal fluid etc.) whereas low water content tissues have very low values of permittivity (breast fat, tooth etc.). The knowledge of the dielectric properties of the body tissues are very important in SAR studies and microwave imaging applications.

2.7 Microwave phantoms

Microwave phantoms are usually used to evaluate quantitative performance of imaging systems [84]. A phantom may be defined as a simulated biological body or as a physical model simulating the characteristics of the biological tissues. Therefore, phantoms can be either experimental or numerical models. The purpose and use of a phantom is to explore the interaction between body tissues and electromagnetic fields. Phantoms are used extensively in medical research on the effects of electromagnetic radiation on health. Phantoms were originally employed for use in 2D X-ray based imaging techniques such as radiography or fluoroscopy, though more recently phantoms with desired imaging characteristics have been developed for 3D techniques such as MRI, CT, Ultrasound, PET, and other imaging methods or modalities. Figure 2.9 shows a whole body phantom which is used for CT studies.

Figure 2.9* Whole body phantom used for CT

Phantoms also serve in development of various methods of medical diagnosis and treatment, such as X-ray, magnetic resonance imaging (MRI) scan, and hyperthermia. For cancer related studies, radioactivity is typically introduced into the phantom by filling hollow volumes with activity in a liquid mixture. A hot tumour is often modelled as a spherical volume contained in a uniform background. Images of such phantoms lend themselves to analysis that provides

*http://img.medicalexpo.com/images_me/photo-m/x-ray-test-phantoms-whole-body-69057-148563.jpg

*PET- Positron Emission Tomography

reproducible measurements of system characteristics. A phantom used to evaluate an imaging device should respond in a similar manner to how human tissues and organs would act in that specific imaging modality. Munro *et al* [50] performed measurements to determine dielectric properties of liquids and gels for use in as microwave phantoms.

With the advent of mobile phones, phantoms became an important experimental component in electromagnetic experimental studies. Specific absorption rate (SAR) is the standard guideline which is followed by many countries for limiting the acceptable level of exposure to electromagnetic radiation. The measurement and experiment of SAR involves the application of phantoms.

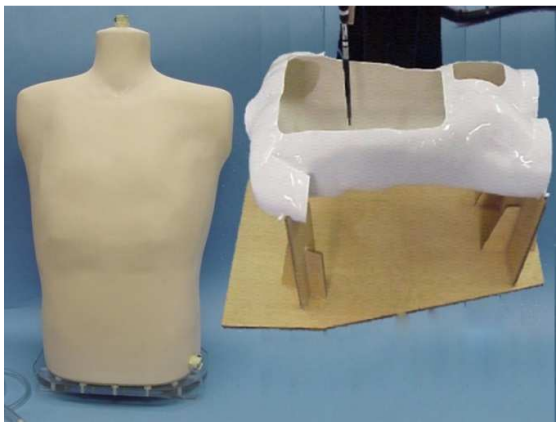

Figure 2.10* Human torso phantom used for measurement

Phantoms may be classified in many ways. They can be classified depending on the frequency range they are used, their physical state, or the type of tissue (low water content/ high water content) they represent. Phantoms in general can be classified as,

i) Physical phantoms

ii) Numerical Phantoms

*http://www.mcluk.org/pics/torsoinuse.jpg,
http://t1.gstatic.com/images?q=tbn:ANd9GcTFYavT_T2YGaiaeNdhVsDRiaEbYRU69ZGUgKHPHclaMOAxzRgG&t=1

2.7.1 Physical phantoms

Physical phantoms may again be divided into three types depending on the physical state of the material after manufacturing process is completed. They can be liquid, semi-solid and solid phantoms.

i) Solid phantoms (Dry phantoms)

A solid phantom is made up of materials which help it to keep its shape for a long period of time. It is mostly used in situations which demand the internal structure of body needs to be preserved. It also becomes useful when SAR has to be measured at the surface of the body. Glycerine phantoms are used to simulate tissue parts such as brain [44]. Table 2.7 shows the composition of a glycerine phantom for simulating a brain-equivalent tissue at 900MHz. The permittivity in a glycerine phantom is adjusted mainly with deionized water, and the conductivity is adjusted by the sodium chloride. The polyethylene powder is used in fine adjustment of the permittivity and conductivity.

Table 2.7 Composition of Glycerine phantom simulating brain tissue at 900MHz

Material	**Weight ratio (%)**
Deionized water	36.31
Glycerol	53.48
Sodium chloride	1.12
Polyethylene powder	3.74
Agar	5.35

ε_r=41.0, σ=0.88 S/m

A typical dry phantom is molded from paraffin, resin and silicon rubber with mixture of the powder of carbon and graphite. The dry phantom does not contain water and therefore avoids the problem of evaporation. Its advantage is that the permittivity and conductivity do not change with time; its drawback is the difficulty of manufacture. It is evident that scanning the electric fields in a solid

phantom for SAR measurement is impractical. Solid phantoms are more appropriate for measuring the temperature rise [71]. A number of solid phantoms have been reported, including a mixture of ceramic and graphite powder [34], silicone rubber mixed with carbon fiber [31], and conductive plastic containing carbon black [45].

ii) Semi solid phantoms

Gel phantoms can be manufactured from a physiological salt solution and polyethylene powder mixed with TX-150 (polyamide resin) or agar. Here, polyethylene powder and sodium chloride are used to control the relative permittivity and conductivity of the material, respectively. It is generally is used to simulate a high water-content tissue. With a gel phantom, it is difficult to have a fix shape, unless a container is used. It also has the problem of water evaporation. All the wet phantom materials degrade over time, due to the loss of water or by the growth of fungi. Several other materials including starch and polyvinyl acetate have been used to make gel phantoms [61, 72]. There is the possibility to visualize the temperature using a high-molecular-gel phantom, because it becomes opaque when the phantom's temperature exceeds a given value. Another solid gel phantom material uses polyacrylamide as its main constituent; this needs special care because of its toxicity. This type of material is capable of simulating both high and low-water content materials. The amount of water content depends on the liquid solvent used in its fabrication.

iii) Liquid phantoms

A liquid phantom permits scanning the electric fields inside it using an electric field probe, which can provide high-precision SAR measurement. It consists of a container filled with a liquid that has the same electrical characteristics as the tissues in the human body, in the defined range of frequencies. Its electrical conductivity is varied by adding appropriate amount of NaCl. The main materials in most liquid phantoms are deionized water, sugar and sodium chloride. Also other materials, such as hydroxyethyl cellulose (HEC), bactericide, and diethylene glycol butyl ether often are used to adjust the

permittivity and conductivity [71]. Because it is based on water, a liquid phantom generally is good at simulating a high water-content tissue. A mixture of a physiological salt solution and ethylene glycol enables the liquid phantom also to simulate a low water-content tissue. The drawback of the liquid phantoms is the evaporation of water, which changes the permittivity and conductivity. This can be managed by proper refilling of water in the container. The permittivity of the liquid is altered by adding sugar solution. Table 2.8 shows the composition of a liquid phantom which simulates brain tissue at 900 MHz.

Table 2.8 A liquid phantom which simulates brain tissue at 900 MHz.

Material	**(Weight ratio %)**
Deionized water	41.45
Sodium chloride	1.35
Sugar	56.50
HEC	1.00
Bactericide	0.10

ε_r=41.5, σ=0.97 S/m

2.7.2 Numerical phantoms

Numerical phantoms are CAD models of the body which have complex structures and shapes. They are used for simulation and computation purposes. The software assigns the dielectric property of a particular tissue to the numerical phantom from a material database. These phantoms are prepared by the assimilation of data obtained from high resolution MR imaging. The CAD format of the organs allows meshing at arbitrary resolution without loss of detail and small features due to repeated sampling. In theoretical analysis, simple shaped phantoms are usually used. The more realistic complex phantoms are known as voxel phantoms.

i) Theoretical phantoms

Theoretical phantoms are homogeneous. Their dielectric properties are constant over a bulk volume. They are also known as layered flat phantoms [3]. Their main purpose is to evaluate electromagnetic dosimetry and their sources are Spherical theoretical models were used for dosimetry study of head and eye [2, 4]. Similarly cylindrical models were used to represent body [6]. These models are used along with electromagnetic simulation tools which employ computational methods like FDTD, FEM and MOM for simulation purposes. Theoretical phantoms are used to assess the influence of anatomical and physiological parameters on complex biological processes and to gain a better understanding of biological mechanisms.

ii) Voxel phantoms

Voxel phantoms are complex realistic phantoms. They are prepared from high resolution MR imaging data. The uses of voxel phantoms in computational purposes demand high processing power. Whole body voxel models are available. Even voxel models of some common animals are available now. Miller *et al.* developed anatomically realistic PET and PET/CT phantoms with rapid prototyping technology [75]. They created the PET image of an example phantom by generating a three-dimensional binary mask of the phantom geometry using cubic voxels 1 mm on a side. Dimbylow developed an anatomically realistic voxel model of an entire body to simulate the reference man (176 cm, 73 kg) [27]. A work on the analysis of RF exposure in the head tissues of children and adults were done by J. Wiart *et. al.*[91]. They analysed maximum specific absorption rate (SAR) over 10 g in the head in seven child and six adult heterogeneous head models.

2.8 Desired features of a phantom for clinical use

Biomaterial based phantoms can also be used for clinical use. The success of such an implant material depends on factors like biocompatibility of the implant, the health condition of the recipient and the efficiency of the surgeon. Below mentioned are the expected requirements for a bone plate implant for stabilizing a fracture.

1. Acceptance of the plate to the tissue surface (biocompatibility)
2. Pharmacological acceptability (nontoxic, non-allergenic, non-immunogenic, non- carcinogenic, etc.)
3. Chemically inert and stable
4. Adequate mechanical strength
5. Adequate fatigue life
6. Sound engineering design
7. Proper weight and density
8. Relatively inexpensive, reproducible, and easy to fabricate and process for large scale production

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Chapter 3
Biomaterials

3.1 Introduction

Biomaterials are defined as materials of synthetic as well as of natural origin in contact with tissue, blood, and biological fluids, and intended for use for prosthetic, diagnostic, therapeutic, and storage applications without adversely affecting the living organism and its components [1]. It is also defined as a nonviable material used in a medical device, intended to interact with biological systems [2]. Biomaterials find application in many fields. The most common application of biomaterials include artificial hip joint, kidney dialysis machine, sutures, bone plates, cardiac pacemaker, intraocular lens, augmentation mammoplasty, chin augmentation, probes, catheters etc [3].

A biofilm is a three-dimensional (3-D) community of microorganisms immobilized at a substratum and frequently embedded in an organic polymer matrix of microbial origin [4]. The chief constituents of natural biofilms typically are many species of bacteria, fungi, algae, protozoa, debris, and corrosion products, with the extra- cellular polymeric substance (EPS) matrix largely responsible for structural integrity [5]. Synthetic films that possess either or any of the characteristic features such as biodegradability, biocompatibility, bioresorption etc. can be termed as biomaterial films. Biomaterial films found significant applications in complex surgeries involving skin transplantation, plastic surgery and they even found use as a medium for drug delivery as some of these films were edible and non-toxic. They were used as transdermal patches and as capsule coatings. Gelatin, Dextran, Chondroin sulphate, Calcium pectinate, Pectin and Chitosan were some polysaccharides which were used in this context [6]. All these materials were found

suitable because of their biodegradability and easy availability. If the film is soluble in water, it can be more useful in pharmaceutical applications. The success of a biomaterial inside a body depends on both the property of the material, design, biocompatibility and external factors such as patient's health and activities.

The biomaterial films can also be used as phantom materials in an electromagnetic simulation environment [7-10]. If their dielectric properties are comparable to the dielectric properties of body parts, those body parts can be represented by phantom materials with a matched dielectric profile in a microwave experimental setup. Biological films can be of animal or plant origin. Some of these films possess medicinal properties. It is by the virtue of the plant from which it is procured. The characteristic features of the films include its mechanical, structural, optical and electrical properties. The mechanical properties include its elasticity, stress withstanding capability etc. Structural properties like heterogeneity and porosity are also important. The optical properties include film's transparency and refractive index. And the electrical properties which are of significant important to us are its electrical conductivity, skin depth, surface resistance, heating coefficient, dielectric constant, loss tangent and attenuation constant. The electrical conductivity tells us about the amount of electric current that can be passed through the film without destroying its properties. Though Skin depth is a term normally associated with conductors, it can be used to characterize the behavior of a film which is subjected to microwaves. The depth of penetration of the signal gives us information such as the capability of the material to reflect a wave and its wave absorption characteristics.

Material characterization using microwaves is a solid field where microwave properties of materials are studied. By studying the dielectric properties [11, 12], several biological effects can be studied. For instance, microwaves are widely used in the field of imaging for finding malicious tissues and tumours. These techniques use tissue characterization based on complex permittivity. The dielectric properties of the malignant tissue will be different from that of the normal tissue. Several advancements have been made on the dielectric property study of materials. The

properties such as permittivity and loss factor are significant in determining material properties. Microwave absorption characteristics gives the amount of microwave power absorbed by the film at different microwave frequencies and will be helpful in the study of effect of non-ionizing radiation [13] on Chitosan and Arrowroot.

3.2 Arrowroot

Figure 3.1. Arrowroot Plant

Arrowroot is from the family Marantaceae [14]. The Arrowroot plant grows up to a height of 80 cm and harvested 9 to11 months after planting. It has tuberous roots which stores starch. Arrowroot powder is valued chiefly for its thickening properties. It has neutral taste and it thickens at a lower temperature than starch of corn. Arrowroot (ARROW) is most commonly used as a chief ingredient in baby food, as substitute for talcum in baby powder and body powder. Because of its

medicinal properties [15], it is considered to be an effective antidote to vegetable poisons.

Arrowroot was first introduced to Europeans by the Arawak tribe in the Caribbean. They used it do draw poison out of the wounds inflicted from poisoned arrows. The Indians used Arrowroot as their chief food and called it *aru-aru* (meal of meals). An interesting pilot study on the use of arrowroot as treatment for diarrhea in irritable bowel syndrome patients by C. Cooke et al [15] shows that Arrowroot is very effective in treatment of diarrhea and plays a significant role in reducing daytime bowel frequency. Its calorie content is low. So it is a popular food among calorie-conscious dieters.

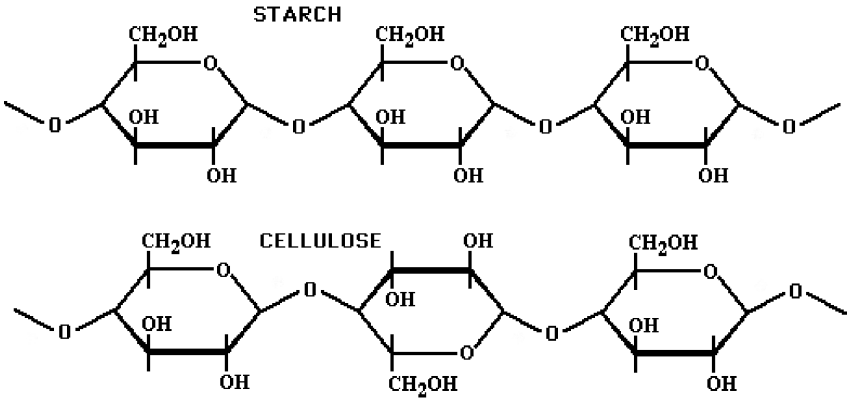

Figure 3.2 Structures of Starch and Cellulose

Arrowroot is basically starch. Starch and cellulose are two terms which are often mistaken for each other. Cellulose is a linear polysaccharide polymer with many glucose monosaccharide units. The acetal linkage is beta which makes it different from starch (figure 3.2). The beta-acetal linkage cannot be broken down by any of the enzymes in animals. Animals such as cows, goats, horses, termite etc has symbiotic bacteria in their intestinal tract. These bacteria produce necessary enzymes to digest cellulose in the gastro-intestinal tract. Hydrolysis of cellulose takes place in intestinal tract. No vertebrate including humans can digest cellulose directly. So humans are not able to digest fibrous food. The indigestible cellulose is

the fiber which acts in the smooth working of intestinal tract. But Starch contains alpha-acetal linkage which can be easily broken down by enzymes within the body. Arrowroot hence is an edible food. It is also used for making cookies, in talcum powder and in biscuits.

3.2.1 Preparation

(i) Arrowroot powder

Arrowroot powder is prepared from the root of Arrowroot plant. Arrowroot is a tuberous plant. So the chief food storage is in the roots. The roots are soaked in hot water and the fibrous covering is peeled off. It is then cut into small pieces and mashed to obtain pulp. The pulp is macerated in water to break down tough cells surrounding starch. It is then washed thoroughly with water and filtered. The washing is done to separate starch from fibrous material. The process is repeated

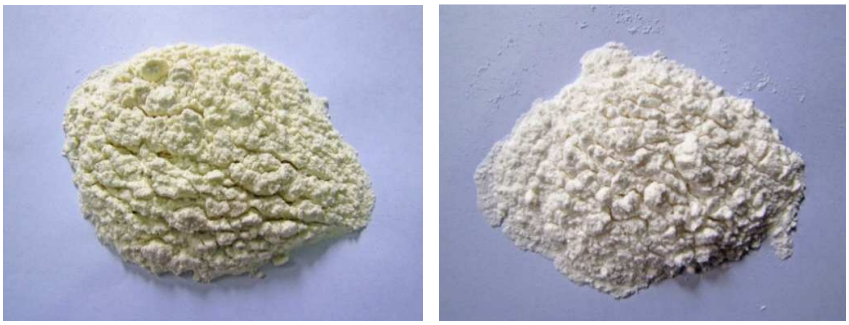

Figure 3.3 Arrowroot powder - Yellow and White

until pure arrowroot powder is obtained. The separated starch is dried and later powdered to obtain Arrowroot powder. Around 20% of the original root is starch. By careful processing, up to 17-18% of the starch can be extracted. There are two kinds of powders obtained from two variants of the same plant. One has pure white color and the other has a slight yellowish tint. But both these powders are very

identical in all other properties. Both are commercially available in the market and are cheap.

(ii) Arrowroot film

Arrowroot film is prepared from Arrowroot powder in a simple process. The powder (10g) is dissolved in water (100ml) and is heated in a glass tumbler. Around 80ºC, it will turn into a transparent gel. This particular soluble: solvent ratio was determined by trial and error. If the amount of powder is high, then it results in excess amount of particles. And the particles tend to coagulate and it is not possible to get a clean gel. If amount of powder is low, the gel wouldn't get sufficient viscosity and the films prepared from the gel won't have any mechanical strength at all. It cannot help in film formation. If we use a conventional heater to heat the solution, then it is necessary to stir the solution so that no coagulation of particles occurs. This method is more susceptible to coagulation problem as the water near to bottom of the vessel gets heated up first rather than the water near the

Figure 3.4 Arrowroot film

top surface. It is possible to get a clean gel, but is difficult to achieve so. As the method suffers from this problem, we had to find other heat sources which can

provide uniform heat to all parts of the solution. As a result, we found microwave heating as the best method for the purpose. In microwave heating, the solution gets a uniform heat from all directions. We were able to obtain a clean gel easily when microwave heating was used. The prepared gel is casted on thick plastic sheets. It is not necessary to use plastic sheet, however, the surface used should be smooth so that the prepared film doesn't get adhered to the surface.

The cast was dried using three methods - conventional shadow drying, microwave drying and hot air drying. Among these methods, shadow drying was the best method to obtain a uniform film. Microwave and hot air drying can also produce good films, but if the temperature given is even slightly high, it will result in deformed film. And the amount of temperature given depends up on the viscosity and thickness of the cast which varies. Hence we have to reduce temperature and increase drying time. But it will eat up electricity and is not as cheap as shadow drying. But the microwave and hot air drying methods has an advantage. They drastically reduce the drying time when compared to shadow drying. The choice of drying method requires a tradeoff between time and economy.

3.2.2 Dielectric Characterization

The dielectric characterization of Arrowroot film was done for S- band of microwave frequencies. Cavity perturbation method was used for the purpose. The properties such as Dielectric constant, Loss factor, Conductivity, Skin depth and Heating coefficient were measured. Microwave absorption study was also performed. These properties are very significant in microwave phantom applications of the material. Arrowroot is an edible food. Also it is biodegradable which makes it suitable for implantation purposes. It is already used in paper coatings and biodegradable plastics. The ability to form thin, transparent and tough film enables it to find applications in many other fields also.

(i) Permittivity and Loss factor

The Permittivity and Loss factor variations of Arrowroot film at various frequencies are shown in Figure 3.5. It can be seen that the dielectric constant of Arrowroot film varies between 5.25 and 6.5. Arrowroot is having low dielectric constant which is closer to the dielectric constants of certain body parts such as bone marrow, collagen, breast fat, etc. Thus Arrowroot can be considered as a phantom material for in vitro studies and can be used for implantation purposes after performing the biocompatibility studies.

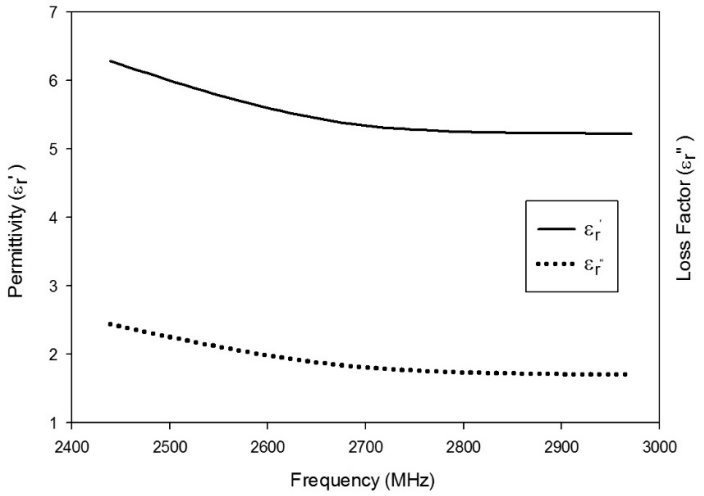

Figure 3.5 Variation of Permittivity and Loss factor of Arrowroot film at microwave frequencies

Loss factor of a material is associated with the dissipation or power loss within the dielectric. The conductivity of the material is a direct function of loss factor and for practical purposes both the conductivity and loss factor are considered indistinguishable [16]. Figure 3.5 shows the variation of dielectric loss. When a field is applied to a dielectric, it tends to polarize the material. The degree of polarizability depends on the relaxation time of the molecules of the medium [11]. For Arrowroot film, the molecules are tightly packed so that the molecules achieve equilibrium with the applied field rapidly. As the relaxation phenomenon is

quick, it has low dielectric loss. Hence the film has a comparatively small loss factor. Thus microwave power is less dissipated in Arrowroot film.

(ii) Conductivity, Skin depth and Heating Coefficient

The dielectric parameters other than permittivity and loss factor are also important for determining material characteristics. The measured properties such as conductivity, skin depth, and heating coefficient are shown in Table 3.1. The conductivity of the material is responsible for the loss within the material. The skin depth determines the depth of penetration of electromagnetic wave within a substance. The skin depth of the material is inversely proportional to the conductivity of the material. The variation of microwave heating coefficient is also shown. The heating coefficient increases with increase in frequency. This means more energy is dissipated via dielectric heating mechanism at low frequencies.

Table 3.1. Dielectric parameters of Arrowroot film

Frequency (MHz)	**Conductivity (Sm^{-1})**	**Skin depth (m)**	**Heating coefficient**
2439	0.3317	0.0176	0.4092
2685	0.2729	0.0185	0.5474
2971	0.2811	0.0174	0.5880

3.2.3 Applications

The dielectric properties of the film sample reveals that it has low dielectric constant which is a typical characteristic of body tissues collagen, bone marrow and human abdominal wall fat. Table 3.2 shows the dielectric chart of these tissues.

The newly developed film may be used as phantom material representing these tissues. For in vitro studies involving these tissues, the film could be useful as an alternative to expensive counterparts. Apart from its use as phantom material in

microwave imaging or SAR studies, it can be of more use in medical field. The remarkable properties of the film such as its transparency, medicinal properties and edibility can be made useful if it is used as capsule material for drugs. We suggest the use of a drug delivery system entirely based on Arrowroot film. The Arrowroot

Table 3.2 Dielectric properties of certain body tissues

Body part	**Dielectric constant**
Collagen	5.5-6.5
Bone marrow	4.2-5.8
Human abdominal wall fat	4.92

film could be easily molded into any shape and is also cost effective at the same time. Drug delivering systems presently use gelatin, dextran, chondroitin sulphate, calcium pectinate, pectin and chitosan as carriers for oral delivery of drugs. These materials are also used for bimodal delivery of drugs [6]. Arrowroot film is insoluble in water, but it swells when dipped in water for a while. The bimodal delivery can be achieved by incorporating hydrophilic degradable polysaccharides in Arrowroot film. The film can ensure sustained drug delivery through this method. It could also be used as transdermal patches which embed drugs in it for sustained delivery over a period of time. Another proposed application is eco-friendly band-aids. The soaking property of the film can be made useful for embedding hydrophilic drugs in it. Low cost, easy preparation and most importantly biocompatible features makes this material a better choice.

3.2.4 Advantages and disadvantages

Advantages	Disadvantages
✓ *Easy availability* ✓ *Medicinal properties* ✓ *Edibility* ✓ *Low cost* ✓ *Easy preparation* ✓ *Transparency* ✓ *Biodegradability* ✓ *Eco-friendly*	▪ *Low mechanical strength* ▪ *Varying thickness in different batches*

3.2.5 Conclusions

The Arrowroot film has been developed and its dielectric properties were analyzed. The prepared films are transparent and can be made into any thickness. They are moldable, edible and biodegradable. The material could find potential applications such as phantom material in microwave imaging, as capsule material in pharmaceutical applications, as transdermal patch material and as eco-friendly Band-Aids. The dissolution properties of the Arrowroot film and its feasibility of use as a drug coating material can only be verified with the use of a dissolution test apparatus and the analysis of data using High Performance Liquid Chromatography (HPLC) system.

3.3 Chitosan

Chitosan (poly [β-1-4) D-glucosamine) is the second abundant polysaccharide and a cationic polyelectrolyte present in nature [17]. It is one of the most versatile biopolymers known to the science community. Its applications are numerous. It is used in applications such as natural seed treatment, ecologically friendly bio

pesticides, plant growth enhancement, water filtration, self-healing coatings, bandages, clarification, chromatography, paper and textiles, photography, transdermal drug delivery etc. [18-22]. It is also used as a soluble dietary fiber owing to its edibility. The property of long chain molecules of dissolved Chitosan to wrap the solid particles suspended in liquids and to bring them together and agglomerate makes it suitable as a coagulant acid. Chitosan facilitates better collagen growth in implants. Its amino group has a pKa value of 6.5 which results in protonation in acidic to neutral solution. This makes Chitosan water soluble and enhances its bio adhesive properties.

Another property of Chitosan is its ability to form gel in diluted acidic solvents. The Chitosan chain contains free amine group which will undergo protonation on treatment with diluted aqueous solution of acids resulting in formation of corresponding Chitosan salt in the solution. Chitosan also has been found to have antimicrobial, hypocholesterolemic, and wound healing properties [23-25]. Chitosan is characterized in many ways such as quality, purity, molecular weight, viscosity, degree of deacetylation and physical forms. The deacetylation process is done by treatment of Chitin with an alkaline solution. Chitin when deacetylated more than 75% gives Chitosan. The degree of deacetylation can be determined by any of the tests such as ninhydrin test, near-infrared spectroscopy, infrared spectroscopy, linear potentiometric titration, nuclear magnetic resonance spectroscopy, hydrogen bromide titrimetry, and first derivative UV-spectrophotometry [26]. Chitosan molecules are positively charged. So it readily binds to negatively charged surfaces. This property of Chitosan is made useful in drug delivery applications. It could carry polar drugs across epithelial surfaces. An exhaustive study on the dielectric behaviour of Chitosan at microwave frequencies has been made and its suitability as biopolymer is analyzed.

3.3.1 Preparation

Chitosan is a biopolymer which is obtained from the shells of sea crustaceans like shrimp and crab [27]. These shells are first oven dried to reduce

the moisture content. A final moisture content of 10-12 % is preferred. The shells are crushed and boiled for an hour in 4% NaOH solution to dissolve proteins and sugars. It is again crushed to fine pieces. The sample is then treated/soaked with 1% solution of HCl for 24 hours to remove calcium carbonate and other minerals. In order to decompose the albumin which is present in the demineralized sample to water soluble amino acids, the sample is treated with 2% NaOH solution for an hour. Thus we obtain Chitin. The sample is washed in deionized water and cleaned. The Chitin on deacetylation by treatment with NaOH gives Chitosan. For deacetylation, 50% NaOH solution is added to the sample and the sample is boiled at 100^{o}C for two hours. Then it is allowed to cool to room temperature. The sample is then washed thoroughly in 50% NaOH and is filtered to obtain the residue, which is Chitosan. It is then kept in an oven and is heated at 120^{o}C for 24 hours. The Chitosan powder thus obtained is kept in air tight containers.

Figure 3.6 Chitosan powder and film

Chitosan is soluble in weak acids due to the low value of pKa. Chitosan powder (1gm) was dissolved in 50 ml dilute acetic acid (14%). The solution was stirred for 4 hours until Chitosan was completely dissolved. The thick gel obtained was then taken in small capillary tubes of approximately 0.8 mm diameter for

cavity perturbation measurements. The Chitosan gel was casted and dried in shadow to obtain thin films of varying thickness. The film was cut into thin strips of 3-5 mm width and 50mm length. The thickness of the films ranged from 0.2mm to 0.8mm. The dielectric characterization of the film was done for S-band of microwave frequencies.

3.3.2 Dielectric Characterization

The dielectric characterization of Chitosan gel and film at microwave frequencies was done using cavity perturbation method. The dielectric properties were evaluated for S-band of microwave frequencies. The aim of the study was to find whether the dielectric parameters resemble the dielectric parameters of any body tissues. If the dielectric parameters are comparable, then these could be used an alternative to the particular body part in microwave tomography and SAR applications.

(i) Permittivity and Loss factor

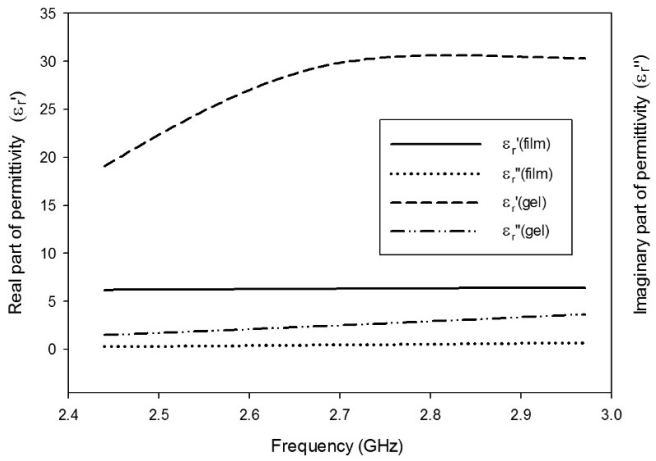

Figure 3.7 Variation of complex permittivity of Chitosan film and gel with frequency.

The permittivity and Loss factor variation of Chitosan film and gel are as shown in figure 3.7. It is observed that Chitosan gel exhibits higher permittivity

and loss factor values as compared to Chitosan film owing to the increased water content. The permittivity and loss factor values of Chitosan film don't show prominent variation for frequency range 2-3 GHz. The large variation in permittivity of the gel for this range suggests that the gel is highly polarized by the incident wave. The dielectric constant of Chitosan film is low because of its lower polarizability. The polarizability of the gel is due to the presence of water which is a polar material. Thus it can be concluded that the permittivity can be altered to any desirable value by varying the water content of the gel (by varying the pH). The Chitosan film shows very low value for permittivity and loss factor. This means that the film is less polarized and dielectric relaxation for the film is very short at microwave frequencies.

(ii) Conductivity, Skin depth and Loss Tangent

The microwave conductivity of a material depends on the dielectric loss factor. It in turn depends on the polarizability of the material and the relaxation time. As Chitosan film is a non-polar material, it has a very low loss factor. And

Table 3.3. Dielectric parameters of Chitosan film and gel

Form of Chitosan	**Frequency (GHz)**	**Conductivity σ (S/m)**	**Skin depth δ_s (m)**	**Tan δ**
Film	2.430	3.7×10^{-2}	5.30×10^{-2}	4.43×10^{-2}
	2.680	6.73×10^{-2}	3.75×10^{-2}	7.17×10^{-2}
	2.970	1.11×10^{-1}	2.77×10^{-2}	1.05×10^{-1}
Gel	2.430	1.06×10^{-1}	3.13×10^{-2}	4.05×10^{-2}
	2.680	2.67×10^{-1}	1.88×10^{-2}	6.06×10^{-2}
	2.970	5.43×10^{-1}	1.25×10^{-2}	1.09×10^{-1}

hence the microwave conductivity is very low for Chitosan film as compared to Chitosan gel. This is evident from Table 3.3. The Skin depth measures the depth of penetration of the microwave signal into the sample. For a highly conducting

material, much of the wave gets reflected back without penetrating deeply into the sample.

It can be observed from Table 3.3 that the Skin depth becomes low as microwave conductivity increases. As Chitosan film is homogeneous, interfacial polar charges will be very low in number. It will result in a low dielectric constant value. Tan δ is the loss tangent of the film and gel. It is observed that the Chitosan gel is lossier due to the polar nature of the sample.

3.3.3 Applications

The film and gel forms of Chitosan can find significant application as phantom materials in microwave imaging. They have dielectric properties similar to that of certain body parts. The dielectric property of the gel depends on the water content in it. Thus by varying the water content, phantoms for various body parts can be prepared. A comparison of the dielectric properties of Chitosan and the corresponding body parts is shown in Table 3.4.

Table 3.4 Dielectric constants of human tissues and equivalent phantoms

Human Organ	Dielectric constant	Equivalent Phantoms
Collagen/Fat tissue	5.5 - 6.5	Chitosan Film
Brain/Breast tissue	26 - 29	Chitosan Gel

The dielectric constant of Collagen/fat tissue falls in the range 5.5-6.5 which corresponds to the dielectric constant of prepared Chitosan film. The equivalent phantom for Brain/Breast tissue can be implemented with Chitosan gel. The study shows that the phantoms corresponding to other body parts can also be developed from Chitosan gel with various pH values. The Chitosan film and gel both are very easy to prepare, low cost and biodegradable. Thus they are ideal candidates for use as phantom materials in microwave imaging applications.

3.3.4 Conclusions

The dielectric characterization studies of Chitosan gel and film were performed. Both the gel and film are transparent and biodegradable. It was found that both of them have dielectric properties similar to that of certain body parts which enables them to be used as phantom materials in microwave imaging applications.

3.4 Arrowroot-Chitosan film

The quest for thin, tough and transparent biocompatible films led to the development of new materials in medical field [28-30]. These films found use as contact lens materials, encapsulation of drugs, as transdermal patches etc. Biocompatibility, ease of preparation, low cost and availability are the important constraints which are to be taken into consideration while preparation of films. The mechanical properties of the film determine the strength of the film. A work on the influence of thickness on mechanical properties for starch films was done by A. Jansson and F. Thuvander [31]. They tested the films in tension and the films were characterized in terms of strength, stiffness and failure strain. Another important work was done for improving the performance of starch film by the use of cellulose micro fibrils [32]. It has been found that the water sensitivity linearly decreases with the cellulose micro fibril content.

The main drawback of Arrowroot film was its comparatively poor mechanical stability. The film was transparent and biocompatible. But it suffered from poor mechanical stability. To increase the mechanical strength of the film, Chitosan gel was added to Arrowroot gel during preparation. The resultant gel was casted to obtain films of varying thickness. The mechanical, morphological and dielectric properties of the film were studied. Dielectric property studies are performed at frequencies from 20 Hz to microwave ranges. The mechanical properties of the film such as stress and strain are also analyzed. Morphological properties are analyzed with the aid of SEM measurements.

The mechanical, morphological and dielectric properties of the film are analyzed. The mechanical properties are procured from Stress/Strain measurement. The morphological characteristics and porosity of the film are determined from SEM measurements. A simple and sure method to find the biocompatibility of a material is to study the dielectric properties of the material. All biomaterials are prone to microwaves. The dielectric properties of the film at low and high frequencies are analyzed with the aid of Impedance and Network analyzers.

3.4.1 Preparation

Arrowroot powder (10gm) is dissolved in water (100ml) and is heated in a glass tumbler using a microwave oven. Around 80^{o}C, it will turn into a transparent gel. Chitosan powder (1gm) was dissolved in 20 ml glacial acetic acid (99-100%) which was diluted with 2ml of water. The gel formed was added to Arrowroot gel and mixed thoroughly. The mix was casted and dried in shadow to obtain thin films of varying thickness. The film was cut into thin strips of 3-5 mm width and 50mm length. The thickness of the films ranged from 0.15mm to 0.8mm. The dielectric characterization of the film was done for 20Hz-2MHz range as well as at S- band of microwave frequencies.

3.4.2 Characterization

(i) Dielectric properties

The dielectric characterization of the film was performed at frequency ranges from 20Hz -2MHz and 2GHz-3GHz. Measurement at low frequencies were done using Agilent E4980A Impedance Analyzer (20Hz to 2MHz) with the aid of Agilent 16451B dielectric material test fixture. The measurements at microwave frequencies were performed using Agilent 8714 ET vector network analyzer.

(a) Characterization at low frequency

Low frequency dielectric property measurements were carried out to find the behavior of film at low frequencies. The properties dielectric constant and loss factor are the most important properties. As shown in figure 3.8, the Arrow-Ch film has low permittivity at small frequencies. After 1 KHz, the films show more or less

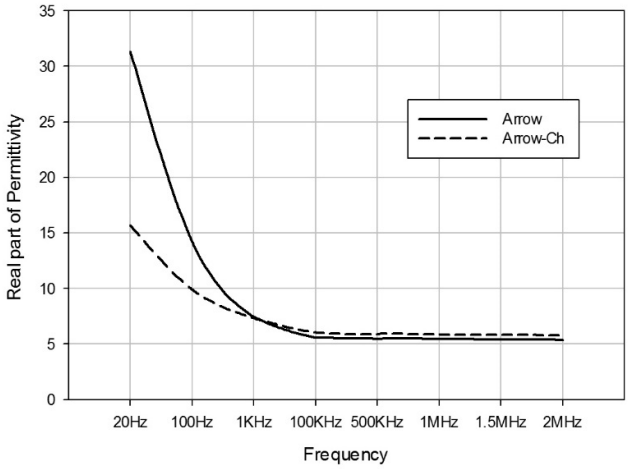

Figure 3.8. Variation of Dielectric constant at low frequencies

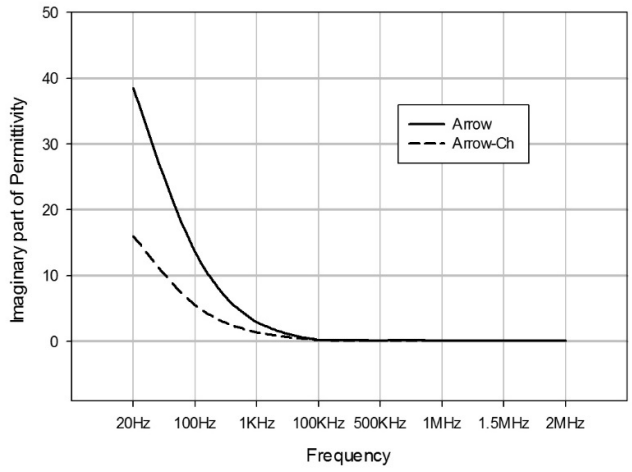

Figure 3.9. Variation of Loss factor at low frequencies

the same characteristics. Figure 3.9 shows the variation of loss factor with respect to frequency. It can be seen that after 100 KHz both are showing the same response. The material is lossy at low frequencies.

(b) Characterization at microwave frequencies

The cavity perturbation technique gives the permittivity and loss factor at microwave frequencies as a function of shift in resonant frequency and variation in quality factor of the wave guide cavity. From the permittivity and loss factor we can obtain other important parameters such as conductivity, skin depth, attenuation constant etc. The measured parameters are shown in Table 3.5.

Table 3.5. Variation of dielectric properties of Arrowroot (A) and Arrowroot-Chitosan (A-C) at microwave frequencies

Frequency (GHz)	Dielectric constant, ε_r'		Loss factor, ε_r''		Conductivity σ (Sm^{-1})		Skin depth, δ (m)		Heating Coefficient, J		Attenuation Constant, α (m^{-1})	
	A	A-C	A	A-C	A	A-C	A	A-C	A	A-C	A	A-C
2.440	6.15	5.78	2.20	1.61	.299	.218	.018	.021	.453	.620	53.76	45.87
2.685	5.28	5.56	1.73	1.50	.259	.225	.019	.020	.575	.663	52.35	48.78
2.972	5.22	5.36	1.70	1.63	.281	.269	.017	.018	.588	.613	57.39	56.15

It can be seen from Table 3.5 that both the films are exhibiting more or less the same characteristics at ISM band of microwave frequencies. The dielectric constants of both the films are low. The Arrow-Ch films used for measurements are prepared by the addition of 5% Chitosan gel to 10% Arrowroot gel. The dielectric constant of Arrow-Ch film can be further lowered to the desired value by increasing the amount of Chitosan in the film. The overall low value of the real part of complex permittivity suggests that the films are hydrophobic. The presence of water or moisture content would have increased the dielectric constant. Hence the films are non-polar in nature. Due to the low dielectric constant, the charge holding capacity of the films will be nominal. The Loss factor and hence the conductivity are slightly low for Arrow-Ch film as compared to Arrow film at low frequencies.

The dielectric loss highly depends on the relaxation process which involves local motion of polar groups. The dielectric loss occurs due to the friction between the molecular chains during this process [33]. The Arrow-Ch film has a structured nature due to the presence of the Chitosan matrix. Hence the friction between chains will be nominal for Arrow-Ch film. This accounts for the lower value of dielectric loss.

The conductivity varies as a function of frequency and dielectric loss of the material. As the dielectric loss is low for Arrow-Ch film, the microwave conductivity is also low for this film. The Skin depth gives a measure of the depth of penetration of the microwave signal. The Skin depth varies inversely with

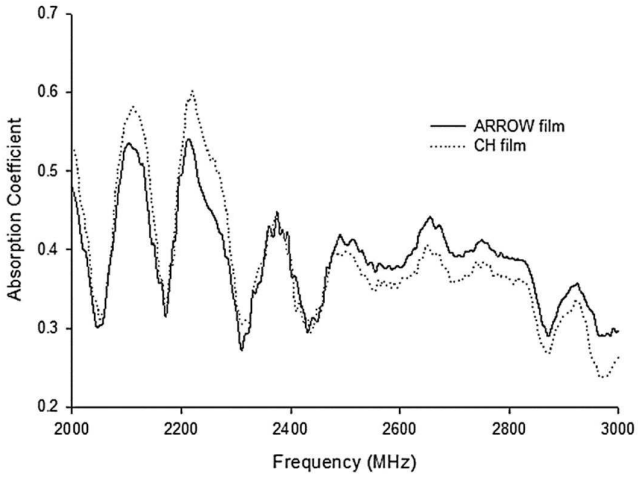

Figure 3.10 Absorption variation of Arrowroot and Chitosan films with frequency

conductivity for a fixed frequency. Hence the Arrow-Ch film exhibits a higher Skin depth. The microwave heating coefficient is high for Arrow-Ch film. This implies that the material is not good for dielectric heating purposes. The attenuation constant represents the amount of attenuation of the wave within the film. The Arrow-Ch film has less attenuation as compared to Arrow film. Hence the wave penetrates more into the film and this can be verified from the value of Skin depth.

The microwave absorption characteristics of Arrowroot and Chitosan films are as shown in figure 3.10. The Absorption coefficient (A) gives a measure of microwave power absorbed by a material. The minimum value of absorption coefficient is 0 and maximum value is 1. The value of absorption is highly dependent on frequency of the incident radiation. Several other important measurements such as Specific Absorption Rate (SAR) depend on the amount of absorbed microwave power. The dielectric heating is also depending on the amount of absorbed power. If microwave absorption is high, it can result in dielectric heating of the material. It can be observed from the figure that Arrowroot and Chitosan films exhibit similar microwave absorption characteristics. The amount of microwave absorption depends on the thickness of the film used.

(ii) Morphological properties

The SEM images of Arrow and Arrow-Ch films are shown in figures 3.11 & 3.12. Figure 3.11 gives 2000 times magnified view of the surface of the film whereas figure 3.12 gives 1500 times magnified view. As we can see, there are no pores on the surface of the films. Both films are also devoid of air gaps. Due to the

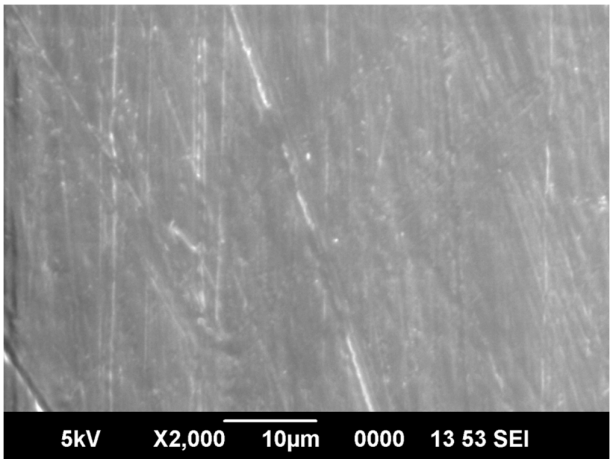

Figure 3.11. SEM image of Arrowroot film

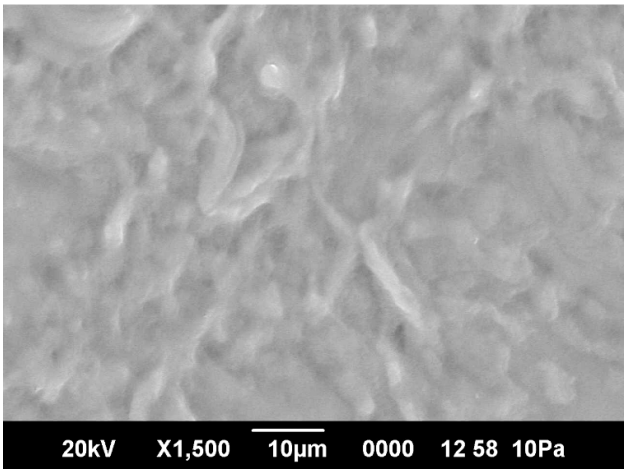

Figure 3.12. SEM image of Arrowroot-Chitosan film

lack of pores, they can be used as capsule material for embedding drugs. The embedded drugs will not interact with atmosphere or get contaminated by any other external factors. The film itself will not interact with air if kept in a dry container. The films prepared in the lab were aged for more than 14 months and still, the films were intact, maintaining the properties.

The capsules prepared from the film can be used either for sustained delivery or burst delivery of the drug in the required areas of the digestive system. We can also make the film porous if necessary. Such porous films can be used as transdermal patches for drug delivery through skin. Both films can be used as capsule coatings but the better tensile properties exhibited by Arrow-Ch film gives it a slight edge over Arrow film.

(iii) Mechanical Properties

The Stress-Strain relationship gives important information about the mechanical stability of the film. The Stress-strain graphs of the prepared films are shown in figure 3.13.

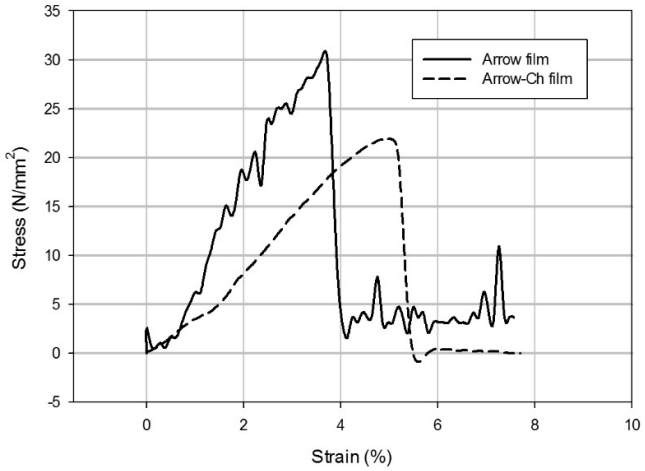

Figure 3.13. Stress-Strain curves of Arrowroot and Arrowroot-Chitosan film (0.8mm thick)

The graph follows an almost linear path for both Arrow and Arrow-Ch. However, it can be seen that the maximum yield point is reached for Arrow film for a smaller value of strain. This means Arrow film is less elastic compared to Arrow-Ch film. The Arrow-Ch film was strained more before it ruptured while Arrow film broke easily. Arrow-Ch film is more flexible and elastic. So it can be used for many biomedical applications where stress resilient features are preferred. Some significant applications may include eco-friendly Band-Aid's, capsule cover, transdermal patch etc.

The Strain energy measured for Arrow-Ch film is 1205 J/m^3 where as that of Arrow film is 1237.5 J/m^3. It means Arrow film consumes more energy with respect to Arrow-Ch film to strain to the maximum yield point. On a close inspection of the graph we can see that high stress is applied to Arrow film to achieve the same Strain as that of Arrow-Ch film. Therefore Arrow-Ch film has low strain energy value.

3.4.3 Applications

The dielectric properties of the prepared film are the same as that of certain biological constituents of human body. A comparative study of human tissues (37°C) at 3GHz [34] and their suggested equivalent phantoms is shown in table 3.6. The dielectric constant of the film can be fine-tuned by varying the amount of Chitosan in the film. This is one of the advantages of using Arrow-Ch film rather than standalone Arrow film. Hence Arrow-Ch film can be used as a phantom material representing these body tissues in scientific/medical applications.

The Arrowroot-Chitosan film shows better mechanical properties as compared to Arrowroot film. Thus it can be used in applications which demand good mechanical properties. The low dielectric constant enables it to be used in microwave phantom applications. It is also suggested to be used in eco-friendly Band-Aids and as capsule material in medical field.

Table 3.6. Dielectric properties of human tissues at 3 GHz and their equivalent phantoms

Biological tissue at 37°C	Dielectric constant of standard sample	Equivalent phantoms in terms of ratio of gels used in preparation (Arrowroot: Chitosan)
Collagen	5.5-6.5	5:1
Bone marrow	4.2-5.8	5:1
Fat	5.28	5:2
Breast fat	5.15	5:2
Human abdominal wall fat	4.92	5:3

3.4.4 Conclusions

Arrowroot-Chitosan film was synthesized. The dielectric, mechanical and morphological characterization of Arrowroot-Chitosan film was done. It has been found that the film can be used as phantom material in microwave compatibility

applications. The dielectric properties of the film can be tuned to the desired value by adjusting the % composition of Chitosan in the film. The Arrow-Ch film has better stress withstanding capability than Arrowroot film. The structural properties of the film are increased by the addition of Chitosan. The film exhibits better strain energy values which say that the film can strain more for an applied stress. The elasticity of the film allows it to be used in applications where mechanical stability is of prime concern. It is also devoid of air gaps and pores. The films prepared are biodegradable as both Chitosan and Arrowroot are edible. With its unique dielectric, mechanical and morphological characteristics, Arrow-Ch film proves to be a versatile material and can find use in many diverse fields.

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Chapter 4
Bioceramics

4.1 Introduction

Ceramic materials are polycrystalline compounds which are inorganic and non-metallic. They include silicates, metallic oxides, carbides and refractory hydrides, Sulfides and Selenides [1, 2]. The ceramic materials are compounds which are often produced by the bonding between metallic and non-metallic elements. The type of bonding can be ionic or covalent in nature. They can be crystalline or amorphous.

Figure 4.1 Ceramic pellets

The ceramics exhibit wide range of properties. Conventional ceramics were suffering from flaws such as brittleness, susceptibility to notches, low tensile and

impact strengths. The advancements in recent research on ceramic materials helped to rectify these flaws to a greater extent. Ceramic compounds are prepared using techniques such as Sol gel method [3, 4], Solid state reaction method [5], Wet chemical method, Gel growth method, Melt growth method etc. Most of the ceramics preparation involves high temperature firing or calcination and subsequent cooling of the compound. They have high melting points.

Bioceramic materials find significant applications in medical field. Their properties such as biocompatibility, bioresorption, biomimic nature, osteo-inductive and osteo-conductive properties [6] make them important alternative to bone reconstruction/ replacement materials. Apart from being used for implantation purposes, bioceramics materials are also used for phantom applications [7-10]. Microwave phantom materials are those materials which have dielectric property profile matching with that of body parts and which can be used in an electromagnetic simulation environment. Table 4.1 shows the desired features of implantable bioceramics. All these features are not necessary for the use of the bioceramics as phantom materials.

Table 4.1 Desired features of implantable bioceramics.

Implantable Bioceramics
➢ Should be nontoxic
➢ Should be noncarcinogenic
➢ Should be nonallergic
➢ Should be noninflammatory
➢ Should be biocompatible
➢ Should be biofunctional for its lifetime in the host body

Calcium phosphate materials are used in bone substitution, augmentation and repair. Their dental applications include fillers for periodontal bony defects, alveolar ridge augmentation, immediate tooth root replacement, coatings for dental implants and maxillofacial reconstruction. The only drawback of most bioceramic

compounds is their poor mechanical stability. Even though they exhibit the same morphological, chemical and dielectric properties of actual bone, they fail in mechanical strength in their pure form. The compressive strength of macroporous calcium phosphate ceramics is very weak; ranging from 0.5 to 10MPa, depending mainly on the porosity percentage, pore size, chemical composition, grain size, and synthesis procedure [11]. Bioceramic composite materials with high mechanical strength have been reported in literature. Hydroxyapatite in bulk form is known to have good mechanical strength [12]. The common bioceramics used in medical field based on composition are,

i) Hydroxyapatite (HAp) - $Ca_{10}(PO_4)_6(OH)_2$
ii) Beta Tricalcium phosphate (β-TCP) - $Ca_3(PO_4)_2$ and
iii) Biphasic Calcium Phosphate (BCP) - mixture of HAp and β-TCP

Although there are many manufacturing techniques, the first two ceramics were prepared using hydrothermal precipitation method. The third one is obtained through a solid state process which involves calcination of a mixture of Hydroxyapatite and Beta Tricalcium Phosphate.

4.2 Calcium Hydroxyapatite

4.2.1. Preparation

Calcium Hydroxyapatite (HAp) is prepared using the hydro-thermal precipitation (sol gel) method [13-15]. In this method, equimolar amounts of Ammonium Dihydrogen Orthophosphate [$(NH_4)H_2PO_4$] and Calcium Nitrate Tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$] are taken. Both are dissolved in distilled water. The solutions are mixed and heated. The temperature is maintained at 80° C. To this solution, Ammonium Hydroxide solution is added and a pH of 8 is maintained. The solution was stirred well using a magnetic stirrer. The resulting precipitation was aged for 24 hours. The precipitate was then washed with water and IPA to remove impurities and dried. The filter cake obtained is then either furnace dried (FUD) or

freeze dried (FRD). The free flowing powder thus obtained was ground in a ball mill and kept in air tight containers. Both the FUD and FRD samples were made into pellets with 5 mm radius and 2.5 mm thickness by using a cylindrical die and applying pressures of 200kg/inch^2 and 1ton/inch^2. HAp in powder and pellet forms are shown in figure 4.2. The pellets and powders are then calcined at 500^{o}C, 1000^{o}C and 1200^{o}C for 4 hours. The unsintered and sintered freeze dried HAp powders are taken for x-ray diffraction studies. The study could reveal the polycrystalline nature of the composite.

Figure 4.2 Calcium Hydroxyapatite powder and pellet

Chitosan is a biopolymer which is synthesized from the exoskeleton of crustaceans such as shrimp and crab [16,17]. The exoskeletons are dried, powdered and subsequently treated with alkali NaOH to separate proteins. The powder is then treated with HCl for removing mineral content. Thus we obtain Chitin. Chitin is again deacetylated to obtain Chitosan. For deacetylation, 50% NaOH solution is added to the sample and the sample is boiled at 100^{o}C for two hours. Then it is allowed to cool to room temperature. The powder thus obtained is heated in an oven at 120^{o}C for 24 hours. Chitosan gel is prepared by dissolving Chitosan in dilute acetic acid. Hydroxyapatite-Chitosan (HAp-Ch) paste is formed by mixing HAp with Ch in different ratios. The paste is ground well. It is pressed using a die

to prepare pellets of 10mm diameter and 3mm thickness for cavity perturbation measurement. The pellets are calcinated at 300^{o}C for 4 hours.

4.2.2 Experimental setup

The dielectric characterization was performed using cavity perturbation technique [18, 19]. The cavity is excited in TE_{10p} mode for cavity perturbation measurement. The microwave absorption measurement of HAp-Ch samples were performed using S- band wave guide adapters of dimensions 34mm x 72mm. A sample holder with thickness 2.5mm was placed in between the wave guides. The system was calibrated before measurement. The S parameters for unsintered and sintered HAp powders were determined using Agilent 8714 ET Network Analyzer. From S- parameters, absorption coefficient is deduced. Experiment was also repeated for sample holder with thickness 5mm. The experimental setup is as shown in figure 4.3.

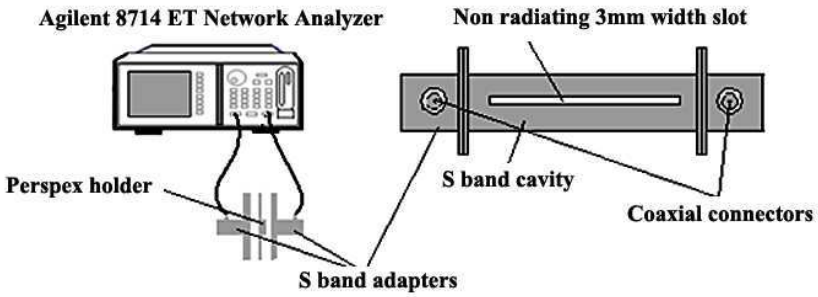

Figure 4.3 Experimental setup for Absorption measurement

4.2.3 Characterization

The dielectric properties of Hydroxyapatite pellet are measured in S band (2-4GHz) which includes the ISM band of 2.4 GHz. The dielectric parameters of the pellets are tabulated in Table 4.2. No significant variation can be observed in the dielectric properties of both freeze dried and furnace dried pellets. The measurement is taken at 2685 MHz. The dielectric constant of the pelletized powder depends on the pressure applied to it. The air between the powder

compacts reduces the dielectric constant. Above 1-ton pressure no substantial variation is noted for $\varepsilon_r^{'}$. The highly packed molecules in the pellet experiences

Table 4.2. Dielectric parameters of HAp pellets measured at center frequency 2684 MHz

Method of Preparation	Pressure (Kg/inch^2)	Sintering Temperature (°C)	Real part of permittivity $\varepsilon_r^{'}$	Imaginary part of permittivity $\varepsilon_r^{''}$	Conductivity σ (S/m)	Skin depth δ (m)
Freeze dried pellet	200	1000	2.67	0.014	0.002	0.197
		1200	3.19	0.073	0.0110	0.093
	1000	1000	3.89	0.063	0.0090	0.100
		1200	3.37	0.020	0.0030	0.178
Furnace dried pellet	200	1000	2.58	0.013	0.0020	0.222
		1200	3.33	0.012	0.0018	0.244
	1000	1000	3.76	0.008	0.0011	0.900
		1200	3.48	0.086	0.0013	0.086

high frictional strain causing low loss factor. The pellet which is subjected to low pelletizing pressure exhibits an increase in the dielectric constant ε'_r when the sintering temperature is increased from 1000˚C to 1200˚C. But the variation of ε'_r for pellets prepared at 1 ton pressure is almost the same for 1000˚C and 1200˚C. However slight variation in ε''_r is observed as temperature is increased. Skin depth

Table.4.3 Dielectric parameters of HAp-Chitosan composite

Ratio of composition of HAp and chitosan (HAp:Ch)	Frequency (MHz)	Real part of permittivity ε_r'	Imaginary part of permittivity ε_r''	Conductivity σ (S/m)	Skin depth δ (m)	Microwave heating coefficient J
1:2	2430	6.48	0.318	.0429	.0493	3.16
	2680	6.19	0.522	.0778	.0349	1.92
	2970	5.93	0.489	.0806	.0326	2.05
1:9	2430	5.78	0.134	.0181	.0758	7.47
	2680	5.59	0.223	.0332	.0534	4.49
	2970	5.47	0.374	.0617	.0372	2.67
2:1	2430	4.77	0.323	.0437	.0488	3.10
	2680	4.64	0.397	.0591	.0400	2.52
	2970	4.53	0.347	.0572	.0387	2.88
4:1	2430	3.93	0.231	.0313	.0577	4.33
	2680	3.83	0.228	.0340	.0527	4.38
	2970	3.74	.320	.0528	.0420	3.12

is the measure of depth of penetration of electromagnetic wave through a material and is inversely proportional to the conductivity. Skin depth of HAp is found to be matching with that of natural bone which is free of water and collagen.

Table. 4.3 shows the variation of dielectric parameters for HAp-Ch combinations. In the case of Hap-Ch composite bioceramics, the dielectric constants at the central frequency 2970 MHz are found to be 5.93, 5.47, 4.53 and 3.74 for HAp-Ch combinations, 1:2, 1:9, 2:1 and 4:1 respectively. Since HAp-Ch is a polymer composite, the microwave heating coefficient J is included in the study. As J is high, the dielectric heating will be poor. The dielectric constants of HAp-Ch composites are low because of their lower polarizability. The nominal water content is the reason behind.

Table. 4.4 Dielectric constants of human organs and their phantoms

Human Organ at 37^{o} C	Dielectric constant at 3000 MHz	Equivalent Phantoms in terms of % composition of HAp: Chitosan
Collagen in vitro	5.5-6.5	1:2
Bone marrow in vitro	4.2-5.8	1:9
Human abdominal wall fat	4.92	2:1
Human chest fat	3.94	4:1

The dielectric parameters of HAp-Ch composite are the same as that of certain biological constituents of human body [20]. A comparative study of dielectric parameters of human organs and their phantoms are given in Table.4.4. The ratio of composite can be appropriately selected according to the required properties of the human sample**.** The HAp-Ch composite having ratios 1:2, 1:9, 2:1, 4:1 falls in the dielectric range of collagen, bone marrow, human abdominal wall fat and human chest fat respectively. Since the dielectric properties of human

abdominal wall fat falls in the range of bone marrow, it can be realized by using 1:9 ratio. HAp-Ch derivatives are known as biomaterials and essentially should be biocompatible.

Their biocompatibility can be confirmed by the close similarity in their dielectric properties with that of human fat tissue, collagen and bone marrow. They will not be rejected when implanted in human body and are capable of becoming part of the body itself eventually through osteoconduction. The absence of other tissues between the newly formed bone and biomaterial surface is used to identify the biomaterial as osteoconductive. Hence HAp-Chitosan composites can be used for biological implant application such as in bioceramics for tissue regeneration.

Since the dielectric properties of HAp-Ch composites match with that of body parts they can be used as phantom materials for imaging studies. An environment with all the dielectric properties of bone marrow, fat, collagen and breast can be simulated using them. It is seen that a composition of 1:2 is nearer to the permittivity of natural bone it can be considered as more compatible bone implant. But a tradeoff has to be attained when strength of the implant is considered, so 1:9 (HAp: Ch composition) will be more appropriate.

Figures 4.4 and 4.5 shows the XRD pattern of unsintered and sintered HAp powders respectively. The XRD pattern of the unsintered and sintered powders are in good agreement with the standard HAp XRD patterns [21]. The XRD pattern of HAp sample sintered at 1000^{o} C shows sharp peaks which represent the well crystallized nature of the sample. An increase in crystal perfection with temperature is observed.

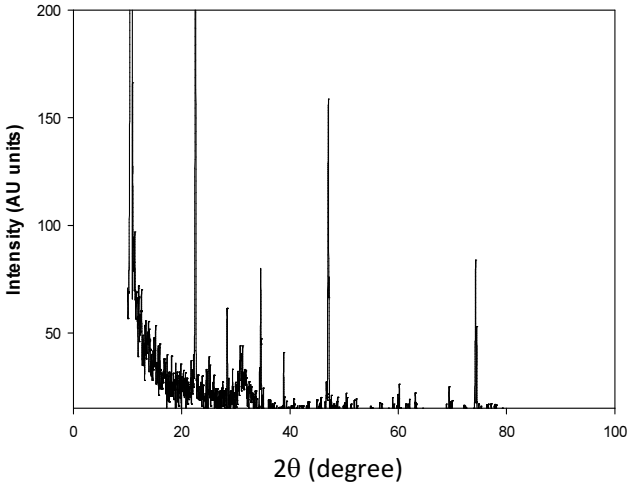

Fig.4.4 XRD of unsintered HAp

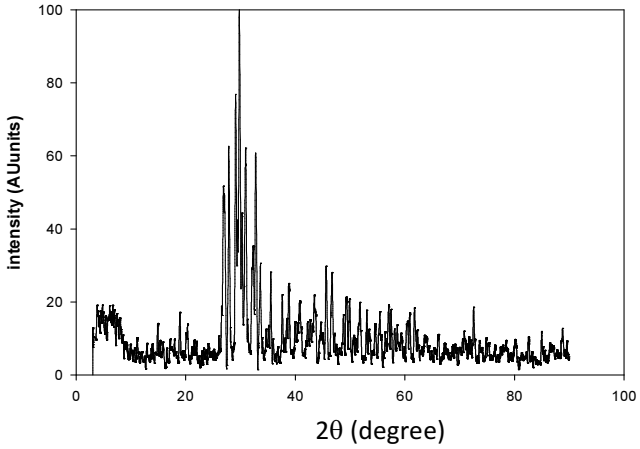

Fig.4.5 XRD of sintered Hap

The variation in microwave absorption coefficient of different ratios of HAp: Chitosan of thickness 2.5mm with frequency is shown in figure 4.7. The Absorption coefficient is found to be highly frequency dependent. Being biological materials they show good absorption of microwave and can be used as microwave absorbing material in microwave tomographic chamber used for imaging. Almost

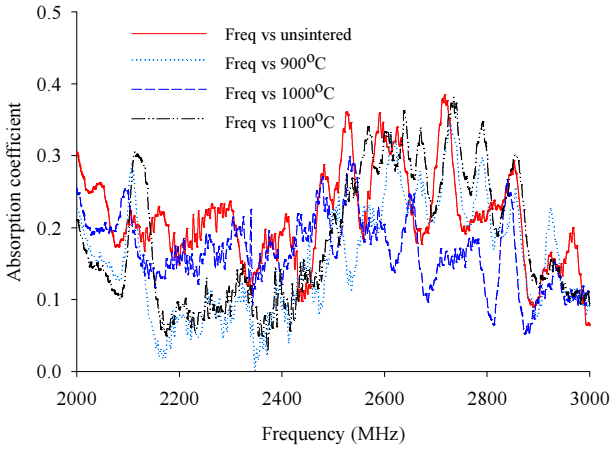

Fig.4.6 Variation of Absorption coefficient of HAp powder sintered at different temperatures with frequency

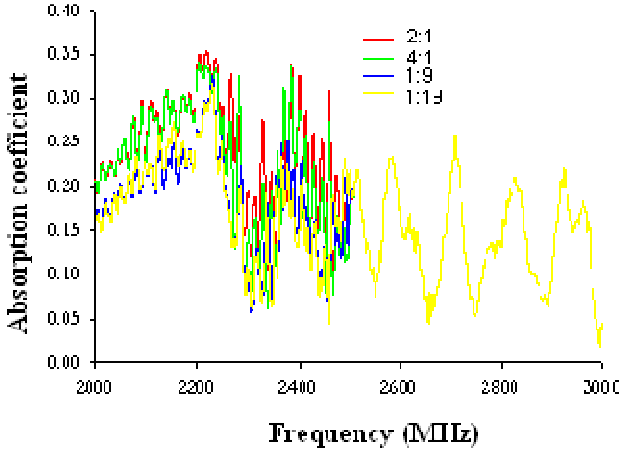

Figure 4.7 Variation of Absorption coefficient with frequency of HAp-Chitosan composite

similar microwave absorption is shown by different composition. But a slight absorption-variation is obvious in the frequency range of 2000-2500MHz. The ratios 2:1 and 4:1 are found to be absorbing power when compared to other compositions.

4.2.4 Applications

The Hap powder can be used as fillers for bone cracks. Its pellets in sintered form can be used for implantation purposes as they are biocompatible. Although its bioresorption rate is low, it can promote bone growth by osteoconduction. Another important application of HAp is its use as microwave phantom material. For studies involving natural bone, Hap can provide an alternative in *in vitro* applications. The dielectric constant of HAp matches with that of natural bone free of water and collagen. HAp-Chitosan composite can find applications as microwave phantoms for Collagen, Bone marrow, Human abdominal wall fat and Human chest fat. The various ratios of HAp-Chitosan representing these phantoms are shown in Table 4.4. Their ease of preparation, biocompatibility and bio functionality make them important in medical applications.

4.2.5 Advantages and disadvantages of HAp

Table 4.5 Advantages and Disadvantages of Hap

Advantages	Disadvantages
✓ Easy preparation	▪ Low mechanical strength ▪ Poor bioresorbability
✓ Availability of raw materials	
✓ Biocompatible	
✓ Low dielectric constant	
✓ Low loss	

4.2.6 Conclusions

HAp was prepared using different drying techniques. The dielectric properties of HAp composites with chitosan are studied. The variations in absorption characteristics are discussed. The dielectric properties of HAp-Chitosan composites are similar to that of fat, collagen, bone marrow and are biodegradable,

non-toxic, and biocompatible. These composites can be easily prepared and be used as phantom materials for microwave medical tomographic applications.

4.3 Beta Tricalcium Phosphate

Beta Tricalcium phosphate (β-TCP) bioceramics and chitosan biopolymers are used as biomedical implants because of their better biocompatibility and good bioresorption characteristics. The Calcium phosphate ceramic materials differ in their dissolution rate and hence bioresorption characteristics [22-24]. β-TCP shows better bioresorption than hydroxyapatite bioceramics [6]. The dissolution rate of β-TCP is higher. β-TCP can be resorbed *in vivo* by osteoclasts or macrophages. Although the resorption rate of β-TCP is affected by both macrostructure and microstructure, β-TCP ceramic is generally considered as a bioresorbable calcium phosphate ceramic. Chitosan (poly [β-1-4]) D-glucosamine) biopolymer is a bioasbsorptive natural medium for surgical correction of periodontal defects. Good haemostatic properties, good ability for guided tissue regeneration, bio absorbability and non-antigenic nature make this membrane unique [25, 26].

4.3.1 Preparation

Figure 4.8 Beta Tricalcium Phosphate (β-TCP) powder

β-TCP is prepared in a solid state reaction which involves thorough mixing of two Calcium compounds followed by calcination at high temperature [27, 31]. Equimolar amounts of Calcium Hydrogen Phosphate Anhydrous ($CaHPO_4$) and Calcium Carbonate ($CaCO_3$) are ground well. The mixture is calcined in furnace at 650^oC for 3 hours to obtain β-TCP. The powder obtained is free flowing and flimsy as shown in figure 4.8.

Chitosan biopolymer (1gm) is dissolved in 50ml of 12% solution of acetic acid (CH_3COOH) to obtain a thick gel of Chitosan. The Chitosan gel is held in a capillary tube of volume 0.2 $\times 10^{-8} m^3$ for measurement of dielectric properties. Dielectric properties of Chitosan film are also measured. For film preparation Chitosan solution is cast on to a smooth surface. It is then allowed to dry at room temperature. The thickness of the films obtained from the cast varied from 0.1 to 0.7 mm. The films obtained are flexible, tough, transparent, clear and have good tensile strength. They were cut into rectangular strips each having 50x3mm^2 area for cavity perturbation measurements. Chitosan film has a special super molecular structure having powerful hydrogen bond formation and high water retention.

4.3.2 Characterization

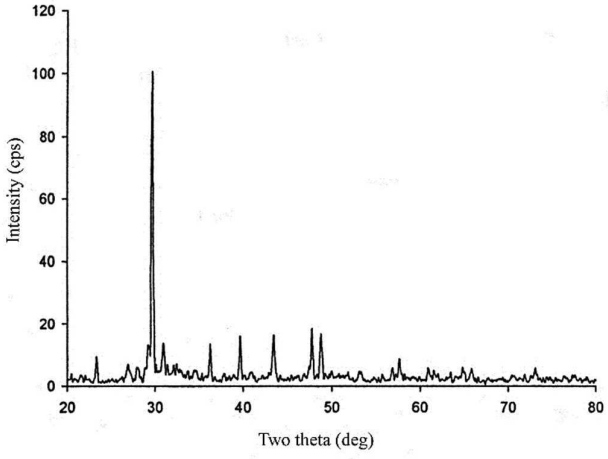

Figure 4.9 XRD pattern of β- TCP

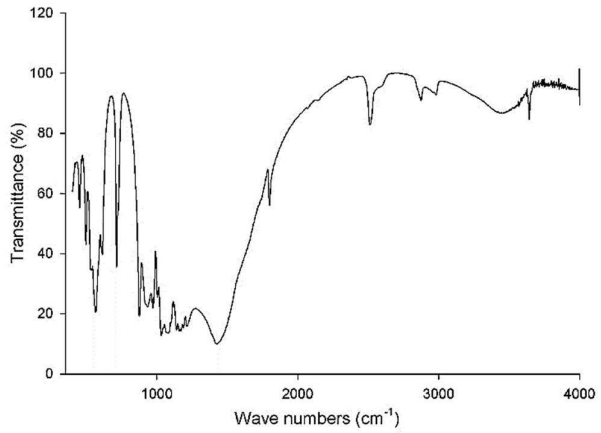

Figure 4.10 FTIR spectrum of β-TCP

The XRD pattern and FTIR spectrum of β-TCP are shown in figures 4.9 & 4.10. The structural properties of β-TCP were analyzed and were found to be agreeing with the XRD pattern and FTIR spectrum of standard samples of the same [28]. The variation in dielectric parameters with frequency was obtained using cavity perturbation technique. Properties such as Permittivity, Loss factor, Skin depth and SAR were evaluated.

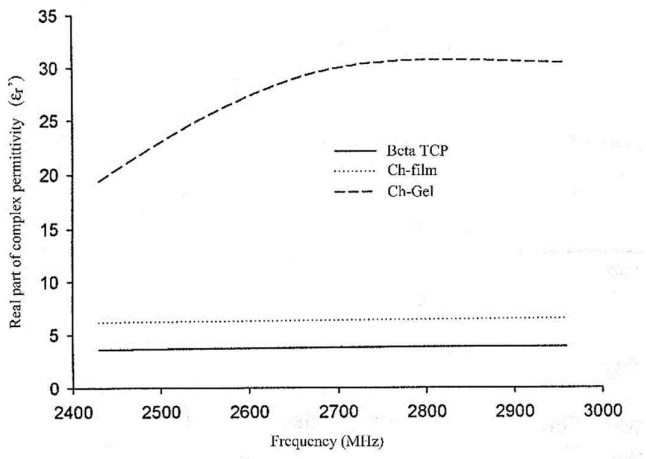

Fig. 4.11 Variation of real part of Complex permittivity with frequency

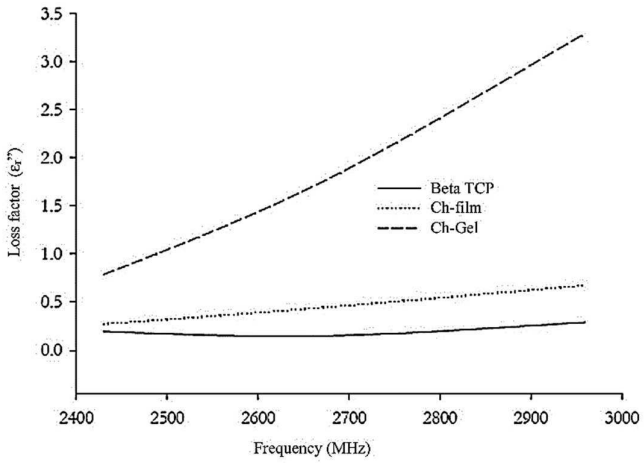

Fig.4.12 Variation of Loss factor with frequency

The frequency dependency of β-TCP and Chitosan is shown in Figs. 4.11 & 4.12. In the frequency range 2000-3000 MHz, β-TCP shows a variation in dielectric constant (real part of complex permittivity) from 3.61-3.80. The low dielectric constant is attributed to low polarizability. The dielectric constants of chitosan film and gel vary from 6.17 to 6.42 and 19.4 to 30.3 respectively in the above frequency range. The lack of air gaps in chitosan film gives it high permittivity when compared to β-TCP. Chitosan molecules are positively charged. Hence it is polarizable in an applied field. The dielectric properties of biological tissues depend largely upon their water content [29]. High water content tissues (muscle, skin) have permittivities and loss factor much larger than those of less water content tissues (bone, fat).

The conductivity of dielectric materials in microwave field depends upon the dielectric loss factor. Here, as frequency increases the dielectric loss factor also increases. The dielectric loss is a direct function of relaxation process, which is due to local motion of polar groups. At high frequencies, the friction between molecular chain increases, which leads to higher dielectric loss. The variation of dielectric loss can be seen from Figure 4.12. Due to the presence of water, Chitosan

gel exhibits the highest loss. The conductivity is inversely proportional to the square of the Skin depth of the material. Hence the skin depth of Chitosan gel will be nominal as evident from Figure 4.13.

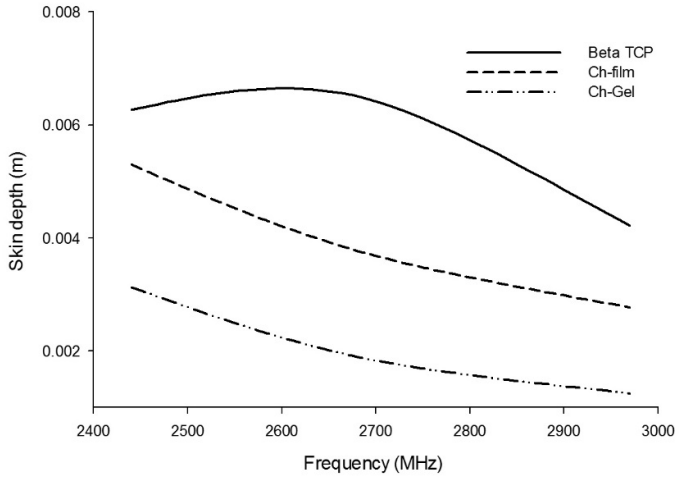

Fig. 4.13 Variation of Skin depth with frequency

Human chest fat, bone marrow and brain falls in the same dielectric range as β-TCP, Chitosan film and gel respectively [20]. Table 4.6 shows the dielectric constant of human organs and their equivalent phantoms. These materials are reproducible, long lasting, non-corrosive, easy to make and cost effective and thus can be used as suitable phantom for biological tissue in microwave medical imaging.

Table. 4.6 Dielectric constants of human organs and their phantoms

Human Organ	**Permittivity at 3GHz**	**Equivalent phantom**	**Method of preparation**
Chest Fat	3.94	β-TCP	Calcination of DCPA and $CaCO_3$
Bone Marrow	4.2-5.8	Chitosan Film (Ch-Film)	Deacetylation of chitin
Human Brain	30-33	Chitosan Gel (Ch-Gel)	Dissolution of chitosan in acetic acid

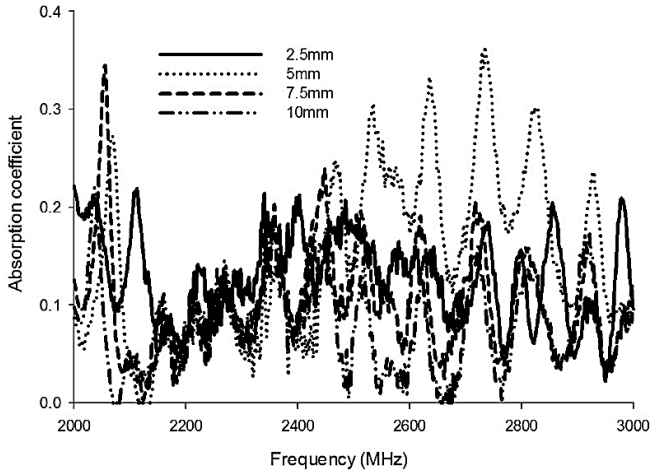

Fig. 4.14 Variation in Absorption coefficient with thickness shown by β-TCP

The S-parameters of β-TCP and Chitosan film have been studied and it is observed that both the samples behave almost identically to microwave radiation. The Absorption coefficient of powder samples of β-TCP with different thicknesses was evaluated from S-parameter measurements. The results are shown in figure 4.14.

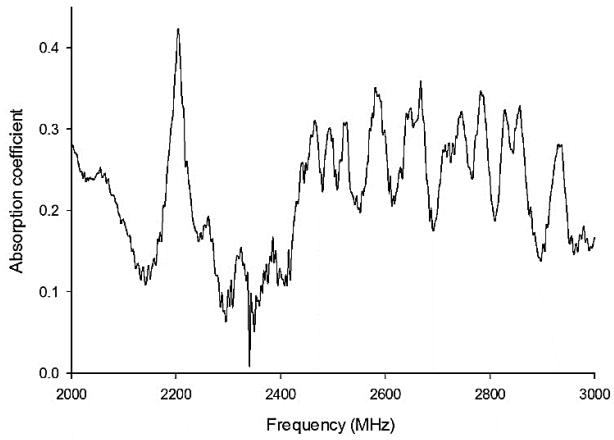

Fig. 4.15 Variation in Absorption coefficient with frequency for 0.5 mm thick Chitosan film

Figure 4.15 shows the variation in Absorption coefficient of Chitosan film with frequency for 0.5 mm thickness. The Chitosan film absorbs maximum power around 2.2 GHz. The reflection of microwave power of samples for different thicknesses is understood from figure 4.16. The information about the transmitted

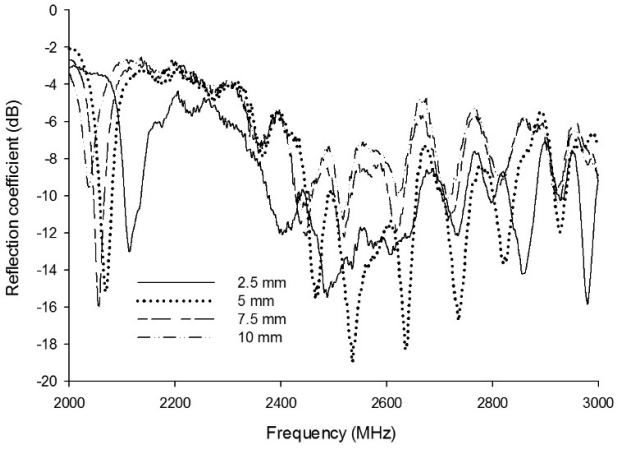

Fig. 4.16 Variation in Reflection coefficient for β-TCP of various thicknesses

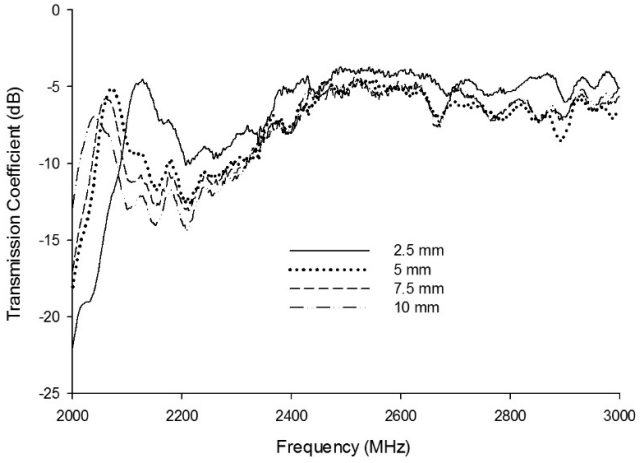

Fig. 4.17 Variation in Transmission coefficient for β-TCP of various thicknesses

power of the samples is obtained from figure 4.17. All the measurements were made in the frequency range 2000-3000 MHz. It is observed that the S-parameters S_{11} and S_{21} and Absorption all vary with frequency. This is expected because the interaction of molecular chains changes with frequency. Figure 4.17 shows that the transmitted power of all samples of β-TCP, irrespective of their thickness is almost the same above 2400 MHz. However slight variation is observed below 2400 MHz.

An observation of figures 4.14 & 4.16 shows that, as reflected power increases the absorbed power decreases and vice versa. This is very clear for the sample with thickness 5mm. Though absorption is high for this sample the reflection coefficient is very low at same frequency range. This is true for all other thicknesses. This supports the earlier statement that the transmitted power of different β-TCP samples are the same.

4.3.3 Applications

β-TCP bioceramics is a potential material which is more biocompatible and bioresorbable than Hydroxyapatite bioceramics. Its microwave absorption characteristic doesn't vary much with increase in thickness of the sample. It could be used for bone filling applications rather than bone replacement because of the flimsy nature of the powder. The samples are difficult to be pelletized and hence suffer from poor mechanical strength. It could be used as phantoms for microwave imaging applications because of the low dielectric constant value and loss factor.

4.3.4 Advantages and disadvantages

Table 4.7 Advantages and disadvantages of β-TCP

Advantages	Disadvantages
✓ Easy preparation	▪ Low mechanical strength
✓ Availability of raw materials	▪ Difficult to form pellets
✓ Better biocompatibility	

- ✓ Better bioresorption
- ✓ Biodegradable
- ✓ Low permittivity
- ✓ Low loss factor

4.3.5 Conclusions

The dielectric properties of β-TCP and Chitosan are studied. Absorption coefficient variation was measured at different frequencies and thickness. Dielectric constant and conductivity of samples are in good agreement with available literature data on biological tissues. The microwave absorption study can be used to check whether the implant is inducing more dielectric heating than that of biological tissue which may be harmful when exposed to microwave radiation. The study facilitates the bioabsorption analysis for microwave imaging and developing phantoms. It can be also used as a method for the verification of microwave compatibility. From the above study, it is inferred that both β-TCP and Chitosan are good for phantom applications in the ISM frequency range.

4.4 Biphasic Calcium Phosphate

In 1970-80s, bioglass (CaP containing glass) and hydroxyapatite ceramic (HAp) were found to be osteoconductive. Since then Calcium phosphate biomaterials became the most interesting artificial bone grafts. In practice, an osteoconductive biomaterial is identified by the absence of other tissues between newly formed bone and biomaterial surface. HAp has good mechanical properties, but is less bioresorptive as compared to β-TCP ceramics. The dissolution of β-TCP ceramics is faster when compared to that of HAp. The Biphasic Calcium Phosphate (BCP) is formed by the mixture of HAp and β-TCP in different ratios [30-32]. Hence the dissolution of BCP highly depends on the β-TCP/HAp ratio.

4.4.1 Preparation

For preparing Biphasic Calcium Phosphate, HAp and β-TCP are mixed in the ratio 1:4 and ground well. The resultant mixture is calcinated at 700^{o}C for 3 hours. The mixture is allowed to cool, ground again and then kept in air tight container. The BCP powder is not as flimsy as β-TCP powder, but is grainier in appearance. The picture of BCP powder is shown in figure 4.18.

Figure 4.18 BCP in powder form

Arrowroot (Maranta Arundinacea) has therapeutic use as it is mainly used as a traditional wound healing medicine [33, 34]. Arrowroot powder (10g) is dissolved in water (100ml) and is heated to obtain Arrowroot gel. To this gel, the BCP is added in different ratios (1:4, 2:3, 1:1, 3:2 and 4:1) and are casted to obtain films. The films are dried in room temperature and are cut into long strips for dielectric characterization studies. The films were of uniform thickness and are devoid of air gaps.

4.4.2 Characterization

The dielectric properties of Biphasic Calcium Phosphate: Arrowroot (BCP: Arrow) film were studied with the aid of HP 8714ET Network Analyzer. The measurements were taken at 2.685GHz which is one of the resonant frequencies of

the cavity. Films with varying BCP/Arrow ratio were used for dielectric characterization measurements. The thickness of the film is immaterial as the films are homogeneous. However uniform thickness was maintained for individual samples.

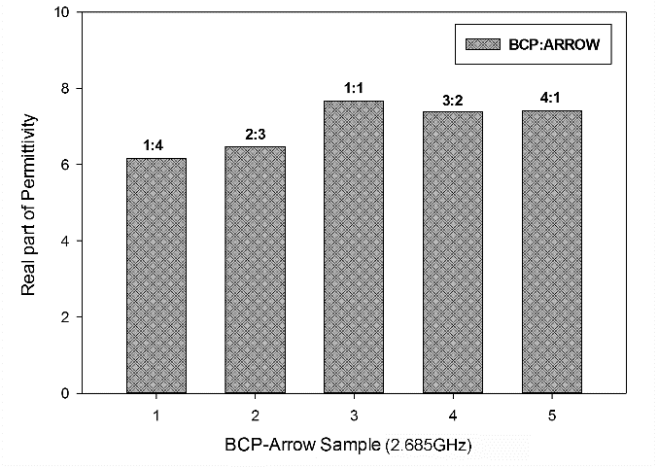

Figure 4.19Variation of real part of Permittivity with Various BCP: Arrow ratios

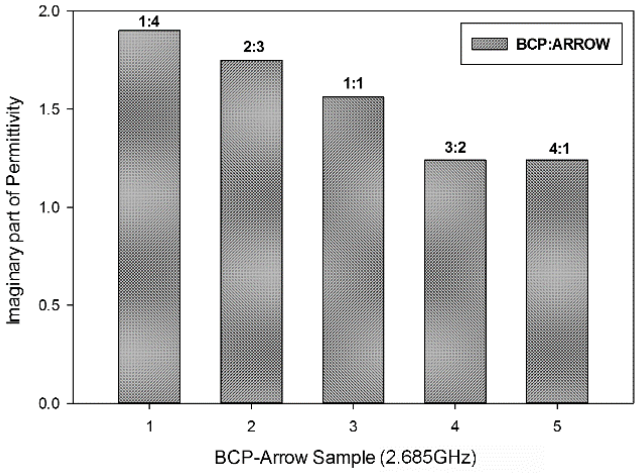

Figure 4.20 Variation of Imaginary part of Permittivity with various BCP: Arrow ratios

Figure 4.19 shows the variation of real part of complex permittivity at 2.685 GHz for BCP: Arrow films with ratios 1:4, 2:3, 1:1, 3:2 and 4:1. It can be observed that the ratio 1:4 shows minimum permittivity which is around 6. As the amount of BCP is increased, an increase in permittivity value is observed. And when amount of BCP exceeds that of Arrowroot, the permittivity doesn't show further variation. It might be due to the saturation of BCP particles in vacant spaces of the film. Further increase of the BCP amount in the film significantly affects its mechanical properties and structural stability of the film. It will make the film brittle and useless.

The imaginary part of permittivity or the Loss factor (figure 4.20) depends on the dielectric relaxation property of the film. The film is assumed to be non-polar due to the absence of water in it. Hence it gets only weakly polarized in an applied field owing to a faster relaxation time. And it accounts for the nominal value of Loss factor. The Arrowroot gel is highly polar in nature when compared to BCP powder. As the amount of BCP is increased in the film, the Loss factor also shows a corresponding variation by lowering its value.

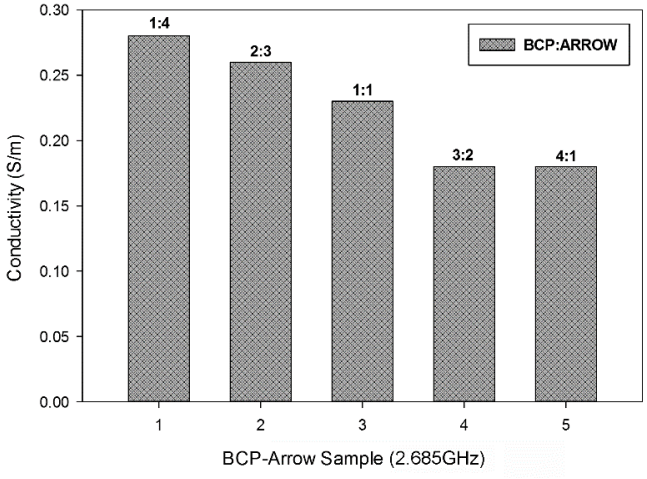

Figure 4.21 Variation of microwave conductivity of BCP:Arrow ratios

Figure 4.21 shows the variation of microwave conductivity for various ratios of BCP:Arrow film. The microwave conductivity is directly related to Loss factor of the material. Hence it shows the same variation as Loss factor. The peak conductivity of 280mS/m is observed for the sample with ratio 1:4. The presence of Arrowroot makes it more conducting. As the amount of Arrowroot decreases, the conductivity of the film also falls.

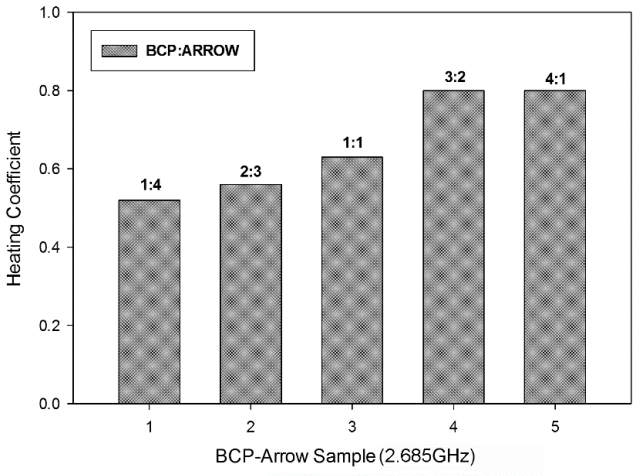

Figure 4.22 Variation of Heating coefficient for different BCP:Arrow ratios

The heating coefficient defines how microwave interacts with a material. Dielectric relaxation phenomenon is responsible for dielectric heating. Heating coefficient is the efficiency of heating of a dielectric material. A low value of Heating coefficient indicates that the material is good for dielectric heating purposes [35]. As evident from Figure 4.22, the BCP: Arrow samples in ratios 3:2 and 4:1 have the highest Heating coefficients. Thus they undergo less dielectric heating. Hence they are better than the other BCP: Arrow combinations for implantation/phantom applications.

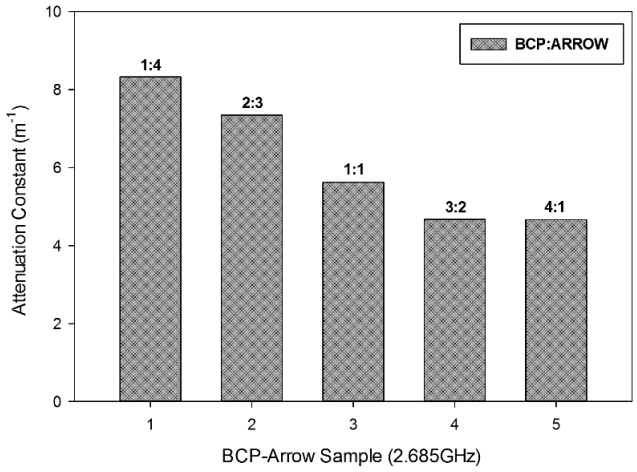

Figure 4.23 Variation of attenuation constant of BCP: Arrow ratios

The attenuation constant (Figure 4.23) shed light on the material's transparency to microwaves. It is directly related to the Loss factor of the material. Hence it shows the same variation as that of the loss factor. It is observed that BCP: Arrow with the ratio 1:4 has the highest attenuation constant which means it

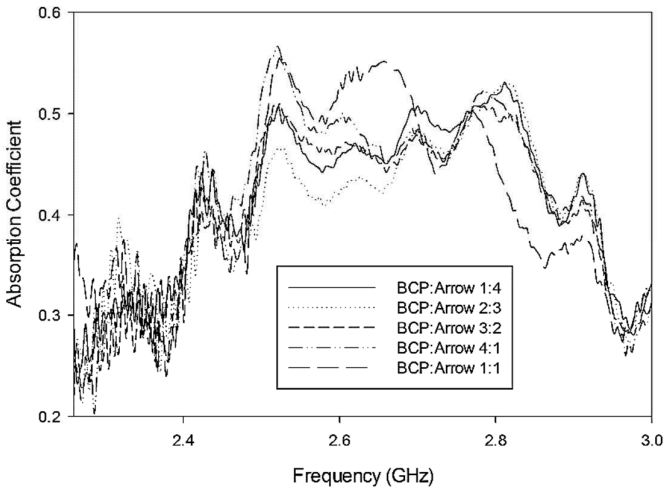

Figure 4.24 Variation of absorption coefficient of BCP: Arrow samples

can attenuate much of the microwave power within the material. This is also evident from the variation of heating coefficient (figure 4.22). The ratios 3:2 and 4:1 are more transparent to microwaves and are better dielectrics.

Figure 4.24 shows the Absorption coefficient variation with frequency for different ratios of BCP: Arrow powder samples. The samples were placed in a sample holder of 2.5mm thickness and hold in between two S-band adapters. It can be seen that there is not much variation between the curves. The minor variations can be attributed to the slight variations in packing density of the samples within the sample holder. The absorption is nominal at the start of the band then increases to reach a maximum and again shows a declination at the upper end.

4.4.3 Applications

BCP:Arrow film could find important applications in medical field. BCP:Arrow samples in ratios 3:2 and 4:1 have the highest Heating coefficients. Thus they undergo less dielectric heating. Hence they could be used for implantation/phantom applications. They could also be used as microwave absorbers. The dielectric properties and dissolution rate of BCP can be controlled by varying the HAp/β-TCP ratio. The desired features of the implants/phantoms can be fine-tuned by this method.

4.4.4 Advantages and Disadvantages

Table 4.8 Advantages and Disadvantages of BCP ceramics

Advantages	Disadvantages
✓ Easy preparation	✓ Trade-off between biocompatibility and mechanical strength
✓ Better control over dissolution	
✓ Biocompatible	
✓ Biodegradable	
✓ Low Permittivity	
✓ Low Loss factor	

4.4.5 Conclusions

The dielectric characterization of Biphasic calcium phosphate-Arrowroot film was done. The amount of BCP is the key factor which determines the mechanical stability of the film. The films obtained have low dielectric constant and loss factor. They could be used as phantom materials representing collagen.

4.5 Conclusion

Bioceramic materials were developed and their dielectric and structural characterizations were performed. Hydroxy Apatite, β-Tricalcium Phosphate and Biphasic Calcium Phosphate ceramics were synthesized. These materials are characterized by their osteoinductive, osteoconductive, bioresorptive and biodegradable nature. These ceramics in pure form and composite form can be used for implantation purposes as well as for applications which require microwave phantoms representing human body parts. They could also be made into pellets, composite mixtures and films. They could be used as bone fillers in their native form.

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Chapter 5
Conducting Polymers

5.1 Polyaniline blends for EMI shielding

5.1.1 Introduction

Conducting polymers have potential applications at all levels of microelectronics [1, 2]. Applications like anticorrosion, static coating, electromagnetic shielding etc. come under first generation. Second generation of electric polymers have applications such as transistors, LEDs, solar cells, batteries etc. Controlled conductivity, high temperature resistance, low cost and ease of bulk preparation make these materials attractive in the engineering and scientific world [3-6]. Polypyrrole (Ppy) and polyaniline (Pani) are especially promising for commercial applications because of their good environmental stability, facile synthesis and higher conductivity than many other conducting polymers [7-9].

Figure 5.1. Polyaniline in powder and pellet forms

Polyaniline ($C_6H_5NH_2$) has received much attention because of its unique reversible proton doping, high electrical conductivity, ease of preparation and low cost. Also its electromagnetic parameters can be adjusted by changing both oxidation and protonation state [10]. Figure 5.1 shows Polyaniline in powder and pellet forms. Pellets are prepared by pressing the powder in a metallic die. Calcination and sintering are not allowed as they will degrade the polymer properties.

The demand of high quality materials for electromagnetic compatibility is alarmingly increasing. This has led to the development of a large number of Pani based composites. The composites of Pani such as Pani-Polyvinyl chloride (PVC), Pani-Polyvinyl butyral-Surfactant (PVB-PS3), Pani-Fly ash (FA), Pani-Single walled carbon nanotube (SWNT) etc exhibit different properties such as semi crystalline nature, high pH sensitivity, sudden fall/rise in conductivity and enhanced electro activity [11-13]. These unique properties make Pani and its composites suitable for various microelectronic applications. A detailed study of PANI-PVB-PS3 composite film by Gill *et al* [11] revealed its excellent pH sensitivity. A similar study was performed on low frequency ac conduction of Pani/Fly ash composites by Raghavendra *et al* [12]. The present knowledge of various transport mechanisms in conducting polymers and the potential use of polymers as EMI shielding materials have encouraged the measurement of dielectric behaviour at high frequencies. A comprehensive study on the microwave conductivity of polyaniline–polyvinyl chloride composites was performed by Honey *et al* [14]. Cyclohexanone soluble conducting polyaniline composite was synthesized in the presence of polyvinyl chloride and its dielectric properties were studied [15]. A detailed study on the effect of different forms of poly *o*-toluidine/poly vinyl chloride composites on dielectric properties in the microwave field was performed [16]. Studies on the dielectric properties of materials such as Natural rubber-Pani composites [17], Poly (3,4-ethylenedioxythiophene), polythiophene, polypyrrole, polyparaphenylene diazomethine (PPDA) [4], poly(o-toluidine) and poly(o-toluidine-aniline) copolymer [18] were also reported. The

beam steering property [19] of Pani made it a strong candidate for automatic beam steering applications. Nagai and Rendell [20] have summarized the theoretical and experimental aspects of ac conductivity and dielectric relaxation of polymers. The dc and ac conductivities of Pani-PVC blends were reported by Dutta *et al* [21]. The frequency range 1 kHz to 5 MHz was adopted for this study.

5.1.2 Electromagnetic Interference (EMI) Shielding

EMI shielding is critical to the proper functioning of many devices [22]. Many electrical devices such as electric motors generate electromagnetic radiation, often at radio and microwave frequencies [23]. Figure 5.2 shows the different ways in which this electromagnetic noise gets coupled to various devices. These noises can result in the malfunction of electrical devices. The plastic casings used in many of these devices are transparent to such radiation. By coating the inside of the

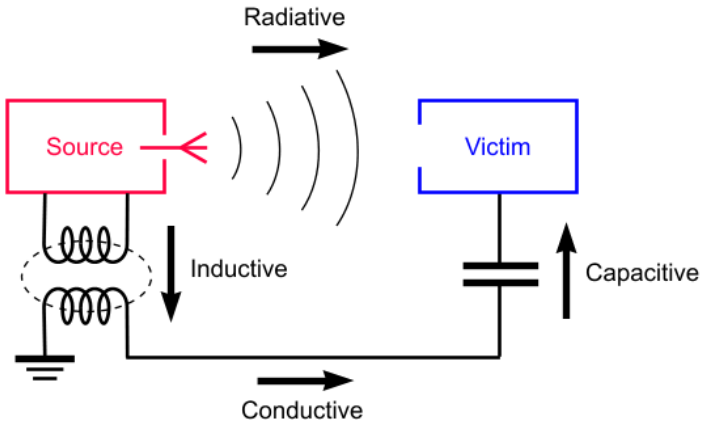


Figure 5.2. Different EMI coupling modes

plastic casing with a conductive surface, these radiations can be blocked. This can best be achieved by the use of conducting polymers. Increase of EMI shielding efficiency with the electrical conductivity results from the increase in shielding by reflection. This in turn is due to the decrease of surface resistivity. A high

reflection coefficient is due to a shallower skin depth of the composite with higher electrical conductivity. The shielding efficiency can be controlled by changing the surface electric conductivity of the material.

Dongxiu *et al* [24] performed a study on EMI shielding of Pani-coated oxidized short carbon fibres (PAOSCF) and came up with good results. The study revealed that the dispersion stability was improved after Pani coated treatment. Though a number of polyaniline based conducting polymers are studied at high frequencies for their dielectric properties, a detailed study on the effect of EMI shielding of these materials has not yet performed. This paper is intended to establish the effect of conducting polymers in electromagnetic interference shielding. Conventional microwave absorbing materials such as carbon and graphite in powder form were blended with polyaniline at different proportions and microwave properties such as transmission, reflection, skin depth and shielding efficiency were evaluated for various thicknesses from S parameter measurements using HP 8714ET network analyzer. The new materials developed exhibit greater electromagnetic interference shielding efficiency.

5.1.3 Polyaniline preparation

The Polyaniline was prepared by the oxidative polymerization of aniline in the presence of HCl as dopant acid. AR grade Aniline ($C_6H_5NH_2$), Ammonium peroxydisulfate ($(NH_4)_2S_2O_8$), Acetone ($(CH_3)_2CO$) and Hydrochloric acid (HCL) were procured from Merck Specialities (P) Ltd, Mumbai. Blending materials, Carbon black (Charcoal activated) and Graphite powder were obtained from Nice chemicals, Cochin and Research Lab, Mumbai respectively. The efficient chemical oxidative polymerization of aniline is achieved only in an acidic medium, where aniline exists as an anilinium cation [25, 26]. The synthesis was based on mixing aqueous solutions of aniline hydrochloride and ammonium peroxydisulfate at room temperature.

Distilled aniline (10ml) was added to 1M hydrochloric acid (250ml) under vigorous stirring. Ammonium peroxydisulfate (34g) was added to H_2O (90 ml) to

form a solution. This solution was added to the previously prepared solution drop by drop at room temperature. The colour of the resultant solution immediately changed from straw yellow to dark green indicating formation of Pani. The solution was stirred thoroughly for 4 hours forcing aniline to polymerize. The Pani precipitate was collected on a filter and washed initially with water and then with Acetone. The collected Pani was kept in a hot air oven and dried overnight at 60^0 C. Pani and carbon black as well as Pani and graphite were blended in ratios 5:1, 5:2, 5:3 and 5:4. Machine blending was used as it provided better mixing.

5.1.4 Experimental Setup

The S parameter measurements were carried out in the S band frequency of ISM band with a wave guide of dimensions (a x b) 34mm x 72mm. Perspex holders of 2.5mm, 5mm, 7.5mm and 10mm thicknesses were constructed for holding the composite material. Perspex was used as the holder material since it has a dielectric constant closer to that of air which means less microwave power will be absorbed in the walls of the holder. The experimental setup is as shown in figure 5.3.

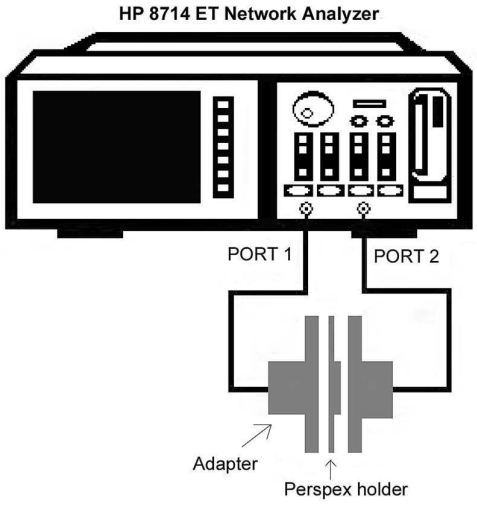


Figure 5.3 Absorption measurement

The sample holder is kept between two coaxial to wave guide adapters and tightened and then connected to HP 8714ET network analyzer. The network analyzer is calibrated for measurement. The calibration can be stored for measurement at a later time. Scattering parameters S21 and S11 of the samples are measured. Samples of varying thickness are studied using Perspex containers of thickness 2.5mm, 5mm, 7.5mm and 10mm at the S-band of microwave frequencies. From the measured data, Reflection coefficient, Transmission coefficient, Shielding efficiency (SE) and Skin depth (SD) of various composite ratios are evaluated.

Scattering parameters, also called S-parameters describe the performance of a two port completely. They relate to the travelling waves (power) to a two port's reflection and transmission behaviour. From the basic theory of wave propagation through matter, the amount of electromagnetic energy reflected and transmitted when incident on a sample material is related by the Reflection coefficient (R) and Transmission coefficient (T). These are related to the S parameters as $R= |S_{11}|^2$ and $T = |S_{21}|^2$. The absorption coefficient A can be obtained from the simple relation A+R+T = 1 indicating that the absorbed power is A = 1-(R+T). The microwave absorption increases as dielectric loss increases [27]. The dielectric loss can be found out using the conventional cavity perturbation technique [28].

If the absolute absorbing capability of a material for a given incident power is the point of interest, then it is necessary to minimize the reflected power. It is most useful in microwave heating applications. But for electromagnetic interference shielding applications, reduction of absorbed energy is preferred. Under such condition, non-conducting shielding material with high reflection coefficient is a good alternative. The EMI shielding efficiency SE is defined [29, 30] as the ratio of the power of the incident wave P_I to that of the transmitted wave P_T.

$$SE = 10 \log (P_I / P_T) \text{ dB} \quad (1)$$

The electrical skin effect describes the effect of current crowding near the surface of a conductor. This effect is important when we try to send an electromagnetic field through a conducting medium. If the skin depth [31] of a particular material at a particular frequency is less than the thickness of the material, then the material is said to be reflective. Conversely, if the skin depth is large compared to the thickness of the material, the material is said to be transparent. If the skin depth is near the thickness of the material, the material is said to be adsorptive. The dielectric parameters of the samples are measured using Cavity perturbation [32] technique.

5.1.5 Results and discussions

The variation of dielectric parameters such as permittivity, loss factor, conductivity and heating coefficient for Graphite and Carbon black are analyzed. The size and shape of the Graphite and Carbon black particles are obtained from Scanning Electron Microscope (SEM) measurement of the samples. The measured properties Reflection, Transmission, EMI shielding efficiency and Skin depth of the developed conducting polymer composites are also analyzed in this section. These properties are very important when EMI shielding applications are taken into account.

i) Dielectric Parameters

The dielectric parameters determine the electrical characteristics of a material. The parameters such as permittivity, loss factor, conductivity and dielectric heating coefficient for resonant frequency 2.43 GHz for Graphite and Carbon black are measured and shown in table 1. It can be seen from table 1 that the permittivity of Graphite is slightly higher than that of Carbon black. However the loss factor and conductivity of Carbon black is higher for the same packing density.

Table 1. Dielectric properties of Graphite and Carbon black at 2.43 GHz

Dielectric Parameters	Graphite	Carbon black
Permittivity, ε_r'	9.23	7.56
Loss factor, ε_r''	1.52	1.95
Conductivity, σ (Sm^{-1})	0.21	0.26
Heating coefficient, J	0.66	0.51

In heterogeneous dielectrics, space charge accumulation occurs at the macroscopic interface due to the differences in the conductivities and dielectric constants of the materials at the interface. This space charge accumulation results in field distortions and dielectric loss. The important factors which determine the interfacial loss are the quantity of filler present and the geometrical shape of the dispersion. Microwave heating coefficient doesn't show much variation for both materials.

ii) SEM Measurements

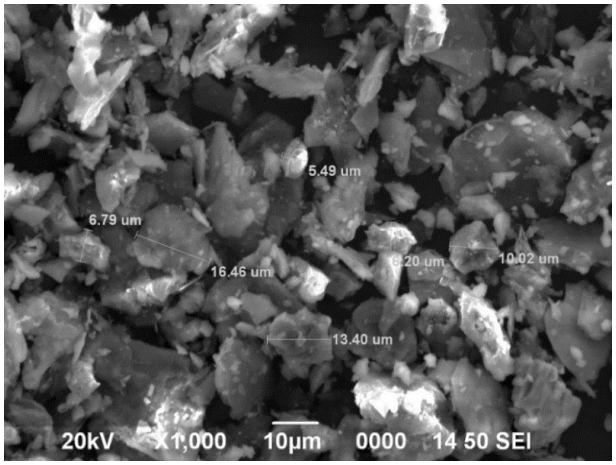


Figure 5.4 SEM image of Graphite powder

The SEM measurements of Graphite and Carbon black samples are taken to study the structural differences of the materials. The SEM images obtained are shown in figures 5.4 and 5.5. The images give thousand times magnified view of the samples in powder form.

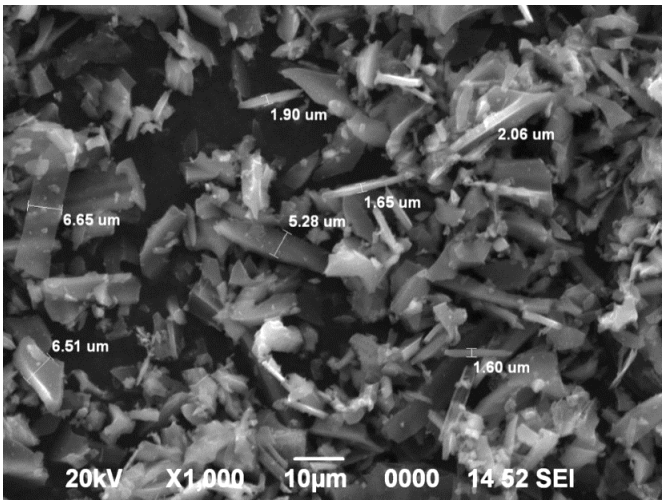


Figure 5.5. SEM image of Carbon black powder

It can be observed from the figures that the Graphite grains are more or less round in shape whereas Carbon black grains show tubular nature. Graphite grains are larger in size compared to Carbon black grains. The difference in the grain size plays a significant role in the shielding efficiency variation of the composites involving these materials.

iii) Reflection Coefficient

The reflection coefficient variation of Pani-Carbon (PC), Pani-Graphite (PG) composites and Pani alone at S band frequencies for different ratios and constant thickness (7.5 mm) is shown in figure 5.6 and figure 5.7. Basic theory states that minimal reflection of the microwave power or matching condition occurs when the sample's thickness, 't' of the absorber approximates to a quarter of the propagating wavelength multiplied by an odd number, that is $t = n\lambda/4$ (n=1, 3,

5, 7, 9, . . .), where n=1 corresponds to the first dip at low frequency. The propagating wavelength (λ) in the material is given by:

$$\lambda = \lambda_0/(|\mu_r*|/|\varepsilon_r*|)^{1/2} \quad (2)$$

Where, λ_0 is the free space wavelength and $|\mu_r^*|$ and $|\varepsilon_r^*|$ are the moduli of μ_r^* and ε_r^* respectively.

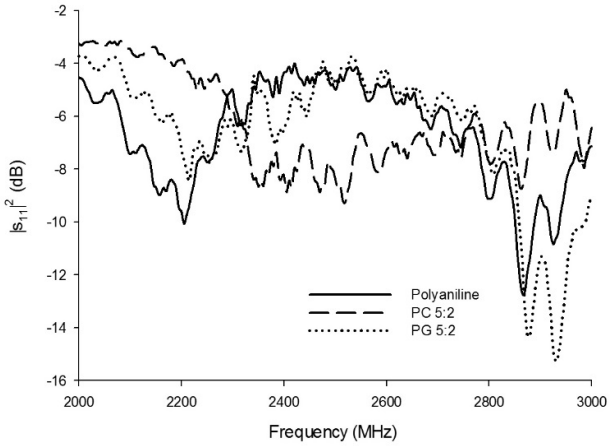


Figure 5.6 Variation of reflection coefficient for various composites in 5:2 ratio

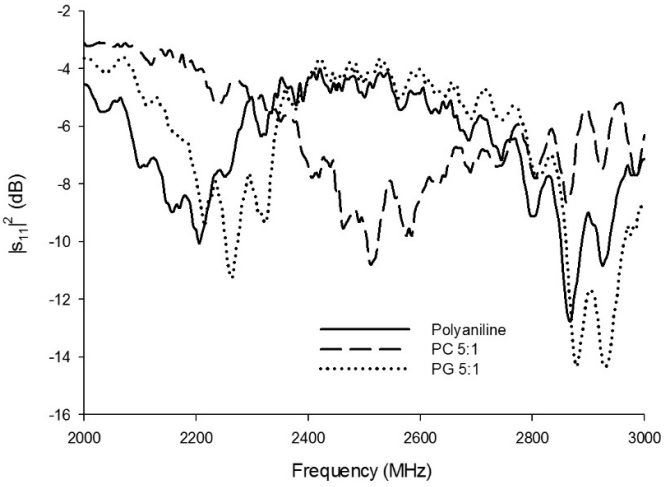


Figure 5.7 Variation of reflection coefficient for various composites in 5:1 ratio

The matching condition can be explained by the cancellation of the incident and reflected waves at the surface of the absorber. The minimum reflection loss or the dip is due to the minimal reflection or maximal absorption of the microwave power for the particular thickness of the sample. The position and intensity of the dip are sensitive to thickness. In figure 5.6, for 5:2 ratio combinations, PC shows high reflection in 2-2.3 GHz and 2.8-3 GHz ranges. At these frequencies, reflection of Pani and PG are quite low but they show good reflection from 2.3-2.8 GHz. Figure 5.7 shows the characteristics of the composite when amount of carbon and graphite are reduced. Here the reflection of PC is low from 2.3-2.8 GHz. PG follows almost the same characteristics as in figure 5.6 except for a dip at 2.265 GHz.

iv) Transmission Coefficient

The Transmission coefficient variation of Pani-carbon (PC), Pani-graphite (PG) composites and Pani alone at S band frequencies for different ratios and constant thickness (7.5 mm) is shown in figures 5.8 and 5.9. Transmission coefficient is the ratio of transmitted power to incident power. Therefore, if

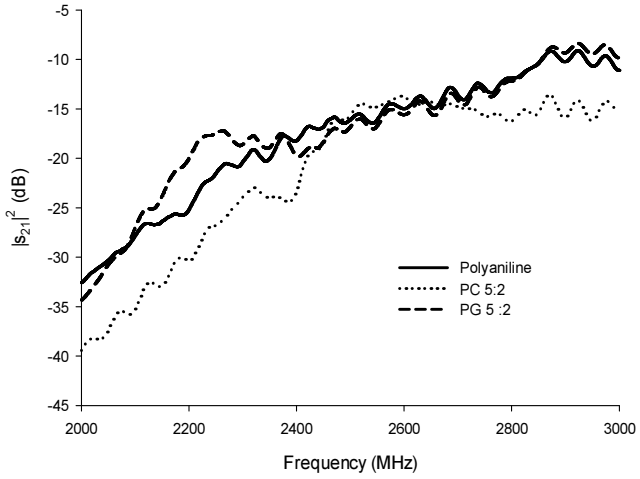


Figure 5.8 Transmission coefficient variation for various composites in 5:2 ratio

Transmission coefficient is low, then the material exhibits either good reflection or good absorption or both. A material which has a low Transmission coefficient and high Reflection coefficient is best suited as a material for EMI shielding applications so that heat generation due to absorption will be nominal. From graph it is clear that Pani-Carbon composite is the best choice for electromagnetic shielding applications. This can be further confirmed by studying the shielding efficiency SE of this composite.

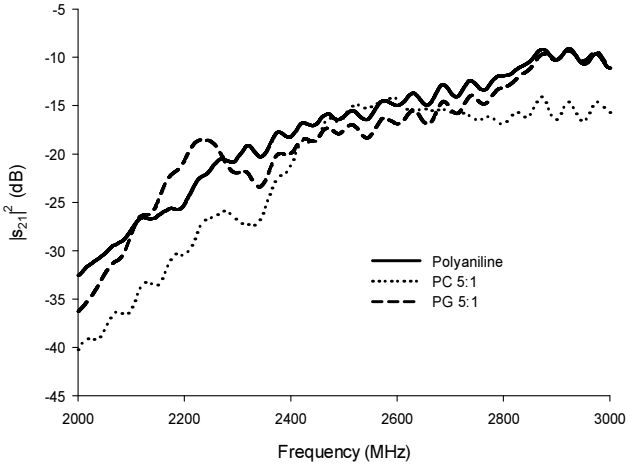


Figure 5.9 Transmission coefficient variation for various composites in 5:1 ratio

v) Shielding Efficiency

The Shielding efficiency variation of different composites at S band frequencies for 7.5mm thickness is shown in figure 5.10 and figure 5.11. Higher the SE value, lesser the energy passing through the sample. All measured SE is the combination of the electromagnetic radiation, i.e. reflection from the material's surface, absorption of the electromagnetic energy and multiple internal reflections of the electromagnetic radiation.

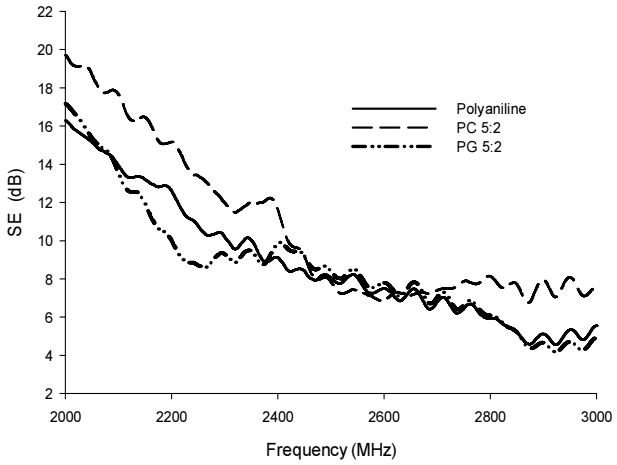


Figure 5.10 Shielding efficiency variation for 5:2 ratio

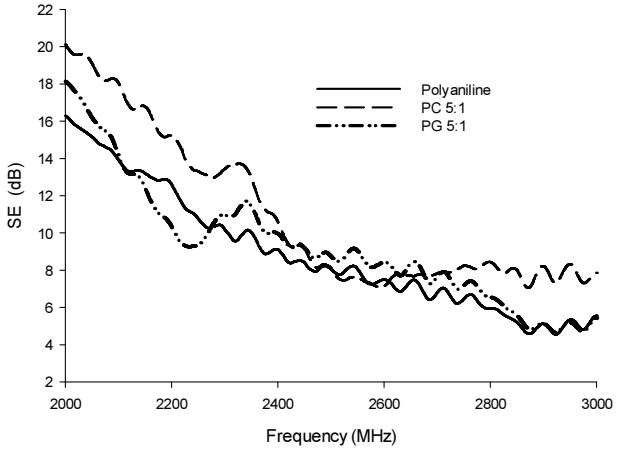


Figure 5.11 Shielding efficiency variation for 5:1 ratio

Observing figure 5.10 and figure 5.11, it is quite obvious that Pani-carbon composite exhibits better shielding efficiency as compared to Pani and Pani-graphite (PG) composites. The difference is quite noticeable at lower frequencies and at higher frequencies. In the frequency range 2.5-2.7 GHz, the shielding efficiencies of composites are more or less similar in nature.

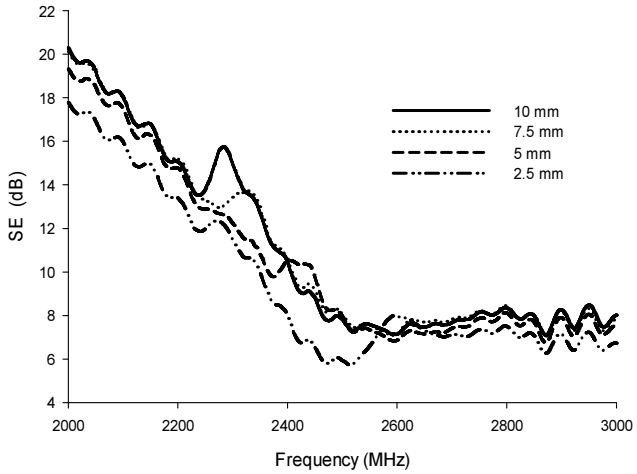


Figure 5.12 Shielding efficiency variation for Pani-carbon in 5:1 ratio

The shielding efficiency variation of the composites for various thicknesses is shown in figure 5.12 and figure 5.13. From these figures, it is clear that Shielding efficiency increases with increase in thickness of the material. For 10mm thickness, maximum shielding efficiency is obtained and for 2.5 mm, the minimum. This is true for both PG and PC composites. Also, for same ratio and

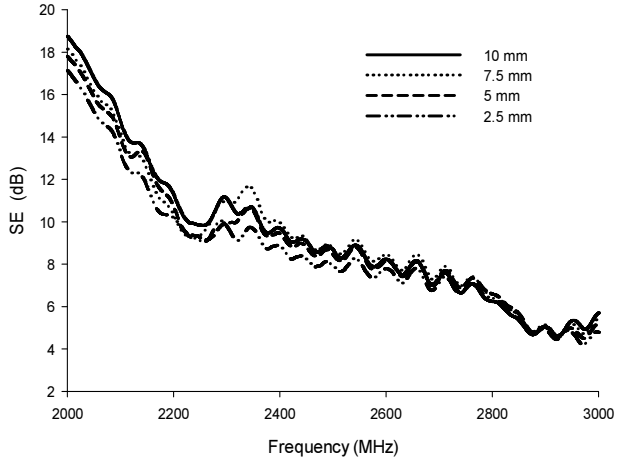


Figure 5.13 Shielding efficiency variation for Pani-graphite in 5:1 ratio

thickness, PC composite exhibits superior shielding efficiency as compared to PG composite. When interfacial loss due to space charge accumulation increases, conductivity increases. This is one of the reasons for high shielding efficiency of Pani-Carbon blend compared to Pani-Graphite. From the graph it can be inferred that SE cannot be measured beyond a thickness limit. The variation in permittivity and the structural differences may contribute to various properties exhibited by both materials. As the grain size of Carbon black is smaller, it can offer a higher packing density when used in a composite. The microwave absorption or reflection will be higher when packing density is higher. Therefore it can be inferred that the smaller grain size of Carbon black also accounts for the increased shielding efficiency of Pani-Carbon composite compared to Pani-Graphite composite.

vi) Skin Depth

The Skin depth variation observed for various combinations at 7.5 mm thickness are shown in figure 5.14 and 5.15. A higher Skin depth value indicates low absorption.

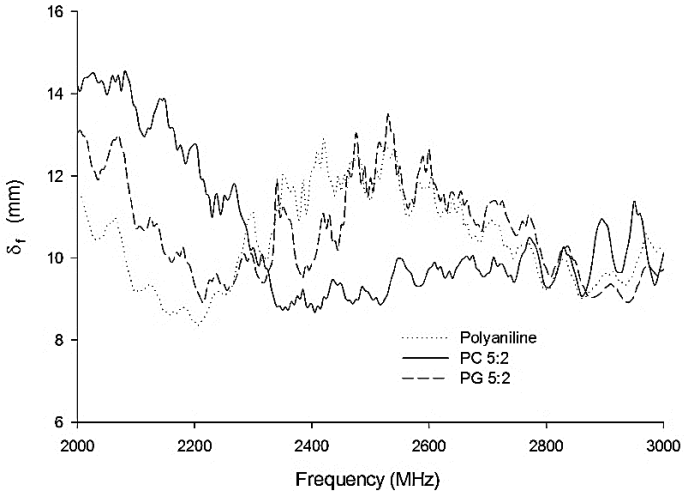


Figure 5.14 Variation of skin depth for various composites in 5:2 ratio for thickness t = 7.5 mm

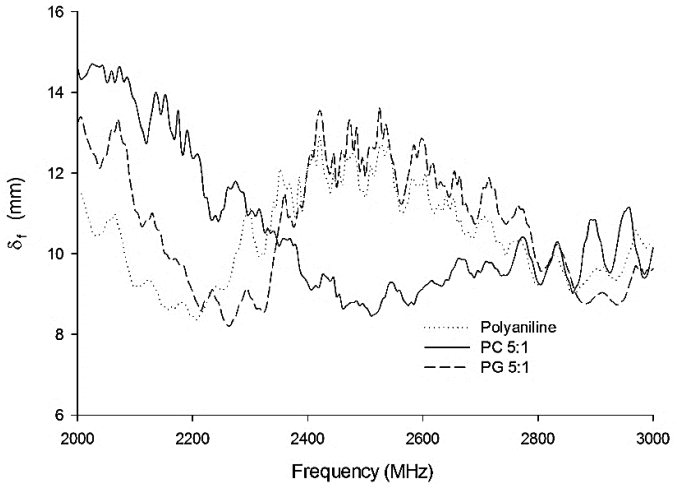


Figure 5.15 Variation of skin depth for various composites in 5:1 ratio for thickness t = 7.5 mm

It can be seen that skin depth is high for PC in ranges 2-2.3 GHz and 2.8-3 GHz, compared to PG. It means absorption is very low for PC at these frequency ranges. From figures 5.8 &5.9, microwave transmission is also very low for PC at these frequency ranges. Therefore, it can be concluded that majority of microwave power is reflected back at these frequency ranges which makes PC a better alternative for EMI shielding.

5.1.6 Conclusions

The detailed study of Polyaniline based conducting polymer blends came up with good results. Our study reveals that the materials we suggested are potential candidates for EMI shielding purposes. Among them, Polyaniline-carbon (PC) composite shows better shielding efficiency compared to Polyaniline-graphite (PG) composite. The structural differences in the constituent elements in the composite play a significant role in various properties exhibited by the material. Pani is the significant constituent which accounts for EMI shielding property of the

composite. The variation in dielectric parameters of the constituent elements as well as the interfacial losses can also be an important factor for variation in shielding efficiency of the composites. Also it has been found that microwave absorption varies with the thickness of the sample and the frequency used. In the present world, where people are connected to each other via mobile phones, study of various EMI shielding mechanisms is significant. The materials we developed can find applications in mobile phones for reducing specific absorption rate (SAR). Because of the unique EMI shielding capabilities, it can be extensively used in anechoic chamber.

5.2 Characterization of Polyaniline pellets using modified cavity perturbation method

5.2.1 Introduction

Conducting polymer field has never stayed out of focus of the science community since the accidental discovery of highly conducting Polyacetylene film by Shirakawa *et al.* in 1967 [33]. The efforts made by Alan J. Heeger, Hideki Shirakawa, and Alan G. MacDiarmid were honored by the Nobel prize in 2000 [34]. Several polymers such as PEDOT, poly pyrrole, poly eurethane, polysulfur nitride are good conductors of electricity. Some have even attained conductivities of the order of 10^3 S/cm and above, nearing to the conductivity of copper (~10^5 S/cm) [33]. Many studies have been performed on the electrical and microwave properties [35-38] of conducting polymers. S. V. Jadhav and Vijay Puri [39] performed a work based on overlay technique for finding the permittivity and microwave absorption of Polyaniline. The effect of drying conditions on dielectric behavior of Polyaniline was studied by Honey *et al* [40].

Cavity perturbation technique is considered to be one of the most accurate methods for determining dielectric properties of materials at microwave frequencies [32, 41]. In this method, the sample which is inserted through the non-radiating slot in the cavity perturbs the field inside the cavity. As a result, changes

in resonant frequency and quality factor occur. These variations in turn depend on the dielectric properties of the inserted sample. For conventional perturbation, the electric field is assumed to be uniform both inside the sample and outside the sample [42]. In the analysis, it is required that the spatial variation of electric field to be minimum throughout the sample and its proximities, with the sample covering the entire height of the cavity. For highly conducting samples, the considerable wave reflection from the cavity upon insertion of the sample demands an elongated geometry for very small volume of the sample, which in many cases may not be practical due to poor mechanical strength of the material. In order to keep the volume to a minimum, the sample length is restricted to be a fraction of the cavity height. When the sample height decreases, it results in depolarization of the sample. Hence a correction term is required in the characterization of samples having length less than the height of the cavity walls. The modified perturbation differs from conventional perturbation by allowing the use of samples with sample length less than the height of the cavity. But the correction factor for depolarization has to be included in calculation of the dielectric properties.

The validation of the results obtained using Modified cavity perturbation is tested by the experimental and theoretical studies of the Reflection coefficient of the Pani pellet. The Reflection coefficient is determined experimentally for the microstrip line fed Pani pellet at S-band frequencies using R&S ZVB-20 Network Analyzer. The same experiment is simulated in Ansoft HFSS using the results from conventional and modified perturbation methods. As it will be seen, the results from the modified perturbation provided better matching between experimental and simulation results thereby confirming the validity of the modified perturbation method.

5.2.2 Theory

The cavity perturbation works on the principle that the change in the electromagnetic field distribution inside the cavity, upon insertion of the sample is nominal. That means the electric field inside the sample nearly equals the

unperturbed field. For this, the sample size should be small and the sample length should cover the height of the cavity. The basic perturbation theory was developed on this assumption and the complex permittivity is related to the resonant frequency shift as [42],

$$\varepsilon'-1=\frac{f_0-f_s}{f_s}\frac{V_0}{V_s} \tag{3}$$

$$\varepsilon''=\frac{V_0}{4V_s}\left(\frac{1}{Q_s}-\frac{1}{Q_0}\right) \tag{4}$$

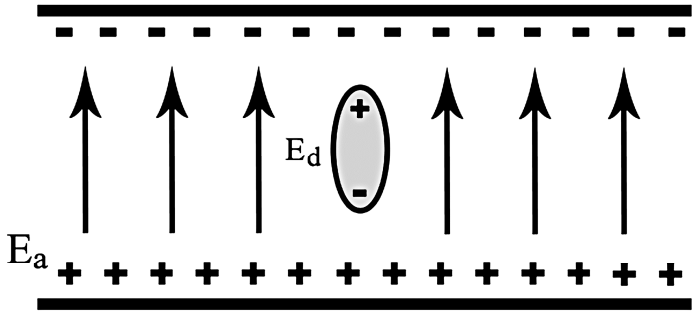


Figure 5.16. Polarization of the sample within the waveguide cavity

As shown in Fig. 5.16, E_a is the applied field and E_d is the depolarizing field. The following relations are given by M. Lin *et al.* [45]

$$\frac{f_s-f_0}{f_s}=\left\{N\left[(\varepsilon_r')^2-2\varepsilon_r'-\varepsilon_r''+1\right]+(1-\varepsilon_r')\right\}\left(\frac{2V_s}{V_c}\right) \tag{5}$$

$$\frac{1}{2}\left(\frac{1}{Q_s}-\frac{1}{Q_0}\right)=\left[\varepsilon_r''-2N\varepsilon_r''(\varepsilon_r'-1)\right]\left(\frac{2V_S}{V_C}\right) \tag{6}$$

Where N is the depolarizing factor which is a function of the dimension ratio, *m* of the sample. For a prolate ellipsoid with semi-axes h, b and c, (h>b=c), N is given as,

$$N = \left(\frac{1}{m^2 - 1}\right)\left[\frac{m}{2\sqrt{m^2 - 1}} \ln \frac{m + \sqrt{m^2 - 1}}{m - \sqrt{m^2 - 1}} - 1\right] \quad (7)$$

Where m=h/b, the dimension ratio of the sample. For small volume of the sample size, the prolate ellipsoid can be replaced with a cylinder of same volume. The effective depolarization factor when the sample is of cylindrical shape is given as

$$N_e = N \frac{\pi h}{2H} \cot \frac{\pi h}{2H} \quad (8)$$

h=length of the sample, H= height of the cavity

The Conductivity is related to loss factor as [36],

$$\sigma = \omega \varepsilon_r'' \text{ S/m} \quad (9)$$

where ω is the angular frequency

5.2.3 Materials and Methods

The key factor which helps the conducting polymers to exhibit conductivity is their π conjugated backbone structure [46]. The conjugated polymer has an alternating sequence of single and double bonds. The longer the chain length, higher will be the electrical properties and lower will be the solubility of the polymer [47]. The conductivity is due to the formation of free radical by treatment of the monomer unit with oxidizing agent at the presence of a dopant acid. The reaction is exothermic. The conductivity can be further tuned by varying factors such as dopant concentration, dopant acids, use of emulsions, treatment with halogens etc.

i) *Material preparation*

Polyaniline was prepared by following the conventional solution polymerization process [26]. During the time of the reaction, the temperature was kept low (around 10^o C). The polymerization can be visualized by the deep greenish colour change of the solution. The polymerization reaction was completed

within an hour, though the stirring continued for four hours. The acid content was removed by filtering first with water and then with acetone. Secondary doping by washing again in HCl was not performed as it decreases the pH value of the sample, which in turn tends to corrode the microstrip line over which the sample pellet is placed for reflection measurements. After filtration, the filtrate was allowed to dry in shadow for 24 hours. The Polyaniline obtained was powdered and was pelletized using a cylindrical die of 13mm diameter. Polyaniline powder cannot be heat treated before pelletizing because the application of heat will degrade its electrical and mechanical properties. The powder was simply compressed in cylindrical die to form pellet by applying pressure which can be varied. The density of the prepared pellets varied in between 1100 and 1200kg/m^3. From the palletized sample, cylindrical shaped samples were cut and smoothened for modified perturbation technique measurement. These samples have lengths varied from 5mm to 3mm and their diameter ranging from 1.2-0.8 mm. Samples were prepared with various dopant acids such as Hydrochloric acid (HCl), Perchloric acid ($HClO_4$) and Nitric acid (HNO_3).

ii) *Experimental setup for Modified Cavity Perturbation*

The experimental setup for modified perturbation is shown in figure 5.17. Coaxial to waveguide adapters are provided at both ends of the S-band waveguide which has dimensions 35x70x350 mm^3. An iris (metallic plate with a coupling hole at center) is placed in between the adapter and the waveguide to convert the waveguide to a resonant cavity. R&S ZVB-20 Network Analyzer was used for the measurements. A movable frame was attached to an S-band wave guide which facilitates the to and fro motion of the sample along the length of the cavity. The wave guide had a non-radiating slot of 3mm width along its broad side.

The Polyaniline sample was inserted to the wave guide through this slot with the aid of a capillary tube to which it is attached. Care was taken to ensure that the capillary tube just reaches up to the cavity walls and only the sample was let to perturb the field inside the cavity. The length of the capillary tube was adjusted by passing it through a rubber holder placed on top of the movable frame.

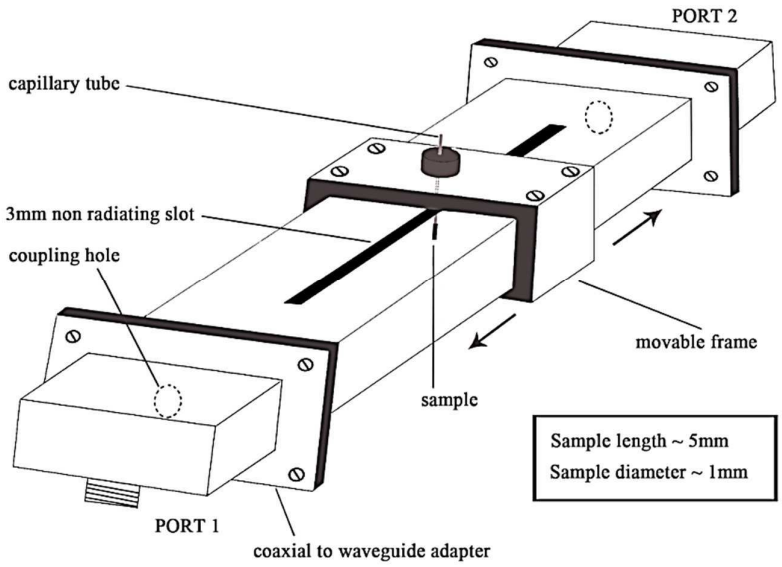


Figure 5.17. Experimental setup for modified perturbation measurement

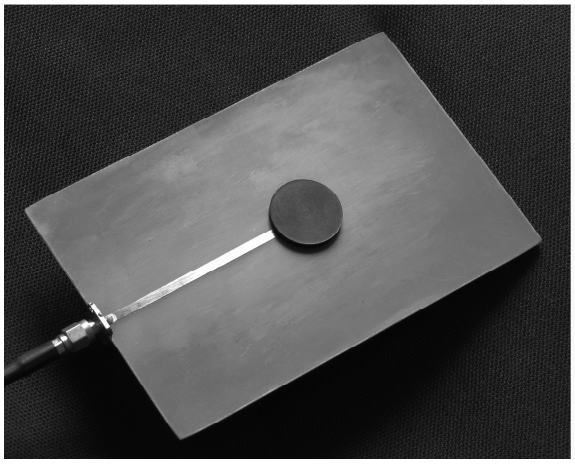
The frequency and quality factor measured with the sample holder alone are taken as the unloaded frequency and Q factor (f_0, Q_0). When the sample is attached to the sample holder and the measurement is made, the frequency and Q factor (f_s, Q_s) of the loaded cavity are obtained. When the sample is inserted to the cavity, it shifts the resonant frequency (f_s) and varies the quality factor of the cavity (Q_s). The variation in resonant frequency is a measure of the dielectric constant (ε_r') and the change in quality factor is a measure of the loss factor (ε_r") of the sample. The resonant frequency and quality factor values 'with sample' (f_s, Q_s) and 'without sample' (f_0, Q_0) are measured. These values along with the cavity volume (V_c) and the sample volume (V_s) are used in equations 3 and 4 to obtain the dielectric properties of the sample.

iii) *Experimental setup for validation of Modified Cavity Perturbation results*

The experimental setup for validation consists of a coaxial line fed microstrip transmission line over which Pani pellet is placed. The pellet was placed

such that the transmission line touches the pellet along its diameter and extends till the edge of the pellet. The Reflection coefficient measured from the experiment was compared with the results obtained from Ansoft HFSS simulations. The simulation conditions are shown in figure 5.18.

Polyaniline doped with HCl was chosen as the pellet material for validation experiment as it is regarded as a standard sample in many studies. The unsintered Pani-HCl powder was pelletized using a cylindrical die and a hydraulic press. The prepared pellet had a diameter of 25mm, thickness of 4mm and density 1161 kg/m^3. The substrate used was FR4 of area 10x15 cm^2 and the length of the feed was 9.4 cm. The simulation result with modified perturbation method was found in good agreement with the experimental results.



Simulation conditions

Simulation conditions	Conventional method	Modified perturbation
Sample diameter	25mm	25mm
Sample height	4mm	4mm
Feed line dimension	94 x 3mm^2	94 x 3mm^2
Substrate dimension	150 x 100mm^2	150 x 100mm^2
Substrate permittivity	4.40	4.40
Substrate loss tangent	0.02	0.02
Sample permittivity	8.20	3.56
Sample conductivity	0.20 S/m	3.27 S/m

Figure. 5.18. Microstrip line fed Pani-HCl sample for Reflection measurement

5.2.4 Results

The dielectric properties of different samples of Pani at S-band frequencies are studied. Dielectric properties of a material determine how an electromagnetic wave interacts with it. These properties such as dielectric constant, loss factor, conductivity etc. are very important for any material that works in microwave environment. The dielectric properties obtained using Conventional and Modified

cavity perturbation methods are compared. Sections (i)-(iii) give a comparison of Conductivity, Permittivity and Loss factor of different samples of Pani using Conventional and Modified perturbation. Section (iv) deals with the validation experiment results.

i) *Comparison of Conductivity*

For a conducting polymer, the most important electrical property is its conductivity. The conductivity variation of samples with conventional and modified cavity perturbation methods is shown in Fig. 5.19. One molar solution of acids was used for the whole experiments. Ammonium salt of peroxidisulphate was considered as free radical initiator instead of its potassium salt because of the better solubility of ammonia salt in water.

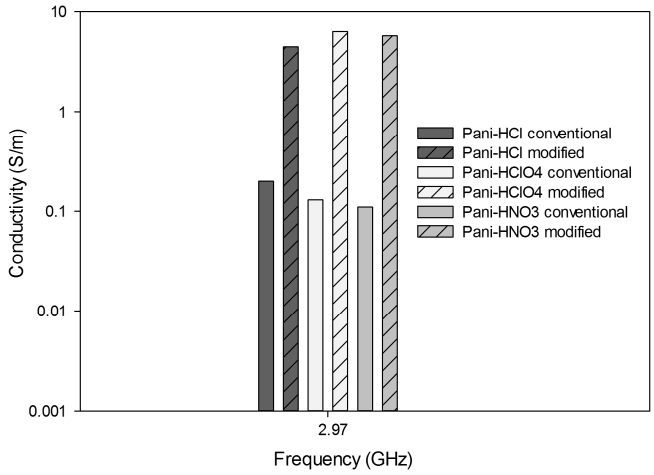


Figure 5.19. Conductivity variation of Polyaniline at 2.97 GHz for various dopant acids using conventional and modified perturbation methods.

The plain bars represent conductivities obtained using the conventional method [15]. And the striped bars represent conductivities measured using modified perturbation method. For y-axis logarithmic scaling is used. In conventional method, Pani doped with HCl is reported to have the highest conductivity. The introduction of modified cavity perturbation method gave

enhanced precision in dielectric property measurements. As it is evident from figure 5.19, the highest conductivities are obtained for Perchloric and Nitric acids which are strong oxidizers. Due to the strong oxidation property these acids can remove more electrons from polymeric π system and can result in more number of radical ions. These delocalized radical ions, also known as polarons represent charged paramagnetic defects in the lattice. They are mobile and they account for the conductivity of the polymer. In metals, the depth of penetration of the wave is limited by Skin depth. Unlike metals, the conduction in Polyaniline is due to delocalized charges [48]. Hence the ratio of bound charges to free electrons increases which in turn increases the capacitance of the polymer. When the material exhibits capacitive properties, it will let higher frequencies pass through it better. It can be seen that the conductivity of the polyaniline at microwave frequencies is significantly higher than the results obtained in other works [36, 40]. This variation can be attributed to the concept of depolarization. If we use the conventional Cavity perturbation method without considering depolarization effects, we will get erroneous complex permittivity results [45]. Although normal dielectrics can be treated using conventional cavity perturbation method, when a conducting sample of poor structural stability is used, the resonant peaks of the transmission coefficient vanishes due to high reflection from the sample. So the only way to overcome this problem is to reduce the sample size, which inevitably brings the depolarization factor in the calculation.

ii) *Comparison of Permittivity*

The permittivity variation of Pani samples with conventional and modified perturbation methods is shown in figure 5.20. In conventional method, Pani doped with HCl had the highest dielectric constant value which is around 8. But when we used modified perturbation method to find the permittivity, we got the permittivity of Pani-HCl minimum among the three. It can be seen from figure 5.20 that the samples which were doped with Perchloric acid and Nitric acid shows higher permittivity value as compared to that of Hydrochloric acid. Both these acids are

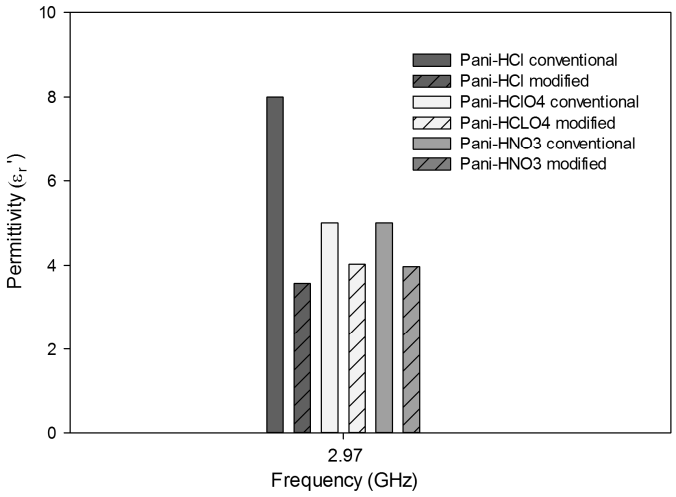


Figure 5.20. Permittivity variation of Polyaniline at 2.97 GHz for various dopant acids using conventional and modified perturbation methods.

strong oxidizing agents. They can more efficiently protonate polyaniline than HCl. Due to the increased number of bound electrons, the material will be able to store more charges. Hence the capacitance of the material increases. Or in other words, the material will exhibit a higher dielectric constant. It is also known that if the size of the dopant acid is large, then the inter chain distance of the polymer increases which in turn results in a decrease in capacitive coupling and it results in low permittivity.

iii) *Comparison of Loss factor*

Loss factor refers to the internal loss of energy caused due to the movement of dipoles. It has a non-zero value only when the real part of permittivity varies as a function of frequency [49]. The Loss factor variation of Pani with different dopant acids at 2.97 GHz using conventional and modified perturbation methods is shown in figure 5.21. From equation 7, it can be seen that the dielectric loss increases with increase in conductivity. Thus the dielectric loss is highest for

polyaniline doped with HClO4 and minimum for the samples doped with HCl. The dielectric loss is a direct indication of the presence of dipoles, which corresponds to the hopping of polaron between structural defects or sites of different energy levels [50]. At any given frequency loss factor ε_r" and conductivity σ both produce the same macroscopic effect in a dielectric material. So practically both are regarded indistinguishable [51].

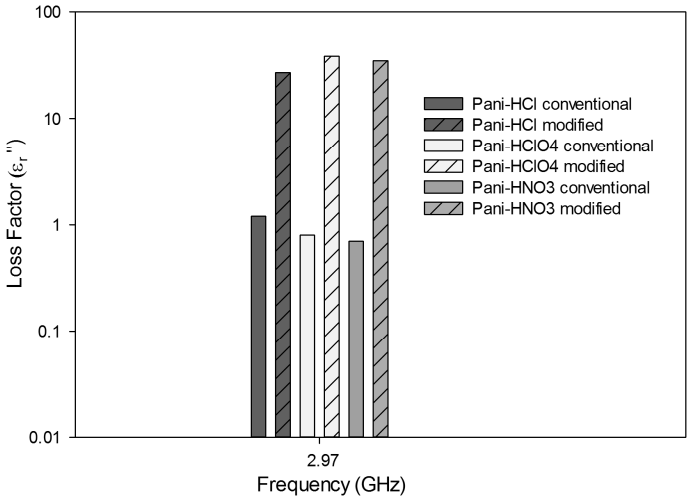


Figure 5.21. Loss factor variation of Polyaniline at 2.97 GHz for various dopant acids using conventional and modified perturbation methods.

iv) *Comparison of experimental and simulation results of validation experiment*

The variation of the experimental and simulated reflection coefficients of Polyaniline sample at microwave frequencies is shown in Fig. 5.22. It can be seen that the reflection coefficient simulated using the dielectric properties derived from modified perturbation method is in good agreement with the experimental value, whereas the reflection coefficient simulated with the conventional perturbation technique, shows a difference of around 10 dB from experimental value. Thus the

modified perturbation method gives results more close to the experimental value. Hence the accuracy of the dielectric property measurement is increased.

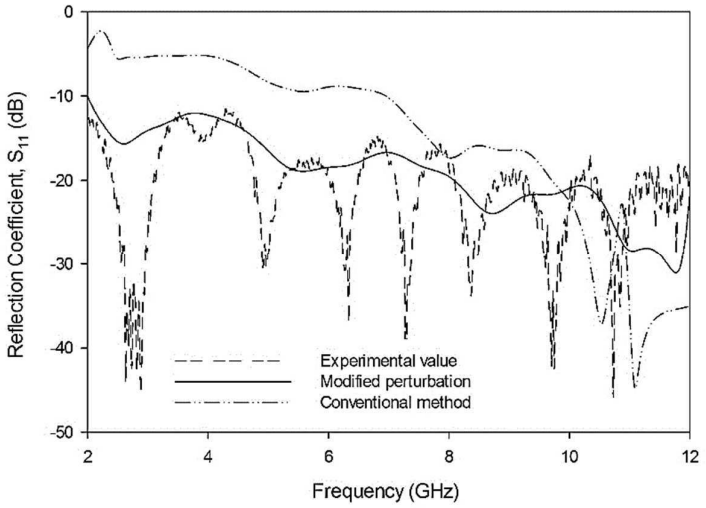


Figure 5.22. Variation of simulated and experimental Reflection coefficients of Pani-HCl sample with frequency

The sample also exhibits good impedance matching for the entire band. The variation in the values of reflection coefficient at resonant dips may be attributed to the packing density variation of the sample. In simulation, the material is considered to be homogeneous where as in a practical sample, the homogeneity of the material depends highly on packing density. Thus any variation in packing density between simulated and experimental readings may slightly alter the reflection coefficient. However, the general nature of the simulated and measured curves is the same.

5.2.5 Conclusions

The dielectric characterization of Polyaniline at Microwave frequencies has been done. One molar standard solution of various dopant acids has been used for the work. Accuracy of the measurement was enhanced with the modified

perturbation method. More than tenfold increase in conductivity is observable. The new method facilitates the use of conducting polymer samples with sample length less than the height of the cavity. Other important dielectric properties such as permittivity and loss factor were also analyzed. The validity of the results from modified cavity perturbation was confirmed by experimental and simulation studies of the Reflection coefficient of Pani-HCl pellet. The prepared conducting polymers can find important applications such as electromagnetic shielding, antistatic applications, RAMs, beam steering of antenna etc. The authors hope that the new measurement technique can bring about changes in the procedure for determining microwave behavior of conducting polymers.

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Chapter 6
Conclusions

Many of the applications at microwave frequencies demand the prior knowledge of the dielectric properties of the materials used. These properties define the interaction between microwaves and the material. The properties collectively called dielectric properties include permittivity, loss factor, conductivity, skin depth etc. In this work the aim was to develop and perform the dielectric characterization of certain materials which can find significant applications at microwave frequencies. The main highlights of the work, the possible applications as well as the scope for future work are discussed in the following section.

6.1 Highlights of the work

1. Biomaterial based films were developed for microwave phantom applications. The developed films are transparent, biocompatible, non-toxic, edible, biodegradable and eco-friendly. The developed phantoms could represent human body tissues such as collagen, bone marrow and human abdominal wall fat at the ISM band of 2.4 GHz.

2. The strength of the Arrowroot film was increased with the introduction of Chitosan into Arrowroot film during gel phase of film preparation. This resulted in better elasticity of the film.

3. Chitosan gel was prepared for microwave phantom applications. The gel could simulate human breast/brain tissue. This gel can be used *in vitro* tests related to mammography.

4. The dielectric properties of Arrowroot-Chitosan biomaterial film could be fine-tuned by varying the amount of Chitosan in the film. This makes the film diverse and provides more flexibility in choice of desired dielectric properties of phantoms.

5. Bioceramic materials Calcium hydroxyapatite, β-Tricalcium Phosphate and Biphasic Calcium Phosphate were synthesized. Their dielectric properties at S band were studied.

6. Hydroxyapatite- Chitosan composite was prepared for use as microwave phantoms. The composite was found to be a good *in vitro* substitute for Collagen, bone marrow, human abdominal wall fat and human chest fat.

7. β-Tricalcium Phosphate bioceramic was synthesized and its dielectric characterization at S-band frequencies is done. Reflection and Transmission studies along with studies on Specific Absorption Rate are done. Its dielectric properties are found to be matching with that of human chest fat.

8. Biphasic Calcium Phosphate ceramic was prepared. It was used along with Arrowroot to make films which are biocompatible. It could be used for implantation or phantom applications.

9. Polyaniline based conducting polymer blends were prepared for shielding applications. Graphite and carbon black were used as blending materials. Shielding efficiency of Pani-Carbon was found superior to that of Pani-Graphite for the same thickness of sample material. Up to 20 dB shielding was obtained at S-band.

10. A study on the dielectric properties of conducting polymers revealed that the accuracy of the conventional cavity perturbation used for measurement can be increased if the equations are modified to include depolarizing factor.

6.2 Possible Applications

The developed biomaterial films (Arrowroot, Chitosan and Arrowroot-Chitosan) could be used as microwave phantoms representing human body tissues. They can also be used as tissue implants, capsule coatings, transdermal patches and

as eco-friendly band aids. The bioceramic materials (Hydroxyapatite, β-Tricalcium Phosphate and Biphasic Calcium Phosphate) can be used as microwave phantoms. They can also be used as periodontal bone filling, treatment of osteomytitis, maxillofacial and orthognathic implantation, alveolar ridge reconstruction, ocular implants, coatings on metallic implant devices etc. The conducting polymer blends (Polyaniline: Carbon, Polyaniline: Graphite) can be used in electromagnetic shielding applications. They can also be used as coating material in anechoic chamber. The modified cavity perturbation method could be used for improving the accuracy in measurement of dielectric properties of conducting samples which have sample length lower than the height of the cavity.

6.3 Scope for future work

1. Arrowroot and Chitosan gels are to be further studied for developing phantoms for other body parts and body fluids. Body tissues like blood and skin have high dielectric constant than fat and bone marrow owing to the increased water content. Materials like gelatin, glycerine etc. can be introduced to Arrowroot and Chitosan gels for varying dielectric and mechanical properties.

2. The developed Arrowroot and Chitosan films are not electrically conducting. Studies to introduce conductivity in these films can be done. This can be achieved by the addition of conductive filler material during gel phase. The conductive films could be used in electromagnetic shielding applications.

3. The use of Arrowroot-Chitosan film as a capsule material demands its dissolution studies. A dissolution test apparatus can be used to find the dissolution rate of a drug which is embedded in a capsule coating. The conditions in stomach, colon or small intestine can be simulated by the dissolution tester.

4. Arrowroot-Chitosan film might provide an alternative to plastic carry bags which are not biodegradable. The possibility of commercial production of carry

bags based on Arrowroot/Chitosan and the moulding capability of the film are to be studied in an industrial environment.

5. Studies are to be performed on increasing the mechanical strength of porous Hydroxyapatite and β-Tricalcium Phosphate bulk bioceramic materials.

6. Study on the substitution of Polypyrrole in place for Polyaniline in Polyaniline-Carbon black/Graphite blends to achieve better shielding efficiency.

7. Preparation of highly conductive Polyaniline film-The solubility of a polymer decreases with increase in chain length. It is difficult to get good Polyaniline films without sacrificing conductivity. Studies to enhance conductivity while maintaining the film properties are to be done.

8. Optimization of modified perturbation method for the dielectric property study of materials with varying packing density.

6.4 Concluding remarks

The development and study of the microwave properties of selected biocompatible materials and conducting polymers and their ISM applications are discussed in this thesis. Biomaterial based films were developed and their microwave, mechanical and morphological properties are studied. Bioceramic materials for microwave phantom and medical implant applications were developed. Also for ensuring radiation safety, conducting polymer based blends were prepared for EMI shielding applications. The developed materials can find significant applications in industrial, scientific and medical fields.

APPENDIX I

Absorption Coefficient Measurement

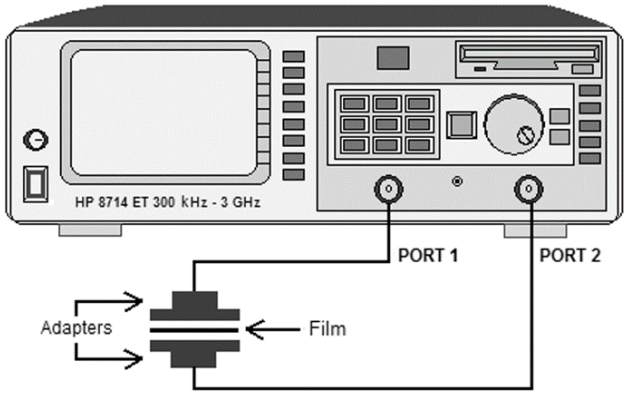

Figure a1. Experimental setup for absorption measurement

Figure a1 shows the experimental setup for measurement of absorption coefficient. The sample film is placed in between two S-band wave guide adapters which are connected to HP 8714ET Vector Network Analyzer.

When electromagnetic wave is passed through the sample material, some of the incident power is reflected back, some power is absorbed and the rest is transferred to the other end. This can be represented as,

$$P_I = P_R + P_T + P_A$$

Dividing throughout with P_I,

$$1 = R + T + A$$

Where,

A is the absorption coefficient $A = P_A/P_I$,

R, the reflection coefficient $R=P_R/P_I$ and

T, the transmission coefficient $T= P_T/P_I$

Thus Absorption coefficient can be found as

$$\boxed{A = 1 - (R + T)}$$

The Reflection coefficient and Transmission coefficient are related to the S parameters as R= $|S_{11}|^2$ and T = $|S_{21}|^2$. The absorption coefficient is a ratio between two powers. Hence there is no unit for it. Ideally, the value of absorption coefficient varies between 0 and 1.

APPENDIX II

Simulation details

The simulation details for Modified perturbation method are shown in figures a2, a3 and a4. The simulation was done in Ansoft HFSS. A transmission line was designed using the 3D modeler (Fig. a2.). A substrate of dimension 150x100mm^2 was modeled and a feed line of dimension 94x3mm^2 was added at the center. FR4 was chosen as the substrate material. Polyaniline pellet was modeled with a cylinder of diameter 25mm and height 4mm.

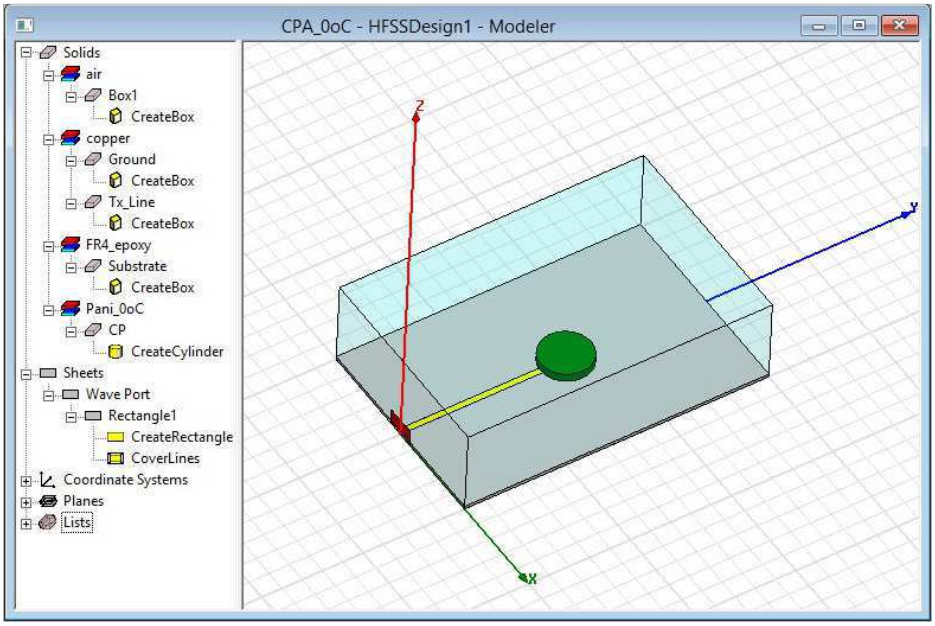

Figure a2. 3D modeler window in HFSS for
Microstrip line-fed Pani-HCl sample

A custom material (Pani_0oC) was added and material properties were assigned in the 'Add material' window (Fig. a3.). Wave port was used for signal input. A frequency sweep from 1 to 12GHz was taken and the solution frequency was set to 4GHz. The variation of S_{11} of Pani-HCl pellet with frequency was found through simulation (Fig. a4).

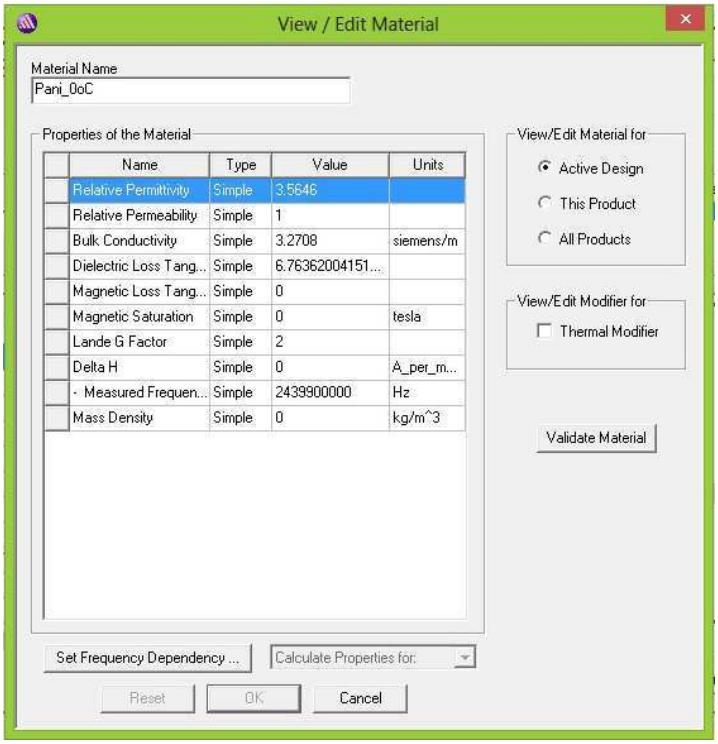

Figure a3. View/Edit material window in HFSS

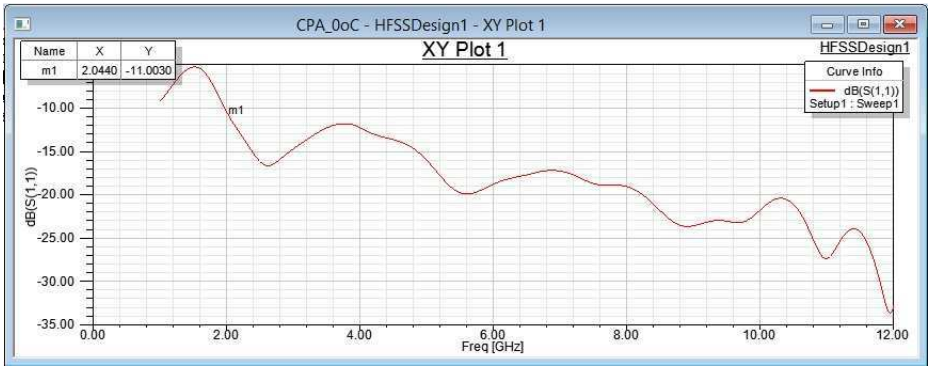

Figure a4. S_{11} vs Frequency of Pani-HCl pellet

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Publications

INTERNATIONAL JOURNALS

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8. "Dielectric Behavior of Aluminium Hydroxide Filled Oil- Extended Ethylene-Propylene-Diene-Monomer Rubber Composites in Microwave Fields", Ajalesh Nair, **Ullas G Kalappura**, Philip Kurian and Rani Joseph, *Polymer Engineering & Science*, 2012

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INTERNATIONAL AND NATIONAL CONFERENCES

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2. " Polyaniline based materials for efficient EMI shielding", K T Mathew, **Ullas G Kalappura** and Robin Augustine XXIXth *URSI General Assembly Chicago,* Illinois, USA, 9-16 August 2008

3. "An investigation of wide band microstripline fed half split cylindrical dielectric resonator antenna", C Gopakumar, **Ullas G. Kalappura**, Jaimon Yohannan and K T Mathew, *National Symposium on Antennas and Propagation*, Department of Electronics, Cochin University of Science and Technology, Kerala, India, 29-31 December, 2008

4. **"***Chitosan Biopolymer for Microwave Tomography Applications",* Robin Augustine, **Ullas G. Kalappura**, K.T. Mathew and P. T. Mathew, *Asia Pacific Microwave Conference*, Hong Kong and Macau, China, 16-20, December 2008

5. "Microwave Dielectric Properties of Strontium Barium Cerium Niobate Ferroelectric Ceramics Using Cavity Perturbation Technique", Jaimon Yohannan, **Ullas G. Kalappura**, K. Vasudevan and K.T. Mathew, *European Microwave week,* CNIT, Paris,France, 26 September - 1 October, 2010.

6. "Automated Network Analyzer measurements for Cavity Perturbation method", Anilkumar K. K., **Ullas G Kalappura**, C. K. Anandan and K. T. Mathew, *International Conference on System Dynamics and Control,* Manipal Institute of Technology, Manipal 576104, Karnataka, India, 19-22 August 2010.

7. "Preparation and characterization of Arrowroot (Starch)-Chitosan composite film", **Ullas G. Kalappura**, Paulbert Thomas, Cyriac M. Odackal and K. T. Mathew, , *National Symposium on Antennas and Propagation*, Department of Electronics, Cochin University of Science and Technology, Kerala, India, 14-16 December, 2010

Resume

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SUMMARY

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- ➢ Microwave property study of Arrowroot and Chitosan in film and gel form for microwave imaging and drug delivery applications
- ➢ Design and measurement of microstrip patch antennas
- ➢ Shielding efficiency studies of Polyaniline-Carbon and Polyaniline-Graphite blends for electromagnetic compatibility applications
- ➢ Microwave measurement techniques like Cavity perturbation, Hakki-Coleman method, Open ended coaxial probe method, Admittance cell (for Static permittivity measurement) for the characterization of materials like liquids, substrate materials, polymers, ceramics etc
- ➢ Automation of Cavity perturbation analyzer measurements
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- Softwares & Packages: Adobe Photoshop, Corel Draw, SigmaPlot, Origin, MS Office, OrCAD, Proteus, MPLAB IDE, Hi-Tech C Compiler

ELECTROMAGNETIC SIMULATION TOOLS

Ansoft HFSS, CST Microwave Studio, CST Microstripes

PRACTICAL EXPERIENCE

SYNTHESIS

- Preparation of conducting polymer Polyaniline using solution and emulsion polymerization pathways.
- Preparation of dielectric resonator antenna material by pelletizing and sintering of ceramic substances
- Preparation of Arrowroot and Chitosan thin films by gel casting method
- Preparation of bioceramic materials such as Calcium hydroxyapatite, Beta tricalcium phosphate and Biphasic Calcium phosphate using sol-gel method.

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REFERENCES

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Relationship : Teacher

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I do hereby declare that the above-furnished details are true to the best of my knowledge and belief.

Kalamassery

Ullas G Kalappura