CERAMIC REINFORCED SILICONE ELASTOMER COMPOSITES FOR FLEXIBLE MICROWAVE APPLICATIONS

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This thesis is a fulfillment of the dream; my family always cherished; coupled with the unstinted support and unfaltering love of my husband & my beloved son

DEDICATED TO MY

FAMILY, TEACHERS & FRIENDS……

DECLARATION

I hereby declare that the Ph. D thesis entitled **"CERAMIC REINFORCED SILICONE ELASTOMER COMPOSITES FOR FLEXIBLE MICROWAVE APPLICATIONS"** is an independent work carried out by me at the Materials Science and Technology Division, National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram, under the supervision of Dr.S.Ananthakumar and the co-supervision of Dr. M.T.Sebastian and it has not been submitted anywhere else for any other degree, diploma or title.

Thiruvananthapuram

April 2016

Namitha.L.K

CERTIFICATE

This is to certify that the work embodied in the thesis entitled **"CERAMIC REINFORCED SILICONE ELASTOMER COMPOSITES FOR FLEXIBLE MICROWAVE APPLICATIONS"** has been carried out by Ms. Namitha. L.K under the supervision of Dr.S.Ananthakumar and the co-supervision of Dr. M.T.Sebastian at Materials Science and Technology Division of National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram, in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy in Chemistry, under the Faculty of Science, University of Kerala, Thiruvananthapuram and the same has not been submitted elsewhere for any other degree. All the relevant corrections and modifications suggested by the audience and recommended by the doctoral committee during the pre-synopsis seminar of Ms. Namitha.L.K have been incorporated in the thesis.

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Abbreviations

IR	Infra Red
Vol. %	Volume %
RF	Radio frequency
CTE	Coefficient of linear thermal expansion
dB	Decibel
GPS	Global positioning system
IEEE	Institute of electrical and electronics engineers
GPS	Global positioning systems
PTFE	Poly tetra fluro ethylene
WiFi	Wireless fidelity
GSM	Global system for mobile communication
RFID	Radio frequency identification
TFT	Thin film transistor
LCD	Liquid crystal display
AMLCD	Active matrix liquid crystal display
OLED	Organic light emitting diode
PDMS	Poly dimethyl siloxane
IC	Integrated circuit
DCP	Di cumyl peroxide

PMC	Polymer matrix composite
CMC	Ceramic matrix composite
MMC	Metal matrix composite
ppm	Parts per million
Q-factor	Quality factor
SEM	Scanning electron microscope/microscopy
SPDR	Split post dielectric resonator
TC	Thermal conductivity
TE mode	Transverse electric mode
V_f	Volume fraction
WLAN	Wireless local area network
XRD	X-ray diffraction
PEEK	Poly ethyl ether ketone
SR	Silicone rubber
UV	Ultra violet
JCPDS	Joint committee on powder diffraction standards
EMT	Effective medium theory
EMI	Electromagnetic interference
UTM	Universal testing machine
HFSS	High frequency structure simulator

PREFACE

Flexible electronics is an important research area for the next generation consumer electronics and is becoming a part of our day today life. The assemblage of electronic components on flexible printed circuit boards is a new way to fabricate electronic systems in stationary, mobile and automotive applications. Flexible electronics are increasingly being used in a number of applications which benefit from their low profile, light weight and favorable dielectric properties. The potential applications of flexible electronics are in various societal sectors, including: healthcare; the automotive industry; human–machine interfaces; mobile communications and computing platform. The flexible circuitry would be able to do many things that rigid circuits cannot. Flexible circuits are also making portable devices more resilient. The flexible circuit connectors find applications in stretchable thermometers, biomedical devices and electronic clothing etc. The soft and rubbery future of electronic industry needs new materials to satisfy their requirements. For some applications, particularly in the biomedical field, electronic circuits are to be conformally wrapped around curved surfaces. The dielectric materials used for flexible electronic applications must have mechanical flexibility, optimum relative permittivity, low dielectric loss, temperature stability of relative permittivity, low coefficient of thermal expansion (CTE) and high thermal conductivity. It is very difficult to identify a single material which possesses all these properties simultaneously. Ceramics with high permittivity and low loss are available but their high processing temperature and brittle nature preclude their single phase use. At the same time low loss elastomer with good flexibility and ease of processing are available but their high CTE, low permittivity and low thermal conductivity limits their single phase use. However, through the composite approach one can improve or tailor the individual properties of both elastomer and ceramics. In such systems, the circuits must be not only flexible but also stretchable.

The thesis entitled **"CERAMIC REINFORCED SILICONE ELASTOMER COMPOSITES FOR FLEXIBLE MICROWAVE APPLICATIONS"** is divided into five chapters. It is the outcome of a detailed investigations carried out on the

synthesis and characterization of silicone rubber reinforced with low, medium and high permittivity ceramic for flexible substrate, electronic packaging and waveguide applications.

The first chapter of the thesis gives a general introduction about flexible electronics, dielectrics, composites and elastomer. The recent developments in flexible electronics also discussed in this chapter. This chapter also gives a brief discussion on the selection of silicone elastomer as matrix for the present study and its characteristics.

The synthesis and characterization of silicone rubber composites filled with low permittivity ceramics are described in chapter 2. The preparation and characterization techniques used for the silicone rubber-ceramic composites are also described in this chapter. The low permittivity ceramics used for the present study are Al_2O_3, AlN and fused SiO_2. The dielectric, thermal and mechanical properties of the composites was investigated as a function of filler volume fraction. The measured properties suggest that silicone rubber-Al_2O_3, silicone rubber-AlN and silicone rubber-fused SiO_2 composites are suitable candidates for microwave substrate and electronic packaging applications.

The chapter 3 deals with the synthesis and characterization of silicone rubber-medium permittivity ceramic composites. The effect of medium permittivity ceramic fillers such as $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Li_2ZnTi_3O_8$ on dielectric, thermal and mechanical properties was studied. The maximum filler loaded composites can find applications as cladding of flexible dielectric waveguide and all other compositions can be used for microwave substrate and electronic packaging applications. A microstrip patch antenna is fabricated using $SRBM_3$ substrate and is found to be a suitable candidate for flexible microwave antenna substrate application.

The synthesis and characterization of silicone rubber- high permittivity ceramic composites are discussed in chapter 4. $BaTiO_3$, $SrTiO_3$ and $Ca_{(1-x)}Nd_{(2x/3)}TiO_3$ are the high permittivity ceramics used and their effect on dielectric, thermal and mechanical properties of the composites are investigated. The composites with maximum filler

loading are suitable candidates for core of flexible dielectric waveguide applications and embedded capacitor applications. The measured properties indicate that all the other compositions of silicone rubber - $BaTiO_3$, silicone rubber - $SrTiO_3$ and silicone rubber - $Ca_{(1-x)}Nd_{(2x/3)}TiO_3$ composites can be used for cladding of flexible dielectric waveguide and also for microwave substrates applications.

The results of the present investigations are summarized in Chapter 5. This chapter also cites the scope for further extension of the work towards the frontier areas of flexible electronics and materials science.

CHAPTER 1

Flexible Electronics

This chapter gives a general introduction to flexible electronics, microwave dielectrics and the recent developments in this field. This chapter cites the importance of elastomer – ceramic composites in today's electronic world. Various scientific and technological features of elastomer – ceramic composites for electronic packaging and microwave substrate applications are also discussed.

1.1 Introduction

Wireless communication is one of the greatest contributions among technologies to the mankind. The wireless communication term was introduced in the 19th century and the technology has developed over the following years. In this technology, the information can be transmitted through the air without requiring any cable or wires or other electronic conductors, by using electromagnetic waves like IR, RF, etc. The first experimental set up to transmit and receive electromagnetic signals was done by Marconi [Smith, 1997]. This invention was a breakthrough to the communication system and following this the electromagnetic waves were used for data transfer from one end to other. Data traffic in wireless communication systems has increased dramatically over the last decades. Present day communication system including military and civil accommodate microwave frequencies. The advent of using microwaves for wireless connectivity drastically improved the information exchange capabilities. Microwaves found applications in satellite communications, radar, mobile phone and global positioning system (GPS) etc. Tomorrow's wireless communication provides: higher throughput, more flexibility, less energy. A lot of systems rely on microwaves to transmit data and it is still one of the most viable technologies for a lot of industries.

Nowadays most of the wireless systems operate at microwave frequencies because they offer wide bandwidths. Spectrum crowding and the need for higher data rates are the main reasons for the migration towards the microwave frequencies for wireless communication. In the electromagnetic spectrum, frequencies ranging from 300 MHz to 300 GHz are known as microwaves since the wave length in this region are measured in microns (wavelengths ranging from 100 cm to 1 mm) [Samuel, 2005]. Institute of Electrical and Electronics Engineers (IEEE) summarized the entire microwave spectrum in to different bands and the band designations are listed in Table 1.1 [Sisodia et al., 2001]. Each band has its own specific applications like L and S band for satellite communications, X band or Ku band for military applications etc. There are

many industrial, scientific, medical and domestic applications of microwaves. The cellular networks like GSM, also uses microwave frequencies of range 1.8 to 1.9 GHz for communication.

Table 1.1 Microwave frequency bands [Sisodia et al., 2001]

Frequency range (GHz)	Designation
0.3 – 1	UHF
1 – 2	L band
2 – 4	S band
4 – 8	C band
8 – 12	S band
12 – 18	Ku band
18 – 26	K band
26 – 40	Ka band
40 – 300	Millimeter

Some of the devices used for wireless communication in today's world are cordless telephones, mobiles, GPS units, wireless computer parts and satellite television. Current wireless phones include 3G and 4G networks, bluetooth and Wi-Fi technologies. Major applications of microwaves are summarized in figure. 1.1. The use of microwaves for wireless communication has several advantages. High operating frequencies allow microwaves to store large amounts of information. Microwaves operate at very high frequencies so they travel much faster and require only smaller infrastructure to transmit. Microwaves travel better through physical obstacles since they're so robust. Microwave communication systems have relatively low construction costs compared with other forms of data transmission, such as wire-line technologies [Pozar, 2008].
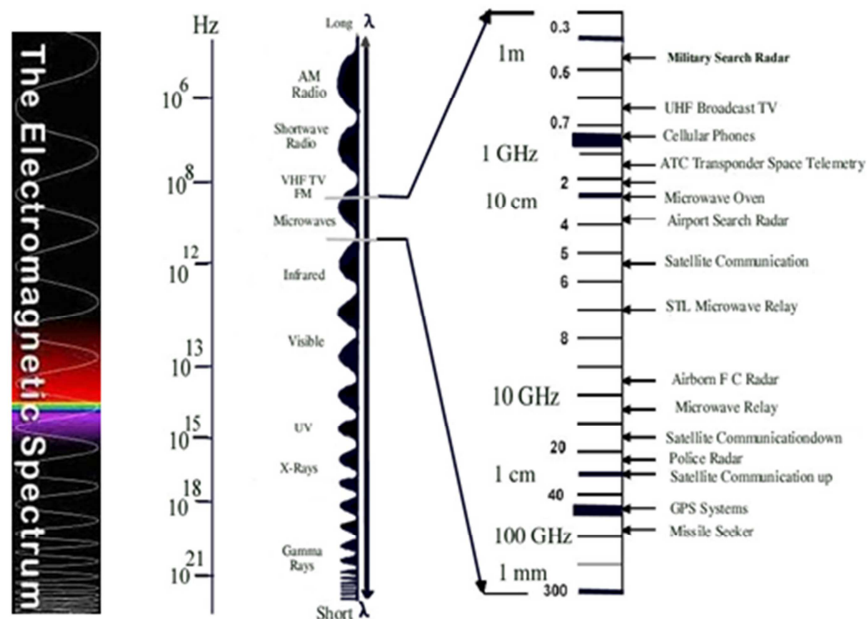
Fig.1.1 The electromagnetic spectrum and various microwave applications

[Sebastian, 2008]

The tremendous growth of RF and microwave wireless products facilitates the scientists to develop new materials, which can deliver improved performance. The cost conscious product miniaturization has been one of the long demanding goals of electronic industries. Flexible and printable electronics have received a great attention in the past decade mainly for consumer electronics such as large area flexible displays, thin film solar panels, flexible and conformal antenna arrays, RFID tags, flexible batteries, electronic circuits fabricated in clothing, biomedical device and smart prosthesis, to name a few.

1.2 What are flexible Electronics?

Flexible electronics is a technology of assembling electronic circuits and devices on flexible substrates, which are significantly of lower cost, lighter and more compact, as compared to the conventional electronic devices [Kim et al., 2008]. It is also known

as flex circuits. Flexible electronics are emerging into the main stream market. Flexible electronics products allow for many new energy conversion and biomedical applications, because the electronics are attached to substrates that are bendable, conformal, lightweight, unbreakable and often cheaper to manufacture. This would significantly expand the applications of modern electronic devices in the areas of computation, communications, displays, sensing, energy harvesting and storage. By thinning single crystal silicon wafer to 100 μm, the first flexible solar cell was made in 1960 which started the development of flexible electronics [Crabb et al., 1967; Ray, 1967]. The first TFTs were reported in 1968 by Brody and colleagues [Brody, 1984]. In 1997, polycrystalline silicon thin film transistor (TFT) made on plastic substrates was reported and received lots of attentions because of its potential applications in flexible display. Since then, flexible electronics has been developed rapidly, and commercialized products have appeared in our daily life. During the 1980s, the liquid-crystal display (LCD) industry began using amorphous silicon (a-Si:H) active matrix TFT backplanes for LCD displays [William et al., 2009]. Now, among which flexible displays occupied more than 80 % of the market of flexible electronics [Liu et al., 2013]. With the development of various flexible devices, display, logic, sensor and memory are expected to be integrated in a multi-functional system and be fabricated on a flexible substrate [Jain et al., 2005].

Flexible display screens are expected to become a common feature of consumer electronics in the next few years and have recently been touted by several top-tier manufacturers. In the mid 1980s, the active matrix liquid crystal display (AMLCD) industry started in Japan. Philips demonstrated a prototype rollable electrophoretic display and Samsung announced a 7" flexible liquid crystal panel in 2005. In 2006 Universal Display Corporation and the Palo Alto Research Center presented a prototype flexible organic light emitting diode (OLED) display with a poly-Si TFT backplane made on steel foil [William et al., 2009]. In January 2013 Samsung officially launched their flexible OLED displays, calling YOUM displays. Samsung announced the world's

first flexible OLED display-the Galaxy Round curved smartphone, in October 2013 [*www.oled-info.com/samsung-youm*]. Recently, Northwestern university scientists have developed first stretchable lithium ion battery. Now it is possible to use stretchable electronic devices anywhere, even inside the body and they can monitor brain waves to heart activity where flat, rigid batteries would fail [Xu et al., 2013]. A new generation of flexible circuit connectors could produce a new class of electronic applications, such as stretchable thermometers, biomedical devices and electronic clothing, all possessing the main advantage of being flexible and washable. Jan Vanfleteren et al. have developed a stretchable thermometer which can wrap around patient's forehead like a headband [*http://news.softpedia.com/news/Flexible-Washable-Electronics-Made-With-Elastic-Circuit-Connectors-59633.shtml*]

Two basic approaches have been employed to make flexible electronics:

- ✓ Transfer and bonding of completed circuits to a flexible substrate
- ✓ Fabrication of the circuits directly on the flexible substrate

First method has the advantage of providing high performance devices on flexible substrate whereas the second method is the most innovative and most direct method to fabricate large area electronics [William et al., 2009].

A generic large area electronic structure is composed of

- ■ Substrate – Flexible substrates that are to serve as drop in replacement for plate glass substrate. They must meet many requirements like optical property, surface roughness, thermal and thermo mechanical, chemical, electrical and magnetic properties etc.
- ■ Back plane electronics - It provides or collects power and signal from or to front plane. An ideal flexible active matrix backplane should be rugged, rollable bendable and should lend itself to low cost manufacturing.

■ Front plane - It carry the specific optoelectronic application. Front plane might also be an X-ray sensor, image sensor, a chemical sensor or an actuator etc. Front plane materials of display include

　　1. Liquid Crystal Displays for transmissive display

　　2. Electrophoretic Displays for reflective display

　　3. Organic Light-Emitting Displays for emissive displays

■ Encapsulation - Polymeric substrates needed a barrier on the substrate side (passivation) and on top (encapsulation) of the device to ensure long life. Thin film encapsulation has been researched and applied for decades. Today metalized plastic foil is widely used for packaging not only food but also for the medical and sensitive electronic components.

Mechanical flexibility in electronic devices would enable new applications which are incompatible with conventionally integrated rigid circuits. Today, the next generation of flexible electronics is driven by wearable electronic systems such as step counters, heart rate monitors, human vision interfaces and other personal fitness or social interaction or wellness tools. Elastically stretchable electronics can undergo large and reversible deformation which is suitable for biomedical applications.

Flexible and stretchable electronics is a hotbed research process. Currently, it has been estimated that there are about 1500 worldwide research units working on various aspects of flexible electronics. The most significant contribution to flexible and stretchable electronics was made by Roger's group at University of Illinois, Urbana Champaign who proposed fully integrated stretchable electronics. They made stretchable and foldable silicon integrated circuits on wavy silicon ribbons in polydimethyl siloxane (PDMS) and have demonstrated appealing devices including electronic eye sensor, smart gloves, implanted medical devices and wearable ergonomic biomedical sensors [Roger,2008]. For stretchable electronic applications, the carrier substrate is an elastic or viscoelastic polymer, e.g., silicones or polyurethanes. Cheng and co workers reported that PDMS and silicone elastomer are frequently used as

stretchable substrates, scaffolds or transfer media for flexible and stretchable devices [Cheng et al., 2012].

Fig.1.2 Images of flexible thermometer and flexible battery [Courtesy: Google images]

Along with the other enabling technologies for flexible electronics, substrates must be designed to meet the needs of this new branch of microelectronics. One of the most fundamental difficulties in flexible electronic systems is the substrate. DuPont™ Kapton® polyimide film has been used in the electronic industry for over 40 years as a dielectric substrate for flexible copper clad laminate. Substrates play a key role in the development and use of electronic devices. Ideally, such a material would present a unique balance of properties that would make it suitable for all applications. Flexible substrates have gained much importance in recent years. polytetrafluoroethylene (PTFE), polystyrene, polyethylene, liquid crystal polymer, parylene-N etc. are widely used as flexible substrates [Thompson et al., 2004].

Flexible and stretchable electronics is the future of electronics. The flexible electronics market is currently in the initial stages of development. Market analysis estimates the revenue of flexible electronics can reach 30 billion USD in 2017 and over 300 billion USD in 2028 [Agnihotri et al., 2013]. Factors responsible for the growth of

this market are flexible electronics devices' small size and low weight [*http://www.futuremarketinsights.com/reports/global-flexible-electronics-market*].
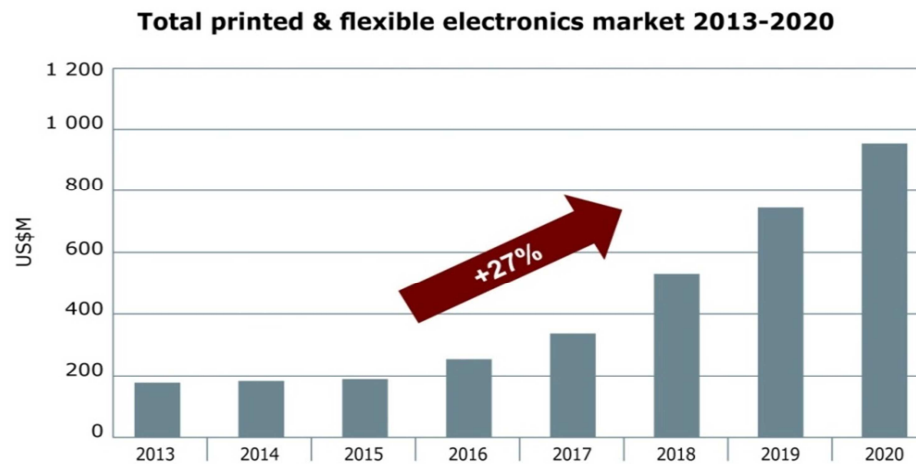
Fig.1.3 Market scenario of future flexible electronics [Courtesy: *www.marketsandmarkets.com*]

1.3 Dielectric materials

A dielectric is an insulating but polarisable material used either actively or passively in an electric field. Such materials usually find applications as either capacitors or microwave resonators. Sometimes the word dielectric and insulator are often used interchangeably. The dielectric can act as a storage device for electrical energy through the generation of electric dipoles and the ability of the material to store its electrical energy is determined by dielectric constant. When a dielectric is placed in an electric field, electric charges do not flow through the material as in a conductor, but slightly shift from their equilibrium positions causing dielectric polarization. The dielectric polarization, P is equal to the total dipole moment induced in the material by the electric field. Thus

$$P = N_i \mu_i \qquad\qquad (1.1)$$

where Ni is the number of dipoles of type i and μi is the average dipole moment [Tareev., 1979]. When a dielectric is placed between two plates of a capacitor, the capacitance of a capacitor will increase by a factor called relative permittivity (ε_r). The capacitance increases because the material effectively cancels part of the applied field and thus "storing" part of the field or charge. Fig. 1.4 shows the parallel plate capacitor without and with the presence of a dielectric material between the plates. The dielectric properties of the material are defined by a parameter called relative permittivity. The permittivity is a complex parameter, which depends upon the materials ability to be polarized under the application of an electric filed. Polarization can be defined as the charge displacement in a dielectric material to produce a net dipole moment under the presence of an electric field. Different polarization mechanisms can occur depending on frequency, temperature and composition. The real part of permittivity represents the material's ability to store electrical charge, whereas the imaginary part implies the dielectric loss factor of the material. Both relative permittivity (ε_r) and dielectric loss (tan δ) factor are dimensionless quantities [Joseph. T, 2011].

Relative permittivity (ε_r) and dielectric loss (tan δ) are the two most important dielectric properties of a material used for high frequencies [Indulkar et al., 2008].
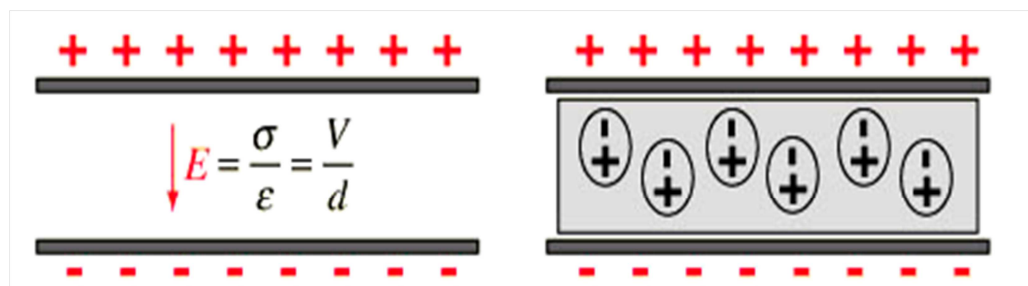
Fig.1.4 Parallel plate capacitor model with and without dielectric medium [Courtesy: *http://hyperphysics.phy-astr.gsu.edu/hbase/electric/dielec.html]*

1.3.1   Relative permittivity (ε_r)

The relative permittivity of an insulator is related to the polarizability of atoms comprising it in response to the field and thereby reduces the total electric field inside the material. The relative permittivity (ε_r) is the ratio of permittivity of a substance (ε) to the permittivity of vacuum (ε_0).

$$\varepsilon_r = \varepsilon/\varepsilon_0 \quad \text{where } \varepsilon_0 = 8.85\text{x}10^{-12}\,\text{F/m.} \tag{1.2}$$

The relative permittivity of a material under given conditions reflects the extent to which it concentrates electrostatic lines of flux. The polarization mechanisms operating in a dielectric depend on frequency, temperature and composition. Therefore the permittivity will also be a function of frequency, temperature and composition.

1.3.2 Dielectric loss (tan δ)

The dielectric loss of a material is quantitatively defined as the dissipation of electrical energy due to different physical processes such as electrical conduction, dielectric relaxation, dielectric resonance and loss from non-linear processes [Choi et al., 2006]. Relative permittivity can be expressed in complex form as

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{1.3}$$

where ε' is real part which is relative permittivity and ε'' is imaginary part which is the dielectric loss. The ratio between the dielectric loss with the relative permittivity is quantified as tan δ ie:

$$\tan \delta = \varepsilon''/\varepsilon \tag{1.4}$$

The loss will be minimum, if the relaxation time is smaller or comparable to the rate of oscillating electric field. However when the rate of electric field oscillates well faster than the relaxation time, the polarization cannot follow the oscillating frequency resulting in the energy absorption and dissipated as heat. It normally occurs in the

microwave region. The total dielectric loss is the sum of intrinsic and extrinsic losses. The losses due to different types of defects show different frequency and temperature dependence [Gurevich et al., 1986].

1.3.3 Different polarization mechanisms in dielectrics

Basically there are four different polarization mechanisms which contribute towards the relative permittivity of a dielectric viz, (1) interfacial (or space charge) polarization, (2) orientation (or dipolar) polarization, (3) ionic polarization and (4) electronic polarization; occurs in dielectrics when subjected to electromagnetic fields. The net polarization of a dielectric material is the sum of the contributions from each mechanism.

$$P = P_{electronic} + P_{ionic} + P_{molecular} + P_{interfacial} \qquad (1.5)$$

The dielectric properties are mainly contributed by the polarization mechanisms arising from the electrical response of individual molecules of a medium. Each dielectric mechanism has a characteristic 'cut off frequency'. As frequency increases, the slow mechanisms drop out in turn, leaving the faster ones to contribute to ε_r. The loss factor (tan δ) will correspondingly peak at each critical frequency.

(a) Interfacial / space chare polarization

This kind of polarization occurs due to the charge accumulation at the interfaces or grain boundaries, i.e. they contain dipoles which may become oriented to some degree in an external field and thus contribute to the polarization of the material. This type involves a longer-range ion movement and may extend to 10^3 Hz. This type gives rise to a high relative permittivity.

(b) Orientation / dipolar polarization

This type of polarization occurs only in polar substances. In thermal equilibrium, the dipoles will be randomly oriented and thus carry no net polarization. When the external field aligns these dipoles to some extent and thus induces a polarization of the material. This is called orientational polarization. The dipolar polarization contributes to the relative permittivity in the sub-infrared range of frequencies. Two mechanisms can be operative in this case; (1) In linear dielectrics dipolar polarization occurs due to the motion of ions between interstitial positions in the lattice. In such cases, the mechanism is active in the 10^3-10^6 Hz range (2) Molecules having permanent dipole moment may be rotated about an equilibrium position against an elastic restoring position. Its frequency of relaxation is very high of the order of $\sim 10^{11}$ Hz.

(c) Ionic polarization

The relative displacement of positive and negative ions in the material under the influence of an electric field is called ionic polarization. The mechanism contributes to the relative permittivity at infrared frequency range ($\sim 10^{12}$-10^{13} Hz).

(d) Electronic polarization

The electronic polarization arises from the displacement of the charge centre of electron cloud relative to the nucleus. It follows the variation of electric field almost instantaneously due to the lighter mass of electrons. It occurs at high frequencies of about 10^{16} Hz. Electronic polarization is present in all materials and, it does not contribute to conductivity or dielectric loss in most dielectrics. The relative permittivity at optical frequencies arises almost entirely from the electronic polarizability [Hench et al., 1990].

At low frequencies all the four polarizations will be active. Dipole orientation and ionic conduction interact strongly at microwave frequencies. Atomic and electronic

mechanisms are relatively weak and usually constant over the microwave region. Orientation polarization is temperature dependent whereas electronic and ionic polarizations are temperature independent and are functions of molecular structure [West, 1984].
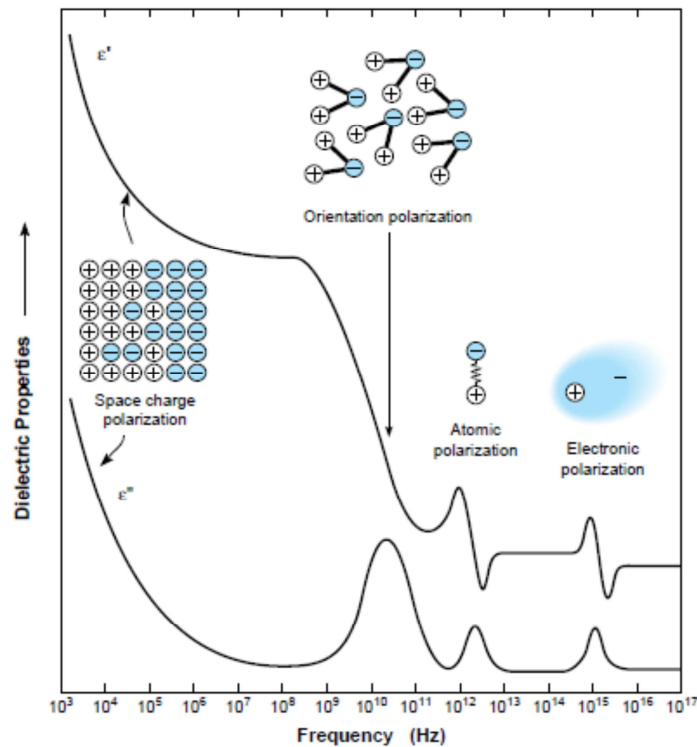
Fig.1.5 Frequency dependence of polarization and its effects on ε' and ε'' [Courtesy: *www.crops.org*]

Figure 1.5 shows the frequency dependence of polarization and its effects on ε' and ε''. At optical frequencies only electronic polarization is operative. Dipolar and ionic contributions are small at high frequencies because of the inertia of the molecules and ions. The frequency dependent response is due to many factors. For electronic and atomic polarization, the inertia of orbiting electrons must be considered. Far below the resonant frequency little contribution to ε' and ε'' is given from these mechanisms. At

the resonant frequency a peak in ε" will occur and a dispersion will occur in ε' [West, 1984; Herbert, 1985]. At microwave frequencies ionic and electronic polarization are the mechanisms responsible for dielectric properties of the material. There are two different types of mechanisms which give rise to frequency dependent behavior of dielectrics: resonance absorption and dipole relaxation.

1.4 Microwave application of dielectric materials

The development of microelectronic industry necessitated the high speed and high frequency devices at microwave frequencies. In electronic industry, dielectric materials are being used as electronic packages, substrates, wave guides, capacitors, resonators, microstrip antennas, filters etc. The accuracy of microwave electronic devices depends upon the material properties of the applied substrate.

1.4.1 Electronic packaging

Electronic packaging is a major discipline within the field of electronic engineering and includes a wide variety of technologies. It is the area dealing with assembly and connections of electronic, electromechanical and electro optical components in an electronic system. Electronic packaging refers to the packing of integrated circuit chips (ICs) and makes it a single compact unit. In electronic systems, packaging materials may serve as electrical conductors or insulators, create structure and form, provide thermal paths and protect the circuits from environmental factors, such as moisture, contamination, hostile chemicals and radiation. Electronic packaging refers to enclosures and protective features built into the product. The electronics packaging is also the bridge between integrated circuits (ICs) and electronic systems. The major functions of electronic packaging are signal distribution, power distribution, heat dissipation and protection from environment. Dielectric properties of packaging significantly influence the performance of high speed microelectronic devices. An important role of packaging materials is to ensure the electrical insulation of the silicon chip and of circuit pins [Gonon et al., 2001].

Packaging materials strongly affect the effectiveness of an electronic packaging system regarding reliability, design and cost [Michael et al., 1998]. Electrical characteristics of microelectronic devices, such as signal attenuation, propagation velocity and cross talk are influenced by the dielectric properties of the packaging materials [Garrou et al., 1998]. The electrical properties in material selection include relative permittivity, dielectric loss, frequency and temperature stability of dielectric properties, dielectric strength and electrical resistivity. Ideally, a low conductivity is needed to avoid current leakage, a low relative permittivity to minimize the capacitive coupling effects and reduce signal delay and a low loss factor to reduce electrical loss [Sun et al., 2005]. The relative permittivity must be as low as possible to reduce propagation delay and must have low loss factor to reduce electrical loss for electronic packaging applications. The actual applications of materials in electronic packaging include interconnections, printed circuit boards, substrates, encapsulations, interlayer dielectrics, die attach, electrical contacts, connectors, thermal interface materials, heat sinks, solders, brazes, lids, housings and so on [Chung et al.,1995].

1.4.2 Substrate application

A substrate is a sheet on which one or more chips are attached and interconnections are drawn, also called a chip carrier. A substrate can be formed either by a single layer or by many layers. The dielectric substrate selection plays very vital role in size reduction and impedance matching. Microwave substrates provide mechanical support and a guided medium for signal transmission. The dielectric properties of the substrate material determine the performance of the microwave module. One important parameter required for substrate application is relative permittivity. The signal propagation delay through the substrate is given by the equation

$$t_d = \frac{l\sqrt{\varepsilon_r}}{c} \qquad\qquad (1.6)$$

where l is the line length, ε_r is the relative permittivity of the substrate and c is the speed of light. Hence the relative permittivity must be as low as possible to reduce propagation delay [Pecht et al., 1999]. The suitable relative permittivity values for a substrate material are in the range of 3-15. The signal cross talk between the conductors can be reduced by decreasing the value of ε_r. The materials used for substrate application should have low dielectric loss to minimize the signal attenuation and power loss. The low loss ceramic produce less heat and thereby they protect the microelectronic devices. The substrate material should have low temperature coefficient of resonant frequency (-10 < τ_f < +10 ppm/^{o}C) to ensure the stability performance while operation. The ceramic substrates for microwave applications should have low CTE. High thermal conductivity for the substrate is also desirable for the proper dissipation of excess heat generated in the module [Sebastian, 2008]. Dielectric substrates found application in the fabrication of transmission line media including microstrip, strip line, coax and even waveguide. This is also used for printed circuit board, microstrip patch antenna, monopole antenna etc. Extensive researches have been invested in developing high performance substrates with excellent microwave properties. Dielectric substrate materials are classified into hard substrates and soft substrates.

1.4.2.1 Hard substrates

Hard substrates are ceramics such as alumina, aluminum nitride and beryllium oxide which can withstand extreme heat during wire bonding [Chung, 1995]. In recent years with the development of electronic industry, the market for hard substrate has also been increased. As hard substrate, ceramics are preferred due to their dimension stability and inertness at typical temperatures. Al_2O_3, BeO, AlN and Borosilicate are some of the commonly used hard substrates. Among the various commercially available substrate materials, alumina has become the most widely used one due to its high mechanical strength and low dielectric losses. Last two decades have witnessed a tremendous research on the development of low permittivity materials as microwave

substrates. The search for new materials with good thermal and dielectric properties is still in progress.

1.4.2.2 Soft substrates

Generally, the polymers or polymer based composites are used as soft substrates instead of hard substrates. Soft substrates are used in applications where packaged parts are soldered on the board [Chung, 1995]. Polymers like polytetrafluroethylene (PTFE), polyethylene, polystyrene, poly-ether-ether-ketone and epoxy shows good dielectric properties [Bur, 1985]. But the high thermal expansion and low thermal conductivity limits their application as substrate in electronic modules. Polymers reinforced with hard ceramic particles is the another category of substrate materials. Through this composite approach the thermal properties of polymers can be tuned. A detailed discussion of the composites and their properties are done in the later section of this chapter.
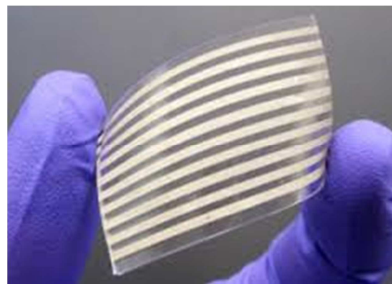
Fig.1.6 Flexible soft substrate [Courtesy*: www.polytechnichub.com*]

1.4.2.2.1 Microstrip patch antenna

There has been a growing interest in the development of antennas using flexible substrates. This gives the advantage of having conformal antennas being placed and attached to uneven shaped structures and surfaces [Babar et al., 2012]. A microstrip antenna is a type of radio antenna with a low profile, which can be mounted on a flat

surface. It consists of a flat rectangular "patch" of metal, mounted over a larger sheet of metal called a ground plane.

The advantages of microstrip antennas over other antenna are low profile, easy to fabricate, conformal structures, easy to form a large array, spaced at half-wavelength or less and light weight. It also has some disadvantages like limited bandwidth, low power handling and efficiency may be lower than with other antennas. Efficiency is limited by conductor and dielectric losses and by surface-wave loss.

1.4.3 Waveguide applications

A waveguide is an electromagnetic feed line used in microwave communications, broadcasting and radar installations. Within many electronic circles, waveguides are most commonly used for microwave RF signals and it will only carry or propagate signals above a certain frequency, known as the cut-off frequency. Below this the waveguide is not able to carry the signals. Waveguides, as the name indicates are a guide for electromagnetic waves and this way they enable them to feed power from one location to another [*ww.radio-electronics.com/info/antennas/waveguide/waveguide-basics-tutorial.php*]. A waveguide consists of a rectangular or cylindrical metal tube or pipe. An ideal dielectric waveguide would have a small core consisting of a flexible, low loss material with large relative permittivity. The cladding would also be flexible and low in loss and its relative permittivity would be much smaller than that of the core, so that the fields of the guided mode would decrease rapidly with distance in the cladding [Bruno et al., 1990]. The electromagnetic field propagates lengthwise. Waveguides are most often used with horn antennas and dish antennas.

Types of RF waveguide

Different types of RF waveguide are available and they are [*ww.radio-electronics.com/info/antennas/waveguide/waveguide-basics-tutorial.php*]

(a) **Rectangular waveguide:** This is the most commonly used form of waveguide and has a rectangular cross section.

(b) **Circular waveguide**: This is less common than rectangular waveguide. They have many similarities in their basic approach, although signals often use a different mode of propagation.

(c) **Circuit board stripline**: This form of waveguide is used on printed circuit boards as a transmission line for microwave signals. It typically consists of a line of a given thickness above an earth plane. Its thickness defines the impedance.

(d) **Flexible waveguides**. These are most widely seen in the rectangular format. Flexible waveguide is often used to connect to antennas, etc that may not be fixed or may be moveable.

Fig.1.7 Images of flexible waveguide [courtesy: *www.atmmicrowave.com, www.ainfoinc.com*]

1.5 Composites

Last decade has seen a significant growth in activity concerned with the technology of composite materials. A composite material is a material made from two or more constituent materials with significantly different physical or chemical properties. The constituents do not dissolve or merge and retain their identity [Button et al., 1989]. Composite materials can be tailored by appropriately choosing their components, proportions, distributions, morphologies, degree of crystallinity,

crystallographic textures as well as the structure and composition of the interface between components for various applications. In modern usage, composites are made by dispersing filler such as particles, flakes or fibres in a matrix of polymer, metal or glass. By combining two or more constituents, it is possible to create materials with unique properties that cannot be achieved in another way. The connectivity of the phases in the composite also plays a crucial role in determining the properties [Dias et al., 1996]. The composite materials find applications in various fields such as electronics, aerospace, automobile, construction, biomedical and in many other industries.

The composite materials consist of basically three phases' matrix, reinforcement and interface [Chung, 2010].

(a) Matrix phase

The primary phase, having a continuous character, is called matrix. Matrix is usually more ductile and less hard phase. It holds the dispersed phase and shares a load with it. It is made up of metals, ceramics or polymers depending on the type of composite.

(b) Reinforcing (dispersed) phase

The second phase is embedded in the matrix in a discontinuous form. This secondary phase is called dispersed phase. Dispersed phase is usually stronger than the matrix, therefore it is sometimes called reinforcing phase. Reinforcing phase can be particles of any shape and size including nanoparticles as well.

(c) Interface

Interfaces are present in a composite material and they tend to govern the properties of a composite material. Interfaces play a profound role in the behaviour of composite materials. The interface between the reinforcement and the matrix needs to

the strong enough in order to allow load transfer to the reinforcement [Chung, 2000]. The properties of the composites are the combined behavior of matrix, reinforcing element and filler/matrix interface. In simple system, bonding at interface is due to adhesion between filler and matrix [Guggilla et al., 2000]. Understanding the science of composite interfaces is crucial to the development and improvement of composite materials.

1.6 Composite properties

Generally the physical and chemical properties of composites are classified into three [Anthony Kelly, 1994]. They are,

(a) Sum properties

Sum properties are those properties in which the property coefficient of the composite depends on the corresponding coefficients of its constituents. Usually the property coefficient will be in between those of the constituent phases. The stiffness and relative permittivity are the best examples for sum properties.

(b) Combination properties

Combination properties of a composite lie between those of its constituent phases, but combination properties involve two or more coefficients which may average in a different way. For example acoustic velocity depends on modulus of elasticity and density of the material and the mixing rules for these two properties are often different. Hence the acoustic velocity of a composite can be smaller than those of its constituent phases.

(c) Product properties

Product properties are more complex. The different properties of the constituents combine to yield a new property, a product property. The combination of different properties of two or more constituents sometimes yields surprisingly large

product properties. Sometimes product properties are found in composites that were entirely absent in the phases that make up the composite. For example in a magneto-electric composite, the piezoelectric effect of on phase acts on the magnetostrictive effect of the second phase to produce a composite magneto-electric effect which is a product property. In such cases, the interaction between the constituent phases produces unexpected properties of the composite. Sometimes, product properties are found in composites that are entirely absent in the phases making up the composite [Newnham, 1986].

1.7 Classification of composites

There are two classification systems of composite materials. One of them is based on the matrix material (metal, ceramic and polymer) and the second is based on reinforcing material structure.

1.7.1 Classification I

On the basis of matrix phase, composites can be classified into metal matrix composites (MMCs), ceramic matrix composites (CMCs) and polymer matrix composites (PMCs).

(a) Metal Matrix Composites (MMC)

Metal Matrix Composites are composed of a metallic matrix (aluminum, magnesium, iron, cobalt, copper) and a dispersed ceramic (oxides, carbides) or metallic (lead, tungsten, molybdenum) phase. MMCs are mainly used in the automotive industry. These materials use a metal as the matrix and reinforce it with fibers. High strength, fracture toughness and stiffness are offered by metal matrices. Most metals and alloys make good matrices.

(b) Ceramic Matrix Composites (CMC)

Ceramic Matrix Composites are composed of ceramic as the matrix and reinforce it with short fibers or whiskers such as those made from silicon carbide and boron nitride. Used in very high temperature environments.

(c) Polymer matrix composites (PMC)

Polymer Matrix Composites are composed of a matrix from thermoset or thermoplastic and embedded glass, carbon, steel or Kevlar fibers (dispersed phase). Most commercially produced composites use polymer as matrix material. PMCs are very popular due to their low cost and simple fabrication methods. The factors affecting the properties of PMCs are interfacial adhesion, shape and orientation of dispersed phase inclusions, properties of the matrix etc. The main advantages of polymers as matrix are low cost, easy processability, good chemical resistance and low specific gravity. The main disadvantages of PMCs are low thermal resistance and high coefficient of thermal expansion. PMCs are used for manufacturing electrical, biomedical, aerospace structures, marine, automotive, sports goods etc [Guggilla et al., 2000].

1.7.2 Classification II

The classifications according to types of reinforcing material structure are particulate composites (composed of particles), fibrous composites (composed of fibers) and laminate composites (composed of laminates) [Guggilla et al., 2000].

(a) Particulate Composites

Particulate Composites consist of a matrix reinforced by a dispersed phase in form of particles. These are the cheapest and most widely used.

(1) Composites with random orientation of particles

(2) Composites with preferred orientation of particles - Dispersed phase of these materials consists of two-dimensional flat platelets (flakes), laid parallel to each other.

(b) Fibrous Composites

In many applications, like in aircraft parts, there is a need for high strength per unit weight (specific strength). This can be achieved by composites consisting of a low-density (and soft) matrix reinforced with stiff fibers. The strength depends on the fiber length and its orientation with respect to the stress direction. The efficiency of load transfer between matrix and fiber depends on the interfacial bond. They are of two types

(1) *Short-fiber reinforced composites* - Short-fiber reinforced composites consist of a matrix reinforced by a dispersed phase in form of discontinuous fibers (length < 100*diameter).

(2) *Long-fiber reinforced composites* - Long-fiber reinforced composites consist of a matrix reinforced by a dispersed phase in form of continuous fibers.

(c) Laminate Composites

Laminates are composite material where different layers of materials give them the specific character of a composite material having a specific function to perform. Sheets (panels) with different orientation of high strength directions are stacked and glued together, producing a material with more isotropic strength in the plane, it is called multilayer (angle-ply) composite. Examples are plywood and modern skis.
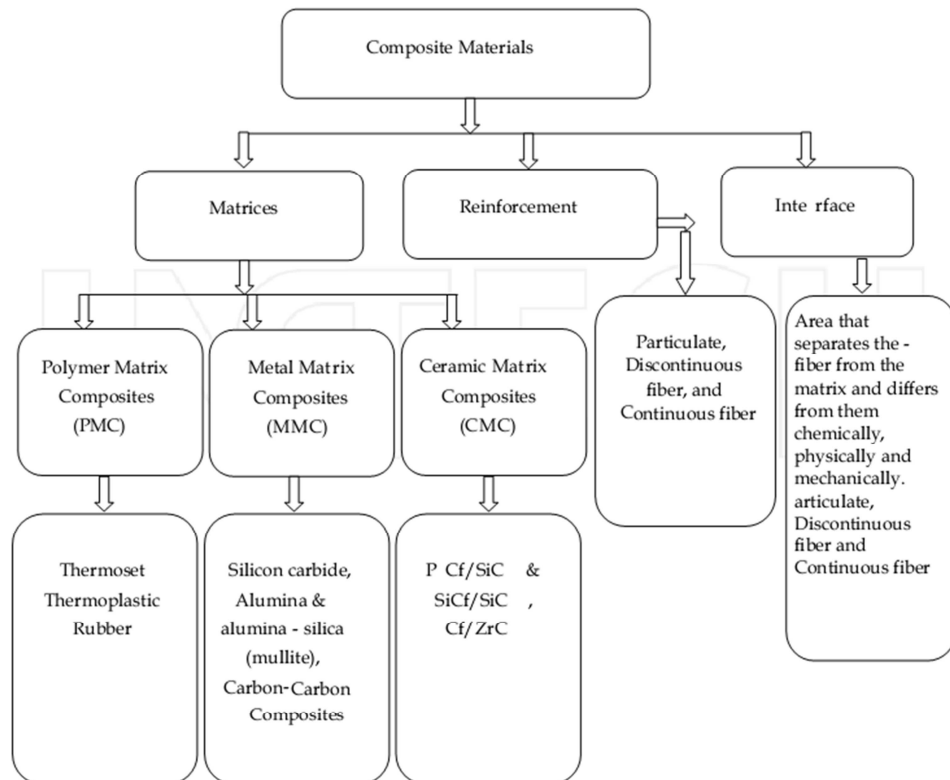
Fig.1.8 Classification of composites [Guggilla et al., 2000]

1.8 Connectivity

Connectivity is a key feature in property development in multiphase solids since physical properties can change by many orders of magnitude depending on the manner in which connections are made. The concept of connectivity was first established by Newnham et al. [Newnham et al., 1978]. The spatial arrangement of components in a multiphase composite is of considerable importance since it controls the mechanical, electrical and thermal fluxes between the phases. Each phase in a composite may be self-connected in zero, one, two, or three dimensions. It is natural to confine attention to three perpendicular axes because all property tensors are referred to such systems. In a two-phase composite system, there can be ten different connectivities, which are 0-0,

0-1, 0-2, 0-3, 1-1, 1-2, 1-3, 2-2, 2-3 and 3-3. The first digit represents the connectivity of inclusions and the second digit represents the host. Generally, the host is a polymer in the case of polymer composite. Based on this concept, the 0-3 connectivity composite is a system in which 0D particulate fillers are randomly distributed in a 3D host polymer matrix ie., the ceramic particles do not contact to each other but the polymer phase is self-connected in all directions in the 0-3 connectivity [Tressler et al.,1999]. The ten different connectivities are illustrated in figure 1.10, using a cube as the basic building block. The most commonly studied composites are 0-3 and 1-3 configurations. 0-3 configuration can be easily prepared at relatively low cost [Dias et al., 1996].

Several methods are available to make ceramic composites with different connectivity such as, extrusion, tape casting and replamine process etc. The preparation of 0-3 ceramic/polymer composites involves proper selection of the ceramic and the polymer. The polymer, determines the way in which the materials can be mixed. Extrusion processing can be used to prepare a 1-3 composite. A 2-2 pattern can be produced by tape casting and stacking alternate layers of two different materials. In 2-3 patterns one phase is two dimensionally connected while the second phase is connected three dimensionally with each other. This pattern can be considered as a modified form of the 2-2 composite. The 3-3 pattern is the most complicated and interesting one. Experimentally 3-3 connectivity composites can be produced by replamine form process [Dias et al., 1996].
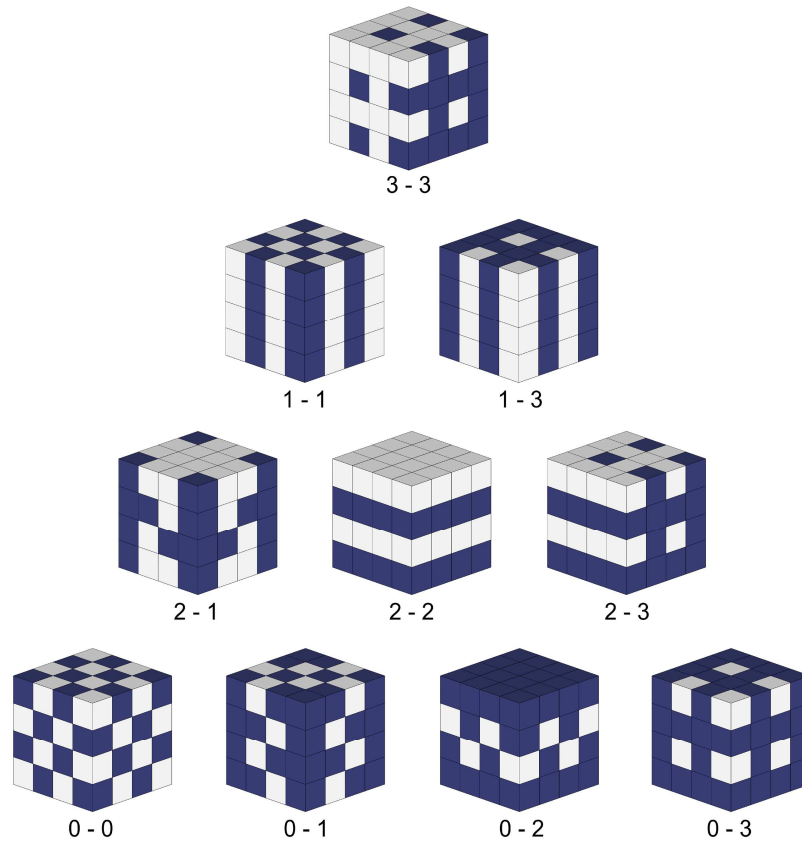
Fig.1.9 Connectivity patterns in a di-phasic composites systems [Safari et al., 2006].

1.9 Polymer - ceramic composites

The growing demand for low cost, large area, flexible and lightweight devices will pave way for material scientists to develop new material systems with improved properties. Polymers play a vital role in the field of electronic industry; such as substrate and electronic packaging applications. Most of the polymers have optimum dielectric properties at microwave frequencies, which is usually required for substrate as well as packaging applications. Polymers also have the advantages of low temperature processability and flexibility. However, the low thermal conductivity and high coefficient of thermal expansion of polymers limits their single phase use in the

electronic applications. Several ceramics have the desired dielectric properties but the high processing temperature and brittle nature greatly limits their practical use. The modern electronic devices and systems require diverse and specific functional properties in materials; which cannot be met in single-phase materials [Batra et al.,2008]. The individual properties of both polymers and ceramics can be tailored through composite approach where they provide useful properties for microwave substrate and electronic packaging applications. Recently, there has been a growing interest in polymer-ceramic composites for microwave applications because they enable inexpensive industrial level realization of microwave devices and packages with advanced electric and mechanical properties. In recent decades, a large number of polymer-ceramic electronic composites have been introduced for applications in the field of telecommunication, medical and microelectronics [Taya, 2005]. There are number thermoplastic polymers like; polyethylene, polystyrene, polypropylene, poly-ether-ether-ketone (PEEK) etc used for making composites with ceramic fillers [Sebastian et al., 2010]. The processing, design aspects and requirements for polymer-ceramic composites for microwave applications are discussed detail in the review "Polymer–Ceramic Composites of 0–3 Connectivity for Circuits in Electronics: A Review" authored by Sebastian et al [Sebastian et al., 2010].

1.9.1 Material requirements for microelectronic applications

Polymer-ceramic composites used in microelectronic packaging have to simultaneously fulfill diverse requirements such as low dielectric loss (tan δ), moderate relative permittivity (ε_r), low temperature coefficient of relative permittivity (τ_ε), low moisture absorption, low coefficient of thermal expansion, high thermal conductivity, high dimensional stability and mechanical stiffness.

(a) Dielectric properties

In polymer-ceramic composites the dielectric properties are controlled by the amount of filler, filler particle size and distribution of the filler, shape and orientation of

the filler and finally dispersion of the filler in the polymer matrix. The dielectric properties include relative permittivity, dielectric loss, frequency and temperature stability of dielectric properties, dielectric strength etc. The relative permittivity of the material should be as low as possible for electronic packaging and substrate applications; since the speed of the signal passing through the dielectric medium is inversely proportional to the square root of relative permittivity [Sebastian, 2008]. A high relative permittivity material is needed for the core of flexible dielectric waveguide. The dielectric loss of the material should be low to avoid electrical losses, especially at very high frequencies [Sun et al., 2005]. The relative permittivity must be stable within the operational temperature range to control the temperature-induced drift in circuit operating characteristics [Walpita et al., 1998]. High electrical resistivity and high dielectric strength is also required for microelectronic applications [Pecht et al., 1998].

(b) Thermal properties

Thermal properties of substrates and packaging materials are very important since it affect the operation of the electronic devices. Thermal properties that are significant in enduring life cycle profiles include thermal conductivity/diffusivity, specific heat capacity and coefficient of thermal expansion (CTE). High thermal conductivity is required to dissipate the heat generated during the operation of the device and low or matching coefficients of thermal expansion to that of silicon (~ 4 ppm/°C) chips to reduce thermal failure. The dielectric properties should not exhibit large variations with operating temperature.

(c) Mechanical properties

Mechanical flexibility is an important property for a substrate material in order to sustain the flexural loading during service. Mechanically flexible systems would improve durability and allow enhanced integration. The mechanical properties affect the material's ability to sustain loads due to vibrations, shock and thermo mechanical

stresses during manufacture, assembly, storage and operation. The mechanical properties of the composites are strongly influenced by the size and shape of the filler, matrix properties as well as the interfacial adhesion between the filler and matrix.

(d) Chemical properties

Chemical properties of the substrate materials are important because of the need to survive manufacturing, storage, handling and operating environments. The chemical properties of significance are water absorption, flammability and corrosion resistance. The dielectric properties of substrates materials are strongly influenced by water absorption, swelling and other dimensional instabilities. The corrosion leads to the formation of more stable compounds and can degrade the physical properties of the materials [Chung, 1995].

Polymer - ceramic composites can combine the advantageous properties of both polymer and ceramics which can satisfy diverse requirements of present - day electronic industry. Modern electronic industry requires systems that can be fitted into non-planar forms which can be folded and unfolded for packaging or storage. The conventional ceramic polymer composites are flexible to a limited extent but they can't be bend or stretch. In this context, the elastomer – ceramic composites can be used for stretchable and bendable electronic applications.

Flexible, bendable and stretchable dielectrics which can cover even curved surfaces are important for applications in communication, automotive and medical electronics. Recently electronic systems that can cover large areas on flexible substrates have received increasing attention because they enable wide range of applications such as flexible displays, electronic textiles, sensory skins and active antennas etc [Sun et al.,2007]. For many applications, particularly in the biomedical field and body-worn antenna, electronic circuits are to be conformally wrapped around curved surfaces. The flexible substrates have many potential applications from neural prosthetics in the medical field to microwave devices in electronics which provides the advantage of

three-dimensional designs of conformal structures [Kramer et al., 2011]. In such systems, the circuits must be not only flexible but also stretchable [Seol et al., 2008]. Stretchability means that the circuits should have the capacity to absorb large levels of strain without degradation in their electronic properties. Elastomer – ceramic composites combine the ceramic hardness and stiffness with the rubbery entropy-elasticity of elastomer [Namitha et al., 2013]. Hence the device engineers are looking for to alternative substrates such as butyl or silicone elastomer which can stretch by tens of hundreds of percent without plastic deformation or breakage.

1.9.2 Elastomer

Elastomer, any rubbery material composed of long chainlike molecules, or polymers, that are capable of recovering their original shape after being stretched to great extents; hence the name elastomer. It is often used interchangeably with the term rubber, although the latter refers to vulcanizates. In the past, "rubber" was used to describe materials that occurred naturally in nature; and "elastomer" was used for materials that were produced synthetically. The term *elastomer*, which is derived from the word elastic polymer. An elastomer is having very weak inter-molecular forces, generally having low Young's modulus and high failure strain compared with other materials [*https://en.wikipedia.org/wiki/Elastomer*]. Elastomers are amorphous polymers existing above their glass transition temperature, so that considerable segmental motion is possible. The mobility of chains is restricted by the introduction of a few crosslinks into the structure. The chemical process for converting the polymer into more durable materials by forming cross-links between individual polymer chains is called vulcanization. Vulcanized materials have superior mechanical properties [*http://www.adhesiveandglue.com/elastomer.html*]. In the absence of applied stress, molecules of elastomers usually assume coiled shapes. Consequently, elastomers exhibit high extensibility (up to 1000%) from which they recover rapidly on the removal of the imposed stress [Ebewele., 2000].

Properties of elastomer materials:

(1) They cannot melt, before melting they pass into a gaseous state

(2) Swell in the presence of certain solvents

(3) They are generally insoluble

(4) Flexible and elastic

(5) Lower creep resistance than the thermoplastic materials

Examples of elastomer materials are natural rubber, silicone rubber, butyl rubber, synthetic polyisoprene, polybutadiene, chloroprene rubber, ethylene propylene rubber and polyurethanes etc.

1.9.2.1 Silicone Rubber (SR)

Among the available elastomers, silicone rubber was chosen as rubber matrix for the present investigation. Figure 1.11 shows the comparison of properties of various rubbers using natural rubber as the reference. From the figure it is clear that silicone rubber satisfy almost all the properties satisfactorily. Silicone rubber is a well-known dielectric elastomer, widely used in electronics and microfluidics due to its elasticity, biocompatibility, optical transparency, permeability, UV transmission and availability [Yang et al., 2012]. Silicones play a key role in all fields including the automotive, cosmetics, electronic industry, chemicals, foods, textiles and the construction industry [Yang et al., 2012; *http://www. Silicone.jp/*]. The first silicone elastomers were developed in the search for better insulating materials for electric motors and generators. Chemists at Corning Glass and General Electric were synthesized the first silicone polymers, heat-resistant materials for use as resinous binders [*en.wikipedia.org/wiki/Silicone_rubber*]. Based on the viscosity silicone rubber are classified in to solid silicone rubber and liquid silicone rubber. In the present investigation we used methyl end blocked solid silicone gum. This is because of the ease of processing compared to liquid silicone rubber. Solid silicone rubber is peroxide

cured system where as liquid silicone rubber is addition cured system (platinum catalyzed).
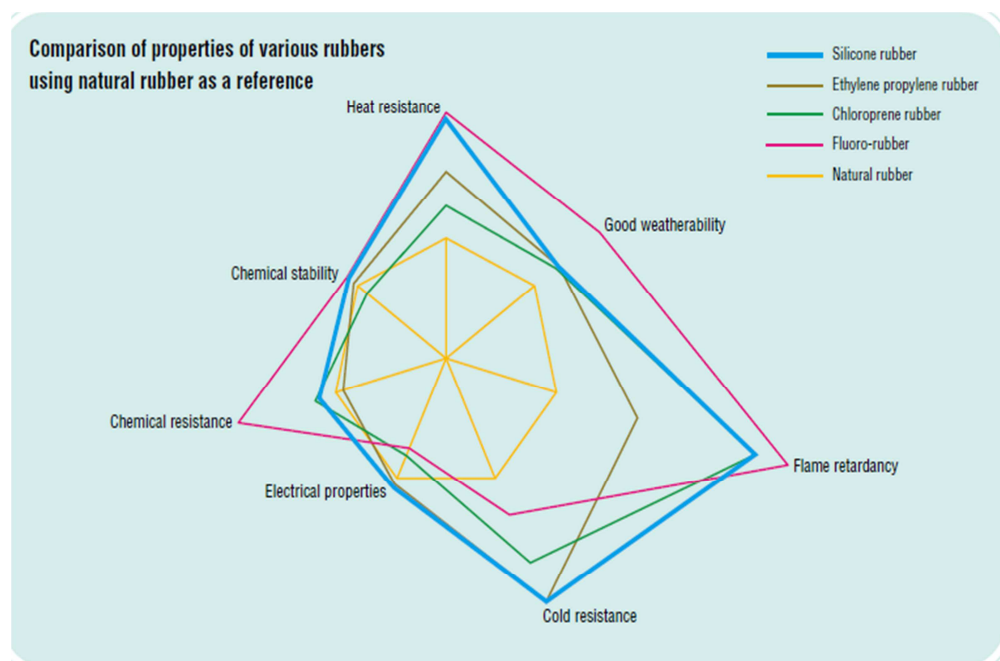
Fig.1.10 Comparison of properties of various rubbers using natural rubber as the reference [courtesy: Shin-Etsu Co .Ltd. *http://www. Silicone.jp/]*

Polydimethyl siloxane (PDMS) is the basic polymer for silicone rubber (SR), the hydrocarbon methyl groups being hydrophobic and water repellent. Pure silicone rubber shows little tracking and erosion resistance. The repeating unit is shown in figure. 1.11a. Some properties of silicone rubber must be improved for practical applications. The specific properties of the polymers are improved by the fillers and also to reduce costs. Silicones are highly functional materials that exhibit both inorganic and organic characteristics. Silicones manifest highly elastic behaviour due to the high flexibility of the siloxane bond. The Si-O bond polarizability in polydimethyl siloxane (PDMS) is higher than that of non polar organic polymers (e.g., polyfluroethylene), the side methyl groups prevent Si-O dipoles from approaching each other too closely and thus the

relative permittivity of PDMS is very low [Gubbels et al.,2007]. Every silicone consists of organic group side chains attached to a main chain of siloxane bonds (-Si-O-Si-). Siloxane bonds have much higher bond energy than the C-C and C-O bonds forming the main chains of organic polymers. Having high bond energy, Si-O bonds will not break even at temperatures around 200°C. Silicones are highly resistant to heat up to a temperature of 200°C; UV rays resist, water repellent and shows a range of other characteristics. They are chemically stable and have weatherability. Silicone molecules are helical and intermolecular forces are low. The methyl group located on the outside the coil structure can rotate freely. This molecular structure gives silicones their unique properties, including water-repellency, cold-resistance, easy release (non-adhesiveness) and they are largely temperature stable. The molecular structure of methyl end blocked silicone molecule (polydimethyl siloxane) is shown in figure 1.11 b.
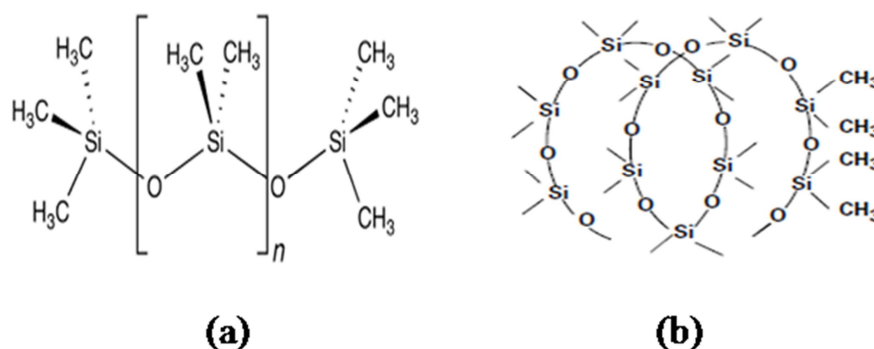
Fig.1.11 (a) Repeating unit of silicone rubber and (b) molecular structure of Polydimethyl siloxane

In the pure form silicone elastomer is a thermo set polymer; once cross linked it cannot be brought back to the former shape. Silicone rubber molecules exist above their glass transition temperature so considerable segmental motions are possible. The glass transition temperature of silicone elastomer is -127°C. The long polymer chains will cross link during curing and the process is known as vulcanization. Dicumyl peroxide is

used for the vulcanization of silicone rubber. The elastomer exhibit large elongation from which they recover rapidly on the removal of the applied stress. The peroxide curing vulcanization mechanism of silicone rubber is shown in figure 1.12.
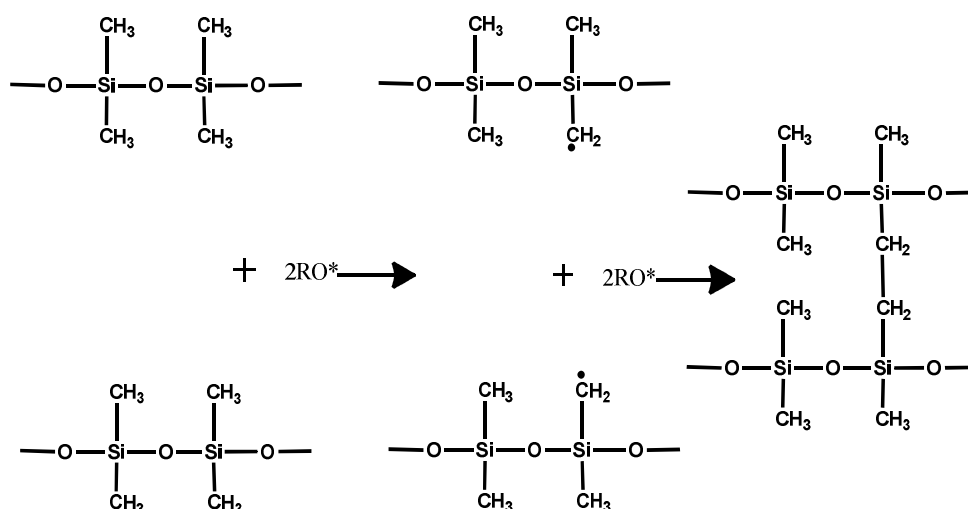
Fig.1.12 Vulcanization mechanism of silicone rubber using dicumyl peroxide

Among the available elastomers silicone rubber has a prominent position due to its unique properties such as good dielectric properties, high binding energy, high elasticity, resistant to extreme environments such as heat, ozone, weather, chemical stability, moisture and steam resistance, better electrical insulation, exceptional weather ability, gas permeability, biocompatibility and physiologically inert character [*http://www. Silicone.jp/*]. Silicone rubbers are extensively used in industry for development of a wide variety of products, including: automotive applications, cooking, baking and food storage products, apparels, electronics, medical devices and implants, and in home repair and hardware with products such as silicone sealants.

Elastomer - ceramic composites are important materials suitable for devices where flexibility is an important parameter. In most of the industrial applications

elastomers are used for composite materials. One of the very attractive features of this ceramic filled elastomer is that the electrical and physical properties can be varied over a wide range by choosing appropriate type, shape, particle size and connectivity or volume fraction of the fillers in the rubber matrix.

1.10 Scope and objectives of current work

Extensive research has been devoted to the development and advancement of flexible electronics and their applications. Flexible electronics is an emerging field in electronic industry which enables a wide range of applications such as capacitors for energy storage, wireless communication, electronic packaging and electromagnetic interference (EMI) shielding etc. It is an important research area for the next generation consumer electronics and is becoming a part of our day today life. For some applications, especially in the biomedical field, electronic circuits are to be conformally wrapped around curved surfaces. In such systems, the circuits must be not only flexible but also stretchable. The conventional ceramic polymer composites are flexible to a limited extent but they can't be bend or stretch. In this context, the elastomer–ceramic composites can be used for stretchable and bendable electronic applications. Silicone rubber is choosing as the matrix for the present investigation due to its excellent dielectric properties, elasticity, biocompatibility, optical transparency, permeability, UV transmission and availability. Silicone elastomer with good flexibility and ease of processing are available but their high CTE, low ε_r and low thermal conductivity limits their single phase use. Moreover, materials with variable relative permittivity are needed for electronic applications. The relative permittivity of silicone rubber can be tailored over a wide range by reinforcing with low-loss ceramics having different range of relative permittivity. Materials having variable relative permittivity are required for practical applications in electronic industry. The dielectric properties of silicone rubber can be tailored over a wide range by reinforcing with ceramics having different range of relative permittivity's, i.e., ceramic particles with i) a high permittivity, ii) a medium permittivity and iii) a low permittivity. In applications like electronic packaging and

substrate, the materials should have low relative permittivity to increase signal transmission speed. High relative permittivity materials are used for the manufacture of embedded capacitor as well as dielectric wave guide applications. Although considerable amount of work has been reported on silicone rubber – ceramic composites, but very little attention was paid on their microwave dielectric properties. In the present study, we discuss the recent advances in low loss silicone composites with ceramics for microwave applications.

Thus the objectives of the present work are

- To develop mechanically flexible, low loss and thermally stable dielectric composites for flexible microwave substrate and electronic packaging applications
- To develop mechanically flexible, low loss and thermally stable dielectric composites for flexible dielectric waveguide and embedded capacitor applications

- To develop a cost effective, flexible microwave antenna using suitable silicone rubber-ceramic composite based substrates with adequate medium of metallization.

CHAPTER 2

Silicone Elastomer-Low Permittivity Ceramic Composites

Preparation and characterization of silicone rubber reinforced with low permittivity fillers are discussed in this chapter. Alumina, aluminum nitride and fused silica have been selected as the low permittivity fillers for the present study. The dielectric properties at radio frequency and microwave frequencies, thermal and mechanical properties of the developed composites as a function of filler volume fraction are investigated. Experimentally observed values of relative permittivity of composites have been compared with the values obtained using various theoretical models. The coefficient of thermal expansion is found decrease whereas the thermal conductivity and moisture absorption increases with filler loading. Almost all the composites show good mechanical property and flexibility.

2.1 Introduction

Recent advancement in electronics technology has resulted in the miniaturization of devices. Microelectronic packaging has been playing a vital role in the rapid development of the electronic technologies. Flexible electronics creates a new era in the fast growing electronic industry. Flexible electronics is expected to make incredible inroads into consumer electronics markets in the coming years. Flexible electronic circuits comprise a flexible dielectric substrate upon which various electronic components are mounted. Flexible electronics are increasingly being used which benefits from their attractive features like mechanical flexibility, light weight and favourable dielectric properties [Jain et al., 2005]. Flexible and stretchable electronics enable a wide range of applications such as capacitors for energy storage, microwave absorbers, flexible dielectric wave guide, flexible displays, sensor arrays, curved circuits, flexible antenna etc [Ryu et al., 2009; Wong et al., 2009]. The iSuppli Flexible Display Report predicts the flexible display market to grow from $1.1 billion in 2015 to $3.89 billion by 2020 [*"Emerging Displays Report-Flexible Displays Technology 2012" http://www.isuppli.com/*]. The requirements for an ideal microwave substrate material are low dielectric loss for better performance, low relative permittivity to increase signal propagation speed, high moisture absorption resistance, good flexibility, high thermal conductivity to dissipate the heat generated and low coefficient of thermal expansion similar to that of silicon chip to avoid thermal failure [Chung, 1995; Garrou et al., 1998; Tian, 2003].

Several low permittivity ceramic like silicates and aluminates are available with excellent dielectric properties and are being used for substrate and electronic packaging applications [Oshato et al., 2006; Sebastian, 2008]. Their high processing temperature and brittle nature greatly limits their practical use. Many of the polymers satisfy the requirement of low relative permittivity (ε_r) and dielectric loss (tan δ) essential for microwave substrate application [Sebastian et al., 2010]. However, unlike the ceramics, polymers exhibit high thermal expansion and low thermal conductivity which are not favorable for substrate application [Rimdusit et al., 2000]. Hence the single phase usage of ceramic and polymer for practical application have facing some major limitations. At this juncture the bonded

technique polymer – ceramic composites are finding increased application in electronic and microwave devices, since they combine the dielectric and electrical properties of the ceramic fillers and the low-temperature processability and mechanical properties of the polymer matrix. Button et al. proposed the composite approach of combining the advantages of polymer and ceramic to get a superior property [Button et al, 1989]. Numerous polymer – ceramic composites have been developed for microwave substrate applications. The commonly used polymers for substrate application are epoxy, polytetrafluoroethylene, polyethylene, polystyrene etc.[Sebastian et al., 2010]. Polymers are flexible to a certain extent and also they cannot be used for stretchable applications and polymer – ceramic composites are rigid. Stretchability is a prime requirement for many applications especially in the biomedical field, where the circuits are to be wrapped around the curved surfaces and movable parts. In the present scenario the elastomer – ceramic composites are getting wide attention due to its flexibility and stretchability. The properties of the composites are depending upon the size and shape of the filler and the interaction between the filler and matrix. Hence through the composite approach we can tune the properties of polymer matrix using suitable ceramic filler.

Among the available elastomer, silicone rubber was chosen as rubber matrix. The most outstanding property of silicone rubber is its excellent dielectric properties including extremely low relative permittivity, low dielectric loss, good mechanical flexibility, stretchability, biocompatibility, chemical stability and moisture and steam resistance. The present work discusses the development of mechanically flexible low permittivity silicone rubber ceramic composites. In order to develop low permittivity composites, the permittivity of ceramic filler should be as low as possible. Enormous number of low permittivity ceramic materials is available. Among them we chose Al_2O_3, AlN and fused SiO_2 for the present study.

Extensive work has been done on ceramic filled butyl rubber for electronic packaging as well as microwave substrate applications [Thomas et al., 2011; Chameswary, 2014]. Considerable amount of work has been reported on silicone rubber – ceramic composites. However, very little attention was paid on the microwave dielectric properties. Koulouridis et al. studied the ceramic ($BaTiO_3$,

Mg-Ca-Titanate and Bi-Ba-Nd-Titanate) reinforced polydimethyl siloxane (PDMS) composite substrates for conformal microwave applications in the frequency range, 100 MHz–20 GHz [Koulouridis et al., 2006]. Dielectric properties of calcium copper titanate – silicone resin composites were reported by Babu et al. [Babu et al., 2012].

The elastomer – alumina composites are widely studied for various applications. Recently Sim et al. examined the thermal properties of silicone rubber filled with thermally conductive, electrically insulating Al_2O_3 and ZnO for elastomeric thermal pads applications [Sim et al., 2005]. Zhou et al. investigated the effect of alumina particle size, the effect of surface modification and hybrid alumina ceramic influence on the mechanical, thermal and physical properties of alumina reinforced vinyl end blocked silicone rubber composites [Zhou et al., 2007; Zhou et al., 2008]. Murali et al. investigated the dielectric properties of magnesia and alumina filled PTFE composites and found that PTFE – alumina composites are suitable candidates for microwave substrate applications [Murali et al., 2009; Goyal et al., 2011]. Recently the effect of particle size on microwave dielectric, thermal and mechanical properties of butyl rubber – alumina composites were done by Chameswary et al. [Chameswary et al., 2014]. Although considerable amount of work was reported on the alumina filled polymer composites, very little attention was paid on the microwave dielectric characterization of silicone rubber – alumina composites.

The unique properties like excellent dielectric properties, low CTE and low cost of AlN led to considerable research on AlN as reinforcing agent in recent years. Some applications like elastomeric thermal pads, electronic packaging etc., require high thermal conductivity and electrical insulation. Many researches have improved the thermal conductivity of silicone rubber by adding thermally conductive inorganic fillers. Research on various polymer/AlN composite have been performed and reported in the literature [Zhou et al., 2012; Goyal et al., 2011; Choudhury et al., 2012; Choudhury et al., 2013]. Zhou and co workers prepared AlN – PMMA composites and reported their microwave dielectric properties [Zhou et al., 2012]. Chiu et al. reported recently the surface modification of AlN filler and its effect on

the mechanical, thermal properties of the silicone rubber composites [Chiu et al., 2014; Chiu et al., 2014].

Commercially available low dielectric ceramic loaded PTFE substrate use fused silica as particulate fillers because of its unique properties. Silica is an important reinforcing filler of elastomer for industrial applications. Several silica loaded polymer composites were reported for microelectronic applications [Todd et al., 2002; Couderc et al., 2012]. Murali et al. developed flexible composite substrates using surfactant-free PTFE powder and micron size fused silica filler through SMECH process [Murali et al., 2009]. They have reported the effect of filler content and size on the dielectric, mechanical and thermal properties of PTFE/ fused SiO_2 composite system. Recently Chameswary et al reported the butyl rubber – silica composites for flexible microwave substrate applications [Chameswary et al., 2013]. The effect of silica on dielectric properties of styrene butadiene rubber were investigated by Hanna et al. in the frequency range of 60 Hz to 10^8 Hz at room temperature [Hanna et al.,1973].

The present work discusses the development of mechanically flexible composites having silicone elastomer matrix containing low permittivity ceramics like Al_2O_3, AlN and fused SiO_2 as fillers. The effects of fillers on dielectric, thermal and mechanical properties of silicone rubber – ceramic composites were investigated. The experimental values of relative permittivity of composites were compared with theoretical models.

2.2 Experimental

2.2.1 Materials

In the present investigation silicone elastomer as matrix and ceramic fillers such as Al_2O_3, AlN and fused SiO_2 were used for the composite preparation.

2.2.1.1 Silicone elastomer

The silicone rubber used for the present investigation was methyl end blocked silicone rubber, molecular weight = 4, 27,000 g/mol, provided by Jyothi

rubbers, Thrissur, India. Dicumyl peroxide (DCP) was used as curing agent and it was of commercial grade. In rubber compounding, it is conventional to use parts per hundred of rubber (phr) to quantify the ingredients used for vulcanization.

The physical properties of silicone rubber is given in Table 2.1

Table 2.1 Physical properties of silicone rubber

Density	1.16 g/cm^3
Water absorption	0.058 vol %
Relative permittivity at 5 GHz	3.0
Dielectric loss at 5 GHz	$\approx 10^{-2}$
Thermal conductivity	0.19 Wm^{-1}K^{-1}
Coefficient of thermal expansion	266 ppm/^{o}C

2.2.1.2 Ceramic fillers

2.2.1.2.1 Alumina (Al$_2$O$_3$)

Alumina is one of the most cost effective and widely used materials in the family of engineering ceramic. Aluminum oxide, commonly referred to as alumina, possesses strong ionic inter atomic bonding giving rise to its desirable material characteristics. It is having good dielectric properties ($\varepsilon_r = 9.8$, tan $\delta = 10^{-5}$), low CTE (6 – 7 ppm/°C), high thermal conductivity (25 Wm^{-1}K^{-1}) and low cost. It offers a combination of good electrical and mechanical properties leading to a wide range of applications in many filled like electrical, electronics, biomedical, chemical industry etc. The dielectric loss of alumina is about 1x 10^{-5} and the temperature coefficient of relative permittivity $\tau_\varepsilon =$~-200 ppm/^{o}C. The quality factor depends on the density and purity of the sintered sample [Alford et al., 1996]. Alumina (<10 µm) procured from Sigma Aldrich, USA was used for the present study. The alumina powder heat treated at 100°C for 24 h to remove the volatile impurities.

2.2.1.2.2 Aluminum nitride (AlN)

Aluminum nitride is a newer material in the technical ceramics family with high intrinsic thermal conductivity (370 $Wm^{-1}K^{-1}$) and high electrical resistivity. Aluminum nitride has a hexagonal crystal structure and is a covalent bonded material. AlN procured from Sigma Aldrich, USA was used for the present study. The AlN powder heat treated at 100°C for 24 h to remove the volatile impurities.

2.2.1.2.3 Fused silica (SiO$_2$)

Fused silica is another low permittivity ceramic having unique properties such as near zero thermal expansion, exceptionally good thermal shock resistance, very good chemical inertness and low dielectric loss. Fused silica is a non-crystalline (glass) form of silicon dioxide (quartz, sand). It's highly cross linked three dimensional structures gives rise to its high resistance to temperature and low thermal expansion coefficient. The dielectric properties are stable up through gigahertz frequencies. The fused silica procured from Chettinad cements, Tamilnadu, India dried at 100°C for 24 h was used for the present study. The physical properties of ceramic fillers are given in Table 2.2.

Table 2.2 Physical properties of ceramic fillers

Material	Density (g/cm^3)	Avg.particle size (µm)	Relative permittivity ε_r	Dielectric loss tan δ	Coefficient of thermal expansion (ppm/°C)	Thermal conductivity (Wm^{-1}K^{-1})
Al$_2$O$_3$	3.95	2.0	9.8	10^{-5}	7.0	25
AlN	3.20	1.3	8	10^{-2}	4.4	160
Fused SiO$_2$	2.20	0.50	4.0	10^{-4}	0.5	1.4

2.2.1.3 Silicone rubber-ceramic composite preparation

Composite materials are increasingly used in applications, such as electronic packaging and thermal management. Polymer composites controllable electrical resistivity, combined with their light and flexible properties, makes them suited for applications in flexible electronics.

2.2.1.3.1 Compounding

The process of sequentially adding the ingredients into the raw rubber is termed 'compounding'. In the present study compounding of silicone rubber was done by sigma blend method. The mixing was done in a kneading machine (Plastomek, Quilandy) at room temperature. The kneading machine consists of variable speed mixer having two counter rotating sigma blades with gear ratio 1:1.2. The silicone rubber was first masticated through the counter rotating sigma blades to make them soft and more processable. Dicumyl peroxide (DCP) was used as vulcanizing agent. Finally appropriate amount of ceramic fillers were added. The mixing was done for about 45 minutes with the rotation speed of 25 rpm to get uniform composites. The uniformly mixed composites were hot pressed at 200°C for 90 minutes under a pressure of 2 MPa with appropriate dies. The optimization of temperature and duration were done by studying the cross linking behavior. After hot pressing, the composites with desired shapes were used for characterization. The photographic images of the kneading machine and hot press used are shown in figure 2.1 (a) and (b) respectively.
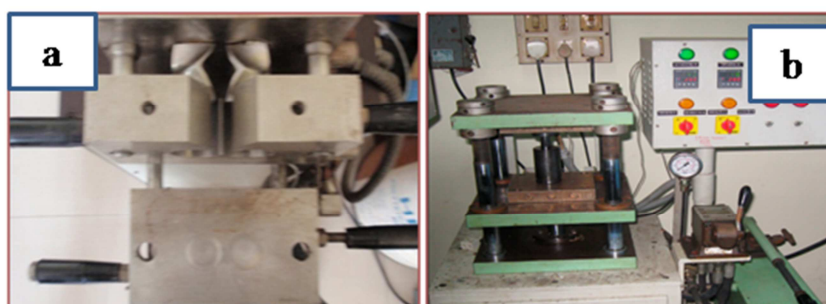
Fig.2.1 Photographic images of (a) kneading machine (b) hot press

2.2.2 Characterization

2.2.2.1 X-ray diffraction (XRD)

The X-ray diffraction technique has been of greatest importance in revealing the structure of the crystals. X-ray diffraction method is most useful qualitative, rather than quantitative analysis (although it can be used for both). The crystals to be examined is ground to a fine powder and placed in a beam of monochromatic X-rays. The incident X-rays will either transmitted or scattered by the electrons of the atoms in the material. In general, the scattered waves interfere destructively with each other, with the exception of special orientations at which Bragg's law is satisfied. The X-ray diffractometer records the intensity data of a diffracted X-ray beam, as a function of angle, so as to satisfy the Bragg's law under the condition of X-rays of known wave length. Diffraction data of many different materials are available in a computer searchable powder diffraction file (JCPDS file). Comparing the observed data with that in the JCPDS allows the phase in the sample to be identified. In the present study the powder XRD spectra were recorded using CuKα radiation (PANalyticalX'PertPRODiffractometer, Almelo, Netherlands).

2.2.2.2 Scanning electron microscopy (SEM)

The scanning electron microscope (SEM) is a microscope that uses electrons instead of visible light to form an image. SEM was used to analyze the microstructure of composites. The SEM has much higher resolution and hence closely spaced specimens can be magnified at much higher levels. The interaction between primary electron beam and the sample produces secondary electrons, characteristic X-rays and back scattered electrons. The signals resulted from electron sample interactions reveal information regarding the sample including texture, chemical compositions, crystalline structure and orientation of materials making up the sample. An electrically conductive (usually gold) coating must be applied to electrically insulating samples for SEM analysis. In the present study scanning electron microscope of JEOL JSM -5600LV, Tokyo, Japan has been used for analyzing the microstructure of the samples prepared.

2.2.2.3 Mechanical properties

The mechanical flexibility is the prime requirement for flexible electronic applications. Tensile test is useful to evaluate mechanical properties of materials in which the sample is pulled to failure in a relatively short period of time. The sample is elongated at a constant rate and the load required to produce a given elongation is measured as a dependent variable. A stress-strain curve may be plotted from the results of a tension test and from the plot the toughness of the material can be assessed [Menard, 1999; Hayden et al.,1984]. In the present study the stress-strain properties of the composites were measured using a Universal Testing Machine (Hounsfield, H5K-S UTM, Redhill, U.K.) with a rate of grip separation of 500 mm/min following the American standard ASTM D-412. Dumb-bell shaped samples of width 4 mm and thickness in the range of 1.5 – 2 mm were used for the tensile measurements.

2.2.2.4 Dielectric characterization

2.2.2.4.1 Radio frequency dielectric measurements

The dielectric properties up to 3 MHz are measured using the parallel plate capacitor method with the help of an LCR meter (HIOKI 3532-50 LCR Hi TESTER, Japan). The working principle of LCR meter is parallel plate capacitor method in which a thin sheet of material is sandwiched between two electrodes to form a capacitor. This is done by uniformly coating silver paste on both sides of cylindrical specimens (11 mm diameter and 1-2 mm thickness). LCR meter measures the complex impedance by auto balancing bridge technique from which the capacitance and dielectric loss are calculated. The relative permittivity is calculated using the equation

$$C = \frac{\varepsilon_r \varepsilon_o A}{d}$$

(2.1)

where C is the capacitance, ε_r and ε_0 are the relative permittivity of material and free space respectively. A and d are the cross sectional area and thickness of the sample.

Fig.2.2 Photograph of Hioki 3532-50 LCR Tester

2.2.2.4.2 Microwave characterization

The microwave characterization of a material plays an important role in microwave electronics. In general, the methods for measurement of microwave dielectric properties fall into two categories: non-resonant method and resonant method. Non-resonant methods are used to get a general idea of electromagnetic properties over a frequency range while resonant methods are used to get accurate knowledge of dielectric properties at single frequency or several discrete frequencies.

2.2.2.4.2.1 Network analyzer

Network analyzer is the major instrument used in the present investigation for the measurement of low loss microwave materials. It gives all network characteristics of the analog circuit by measuring and phases of transmission and reflection coefficients. A vector network analyzer (Agilent Technologies, E5071C, ENA Series Network Analyzer) is used for the present investigations.

Fig.2.3 Photographic image of the network analyzer

[courtesy: *www.metrictest.com*]

2.2.2.4.2.2 Split Post Dielectric Resonator (SPDR)

Split Post Dielectric Resonator method is suitable for the measurement of dielectric properties of samples in the form of thin sheet [Krupka et al., 1996]. The SPDR uses a particular resonant mode which has a specific resonant frequency depending on the resonator dimensions and the relative permittivity. The resonator mainly consists of two dielectric discs separated by a small air gap in a metal enclosure. The schematic representation of the SPDR is shown in the figure 2.4 [Sebastian, 2008]. The dielectric discs are thin and the height of metal enclosure is relatively small, so the evanescent electromagnetic field is strong not only in the air gap region outside the cavity but also in the cavity region for radii greater than the radius of the dielectric resonator. Therefore the electromagnetic fields are also attenuated in the cavity so it is necessary to take them into account in the air gap. This simplifies the numerical analysis and reduces possible radiation. The sample under test is placed in the gap between the two parts of the resonator usually at the place of maximum electric field. The loading of a dielectric sheet sample changes the resonant properties of a split resonator and the dielectric properties of the sample can be derived from the resonant properties of the resonator loaded with sample and the dimensions of the resonator and the sample [Chen et al., 2004]. The SPDR usually operates in TE$_{01\delta}$ mode, which has only azimuthal electric field component.
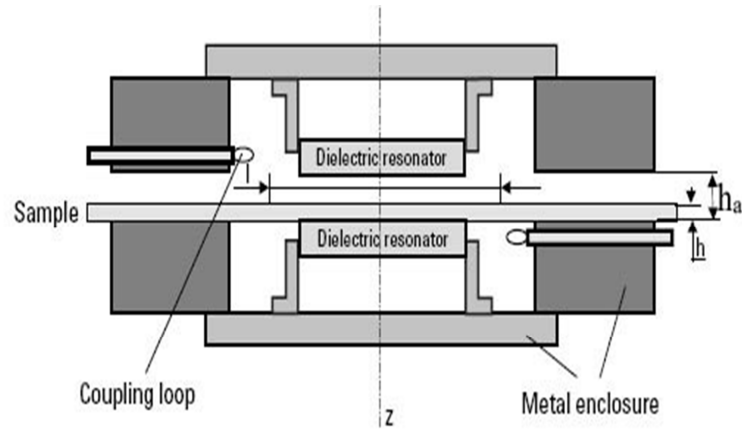
Fig.2.4 Schematic representation of a split post dielectric resonator

[Ssebastian ,2008]

The dielectric properties of the sample are derived from the changes of resonant frequency and unloaded Q-factor due to the insertion of the sample. The relative permittivity of the sample is an iterative solution to the following equation

$$\varepsilon_r = 1 + \frac{f_o - f_s}{h f_o K_\varepsilon(\varepsilon_r, h)} \qquad (2.2)$$

where h is the thickness of the sample under test, fo is the resonant frequency of empty resonant fixture, fs is the resonant frequency of the resonant fixture with dielectric sample, K_ε is a function of ε_r and h;it has been evaluated using Rayleigh-Ritz technique [Krupka et al., 2001]. The dielectric loss of the sample can be determined by

$$\tan \delta = (Q_u^{-1} - Q_{DR}^{-1} - Q_C^{-1})/\rho_{es} \qquad (2.3)$$

In equation (2.3)

$$p_{es} = h \varepsilon_r K_1(\varepsilon_r, h) \qquad (2.4)$$

$$Q_c = Q_{c0} K_2(\varepsilon_r, h) \qquad (2.5)$$

$$Q_{DR} = Q_{DR0} \cdot \frac{f_o}{f_s} \cdot \frac{p_{eDR0}}{p_{eDR}} \qquad (2.6)$$

where p_{es} and p_{eDR} are the electric energy filling factors for the sample and for the split resonator respectively; p_{eDR0} is the electric energy filling factor of the dielectric split resonator for empty resonant fixture; Q_{c0} is the quality factor depending on metal enclosure losses for empty resonant fixture; Q_{DR0} is the quality factor depending on dielectric losses in dielectric resonators for empty resonant fixture; and Q_u is the unloaded quality factor of the resonant fixture containing the dielectric sample. The values of p_{eDR}, p_{es} and Q_c for a given resonant structure can be calculated using numerical techniques. The uncertainty of the permittivity measurements of a sample of thickness h is $\Delta\varepsilon/\varepsilon = \pm (0.0015+\Delta h/h)$ and uncertainty in dielectric loss measurements are $\Delta (\tan \delta) = 2\times10^{-5}$ [Krupka et al., 2001].

Microwave dielectric properties of silicone rubber - ceramic composites in the present investigation were measured by this method. The SPDR operating at 5.155 GHz and 15.155 GHz is used for the present study. Figure 2.5 shows the photograph of split post dielectric resonator used.
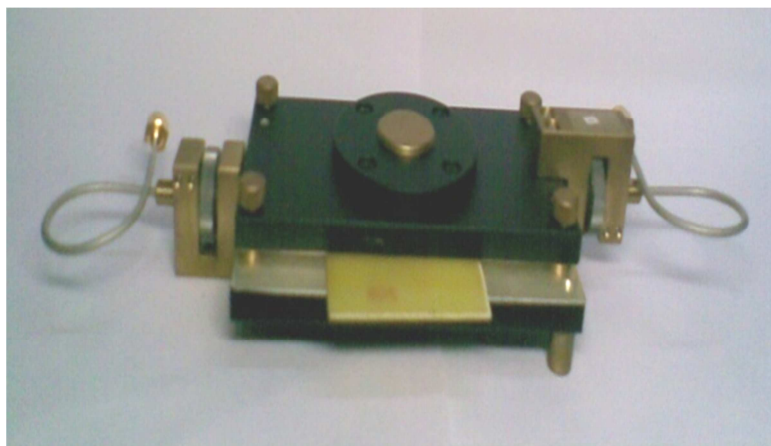
Fig.2.5 Photograph of QWED split post dielectric resonator

2.2.2.4.3 Theoretical modeling of relative permittivity

The precise prediction of relative permittivity of the composite from the relative permittivity of the components and the volume fraction of the filler is very important for the design of composites for electronic applications. Several theoretical models have been developed to estimate the relative permittivity of

polymer - ceramic composites structures. The dielectric properties of the composites are influenced not only by the relative permittivity of the components but also by other factors such as the morphology, dispersion and the interaction between the two phases. The theoretical modeling enables the material scientists to arrive at novel composite systems without much experimental iterations. The following equations are used to predict the relative permittivity of the present composites theoretically:

(a)   Maxwell-Garnett equation:

$$\frac{\varepsilon_{eff} - \varepsilon_m}{\varepsilon_{eff} + 2\varepsilon_m} = v_f \frac{\varepsilon_f - \varepsilon_m}{\varepsilon_f + 2\varepsilon_m} \tag{2.7}$$

Where ε_{eff}, ε_f, ε_m are the relative permittivity of the composites, filler and matrix respectively and V_f is the volume fraction of the filler.

The Maxwell-Garnett mixing rule was initially used to calculate the effective permittivity of a system where metal particles are encapsulated in an insulating matrix. This mixing rule was modified for polymer - ceramic composites incorporating homogeneous distribution of spherical ceramic particles and the excitation of dipolar character is considered [Maxwell Garnet, 1904].

(b)   Jayasundere-Smith equation:

$$\varepsilon_{eff} = \frac{\varepsilon_m\left(1 - v_f\right) + \varepsilon_f v_f \left[\dfrac{3\varepsilon_m}{\varepsilon_f + 2\varepsilon_m}\right]\left[1 + \left(\dfrac{3v_f\left(\varepsilon_f - \varepsilon_m\right)}{\varepsilon_f + 2\varepsilon_m}\right)\right]}{1 - v_f + v_f\left[\dfrac{3\varepsilon_m}{\varepsilon_f + 2\varepsilon_m}\right]\left[1 + \left(\dfrac{3v_f\left(\varepsilon_f - \varepsilon_m\right)}{\varepsilon_f + 2\varepsilon_m}\right)\right]} \tag{2.8}$$

Jayasundere-Smith equation is a modification of well-known Kerner equation by including the interactions between neighboring spheres. This equation considers composite as a bi-phase system of dielectric spheres (ε_f) dispersed in a continuous medium (ε_m) and is valid only when $\varepsilon_f \gg \varepsilon_m$ [Jayasundere smith, 1993].

(c)   Lichtenecker equation:

$$\ln\varepsilon_{eff} = \left(1 - v_f\right)\ln\varepsilon_m + v_f \ln\varepsilon_f \tag{2.9}$$

The most widely used relation for the prediction of ε_r is Lichtenecker's logarithmic law of mixing. It considers the composite system as randomly oriented spheroids that are uniformly distributed in a continuous matrix [Lichtenecker, 1931].

(d)   Effective Medium Theory (EMT):

$$\varepsilon_{eff} = \varepsilon_m \left[1 + \frac{v_f \left(\varepsilon_f - \varepsilon_m \right)}{\varepsilon_m + n\left(1 - v_f\right)\left(\varepsilon_f - \varepsilon_m\right)} \right] \tag{2.10}$$

Where n is empirically determined parameter in the EMT model.

In EMT model, composites are treated as an effective medium whose relative permittivity is obtained by averaging over the relative permittivity of the constituents. The basic concept of EMT model is that when a random unit cell (RUC) is embedded in an effective medium it cannot be detected in the electromagnetic experiment. A random unit cell is defined as a core of ceramic surrounded by a concentric shell of the polymer [Rao et al., 2000]. A correction factor 'n' is used to compensate for the shape of the fillers and is called morphology factor which is related to ceramic particle and can be obtained empirically. A small value of 'n' indicates a near spherical shape for the filler, while a high value of 'n' shows a largely non-spherically shaped particle.

2.2.2.4.4 Bending

Bending measurements of the composites were carried out by bending the samples manually in such a way that every part of the sample had undergone 180° bending. The bending cycle was repeated for 125 times and the microwave dielectric properties were measured by SPDR operating at 5.155 GHz after every 25 cycles.

2.2.2.4.5 Temperature coefficient of relative permittivity ($\tau_{\varepsilon r}$)

Temperature coefficient of relative permittivity ($\tau_{\varepsilon r}$) of material should be stable within the operational temperature range of electronic devices for practical applications. The temperature coefficient of relative permittivity of the present

composites was measured by SPDR operating at 5.155 GHz from 25 to 60°C. The temperature stability may be examined using the relation given below

$$\tau_{\varepsilon r} = \frac{1}{\varepsilon_r} X \frac{\Delta \varepsilon_r}{\Delta T} \qquad (2.11)$$

In order to measure the $\tau_{\varepsilon r,}$ the sample is kept in the SPDR and the corresponding peak is identified in the network analyzer. Then the entire setup is heated up in the temperature range of 25 to 60°C. The shift in the resonant frequency with temperature is noted at regular intervals.

2.2.2.5 Thermal characterizations

Thermal analysis includes the techniques in which some physical parameters of the system is determined and recorded as a function of temperature. Some of the thermal characterizations used in the current study are discussed below

2.2.2.5.1 Coefficient of thermal expansion (CTE)

Dilatometry is a thermo analytical technique used to measure shrinkage or expansion of materials. Dilatometry [Pennisi, 1991; Wang et al., 2006] is the continuous measurement of the length of the sample as the specimen is subjected to a controlled linear heating rate. In this technique, dimensional changes in a sample are primarily measured with negligible force acting on it, while the sample is heated. The value of coefficient of thermal expansion is calculated using the relation

$$\alpha_l = \frac{1}{L} \frac{\Delta L}{\Delta T} \qquad (2.12)$$

where L is the original dimension of the sample and ΔL is the change in length when the change in temperature is ΔT. In the present study, Dilatometer (DIL 402 PC, NETZSCH, Selb, Germany) is employed for thermal expansion measurements of the composites. Cylindrical samples (diameter 8 mm and thickness 10 to 14 mm) are required for dilatometric studies.
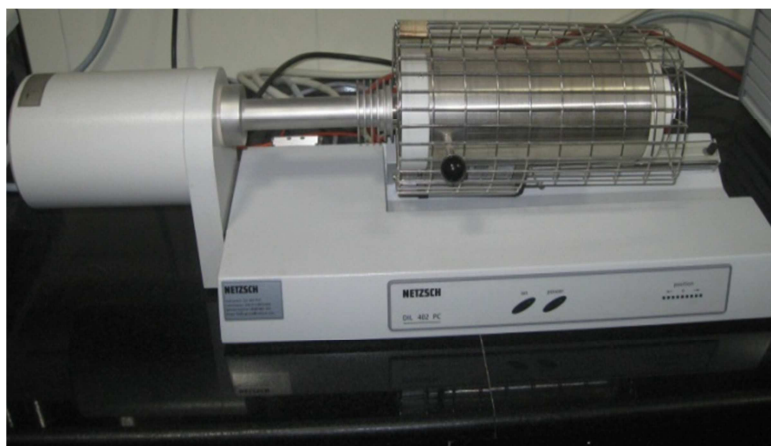
Fig.2.6 Photograph of DIL 402 PC, NETZSCH dilatometer

2.2.2.5.2 Thermal conductivity (TC)

The thermal conductivity of the composites was measured by laser flash technique using the relation

$$TC = \lambda \times Cp \times \rho \qquad (2.13)$$

where λ is the thermal diffusivity, Cp is the specific heat capacity at room temperature and ρ is the density of the sample.

Fig.2.7 Photograph of Flash Line[TM] 2000 thermal properties analyzer

The laser flash method is a vertical set up in which Xenon flash heats the sample from the bottom side and a detector on top detects the time dependent temperature rise. The thermal diffusivity can be calculated from specimen thickness and the time required for the rear face temperature rise to reach certain percentage of its maximum value [Hasselman et al., 1985]. The heat capacity of the sample also measured simultaneously comparing the temperature rise in the sample with that in a reference material [Parker et al., 1961].

In the present study, thermal conductivity was measured by thermal properties analyzer (Flash Line^{TM} 2000, Anter Corporation,Pittsburgh,USA). Graphite coated samples of diameter 12.57 mm and thickness ≈1 mm was used for thermal conductivity measurements.

2.2.2.6 Water absorption of composites

The water absorption characteristic of the composites was measured by following the ASTM D 570-98 procedure. The dimensions of the samples used for the water absorption study is 50 mm×50 mm×2 mm. The samples were weighed accurately and immersed in distilled water for 24 h. The samples were then taken out and again weighed after removing the excess water from the surface. The vol. % of water absorption was then calculated using the relation,

$$\text{Volume \% water absorption} = \frac{(W_f - W_i)/\rho_w}{(W_f - W_i)/\rho_w + W_i/\rho_c} \times 100 \qquad (2.14)$$

Where W_i and W_f are the initial and final weights of the sample and ρ_w and ρ_c are the densities of distilled water and composite respectively. The density of the composites was measured using Archimedes method.

2.3 Results and discussion

The silicone rubber ceramic composites of alumina, aluminum nitride and fused silica were prepared as described in section no 2.2.1.3.1. The density of fused SiO_2 ($\rho = 2.20$ g/cm^3) is lower than Al_2O_3 and AlN. So the silica filled composites can be mixed upto a filler loading level of 0.51 V_f (200 phr) where as the mixing is found to be difficult for more than 0.41 V_f (200 phr) for SR-AlN (SRAN)

composites and for SR-Al$_2$O$_3$ (SRAL) composites it is upto 0.45 V$_f$ (300 phr). Zhou et al. reported that after certain volume percentage (40 vol %) of filler loading, hardening and difficulty in processing occurs with degraded mechanical property [Zhou et al., 2007]. Ceramic fillers can be incorporated in the rubber matrix only up to a certain loading fraction beyond which the composite becomes porous as a result of insufficient rubber to encapsulate the filler. The optimum filler loading also depends on the particle size, distribution and morphology of the filler [Zhou et al., 2007]. Consider the case of nano fillers they can provide better mechanical properties, lower CTE, better relative permittivity compared to micro fillers but the dielectric loss and the moisture absorption may be higher for nano composites than that of micro composites. The large surface area may be the reason for higher moisture absorption; which in turn increase the dielectric loss which is not favorable for electronic packaging as well as microwave substrate applications [Namitha et al., 2013; Chameswary et al., 2014]. Hence in the present work nano fillers have not been considered. The sample designation and the formulations of composites are given in Table 2.3. The composites thus prepared were characterized for microstructural, dielectric, thermal and mechanical properties using the techniques mentioned earlier in the chapter (section 2.2.2 and subsections). In the present chapter we report the development of flexible as well as stretchable, thermally conductive, low relative permittivity and low dielectric loss silicone rubber composites for microwave substrate application. Photographic images of some of the developed composites are shown in figure 2.8.
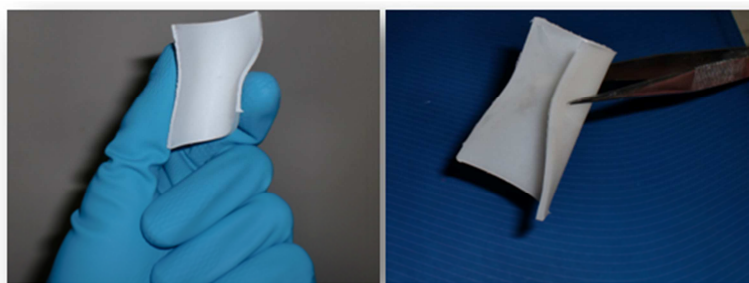
Fig.2.8 Photographic images of developed composites

Table 2.3 The formulations of silicone rubber composites (Ingredients in phr [a])

Composite material	Sample designation	Silicone rubber in phr[a]	Dicumyl peroxide (DCP) in phr[a]	Filler in phr[a] [][b]
Silicone rubber-Al_2O_3 (SRAL)	$SRAL_0$	100	2	0[0]
	$SRAL_1$	100	2	10[0.02]
	$SRAL_2$	100	2	50[0.12]
	$SRAL_3$	100	2	100[0.22]
	$SRAL_4$	100	2	200[0.35]
	$SRAL_5$	100	2	300[0.45]
Silicone rubber-AlN(SRAN)	$SRAN_0$	100	2	0[0]
	$SRAN_1$	100	2	10[0.03]
	$SRAN_2$	100	2	50[0.15]
	$SRAN_3$	100	2	100[0.26]
	$SRAN_4$	100	2	200[0.41]
Silicone rubber-fused SiO_2(SRFS)	$SRFS_0$	100	2	0[0]
	$SRFS_1$	100	2	10[0.04]
	$SRFS_2$	100	2	50[0.20]
	$SRFS_3$	100	2	100[0.34]
	$SRFS_4$	100	2	200[0.51]

[a]Parts per hundred of rubber [b]Volume fractions of filler given in parenthesis

The X-ray diffraction patterns of the ceramic fillers are shown in figure 2.9. Only a diffused peak has been observed for the fused SiO_2 powder, which indicates the pure amorphous phase where as all the peaks of Al_2O_3 and AlN were indexed using the standard JCPDS files; no 46-1212 and 65-1902. The phase purity of the ceramics is clear from the XRD patterns.
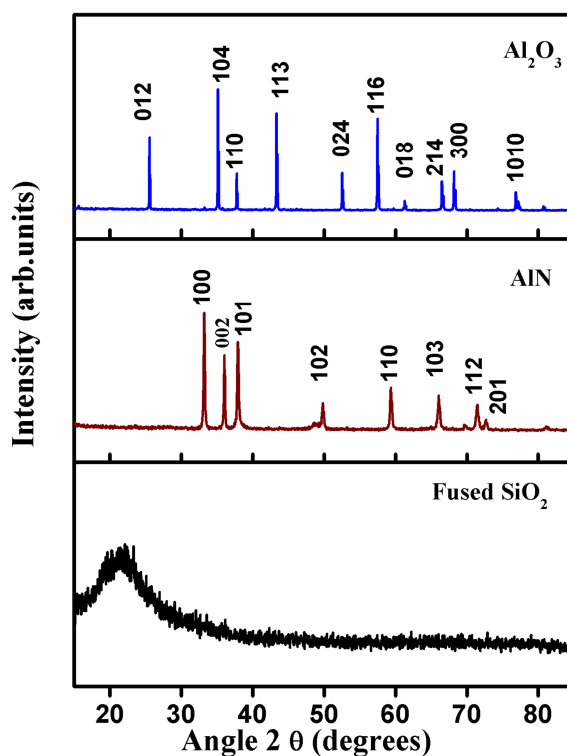
Fig.2.9 XRD patterns of (a) fused SiO_2 (b) AlN and (c) Al_2O_3

The morphology of Al_2O_3, AlN and fused SiO_2 powders and the fractured surface of the corresponding silicon rubber composites with different filler content is shown in the figure.2.10. Figure (a_1), (b_1) and (c_1) shows the microstructure of Al_2O_3, AlN and fused SiO_2 powder respectively. Figure a_2 and a_3 showed the fractured surface of SR+0.02 V_f of alumina and SR+0.45 V_f of alumina, b_2 and b_3 the fractured surface of SR+0.03 V_f of AlN and SR+0.41 V_f of AlN, c_2 and c_3 shows the fractured surface of SR+0.04 V_f of fused SiO_2 and SR+0.51 V_f of fused SiO_2 composites respectively. Filler particles are uniformly dispersed throughout the matrix at low volume fractions. At lower filler loading the matrix covers the ceramic particles but as the filler loading increases the inter particle distance decreases and

this may leads to the agglomeration of filler particles which leads to porosity which is evident from the figure.
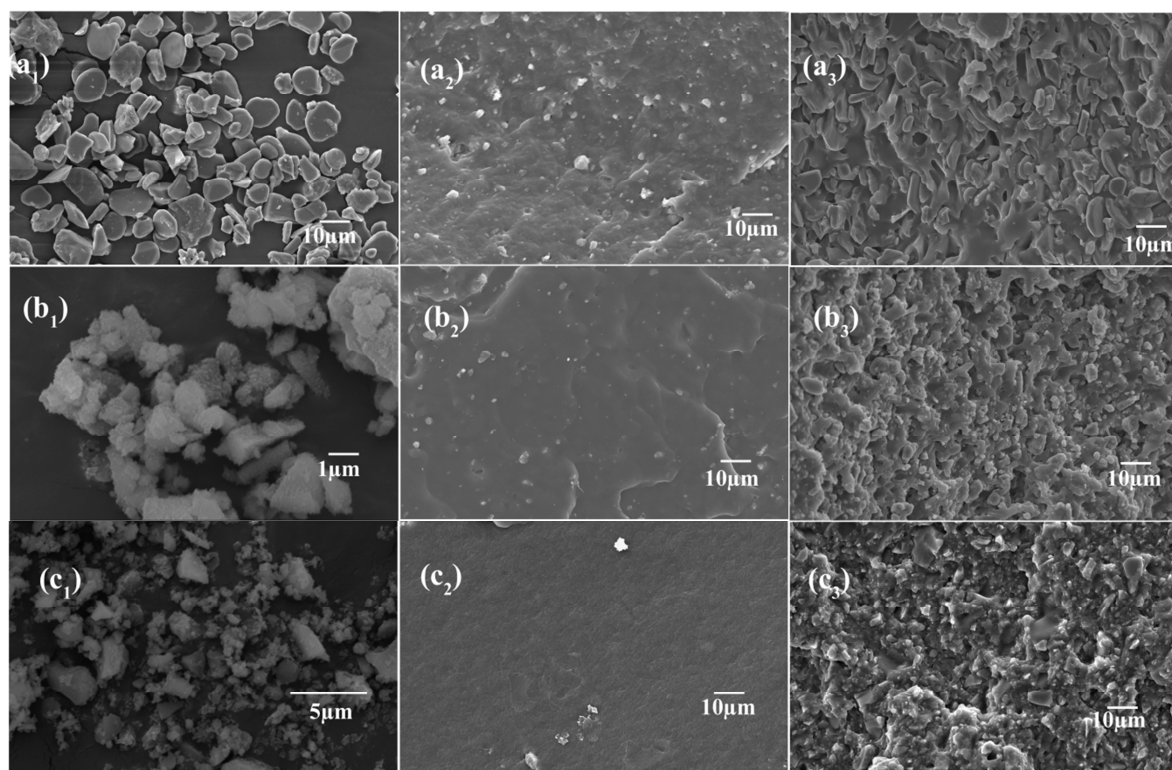
Fig.2.10 SEM images of (a_1) Al_2O_3powder (b_1) AlN powder (c_1) fused SiO_2,(a_2), (b_2) and (c_2) fractograms of low filler loaded composites and (a_3), (b_3) and (c_3) fractograms of higher filler loaded SRAL, SRAN and SRFS composites respectively.

The stress – strain curves of pure elastomer and the different composites are shown in Figure 2.11. For practical applications, good mechanical properties of the elastomer are essential and are normally improved by the addition of fillers. The mechanical properties of the composites are strongly influenced by the size and shape of the filler, matrix properties as well as the interfacial adhesion between the filler and matrix. The addition of the filler increases the flexural strength of the silicone rubber [Mohamad et al., 2008]. From the figure it is clear that the stress for elongation increases with ceramic loading. This is attributed to the filler – matrix and filler – filler interaction that restrict the mobility of the elastomer matrix. As the filler loading increases the flexibility of the composite decreases. It is found that the

maximum filler loaded silicone rubber broken at an elongation. This may be due to the formation of agglomerations at higher ceramic loading which act as weak points in the composite and it easily break when stress is applied [Nielsen et al.,1994].
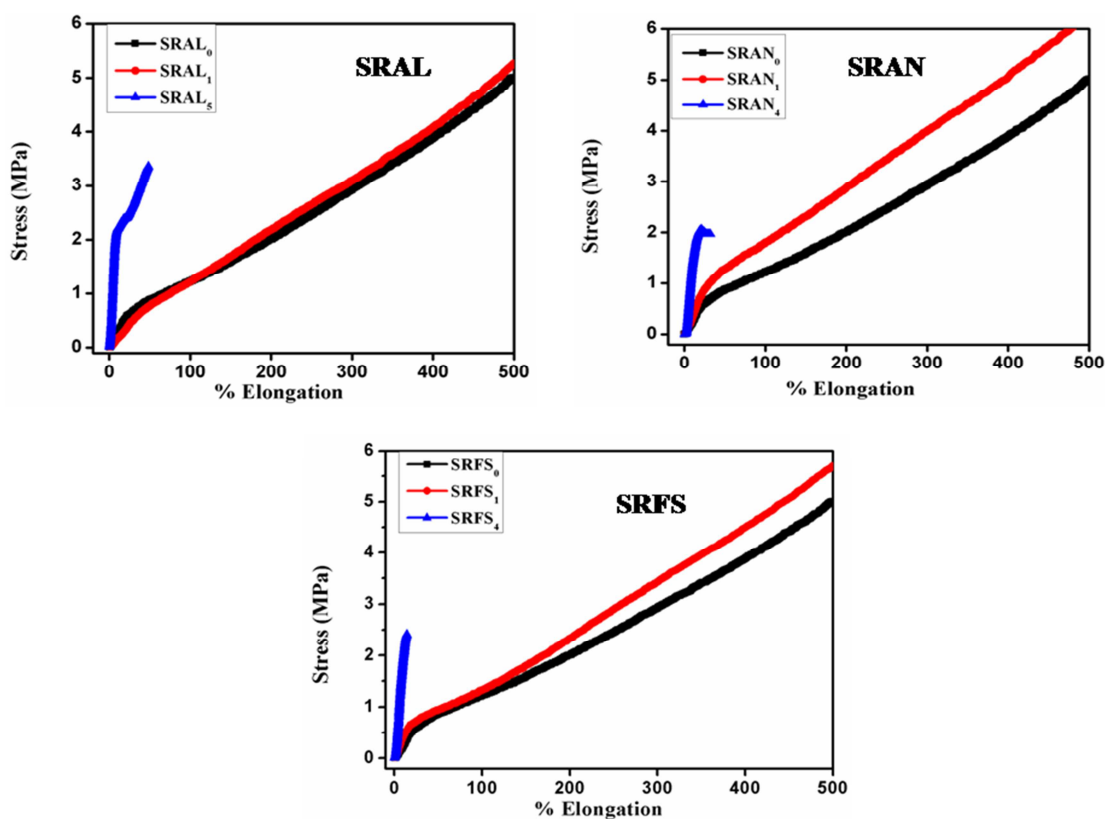
Fig.2.11 Stress-strain curves of SRAL, SRAN and SRFS composites

A low relative permittivity is desirable for microelectronic packaging to increase the signal transmission speed. The relative permittivity of composites varies between the relative permittivity of polymer and filler. The variations in relative permittivity and the dielectric loss of the composites with varying filler fraction at the radio frequency (1 MHz) as well as at microwave frequency region (5 GHz & 15 GHz) are shown figure 2.12. It is clear from the figure 2.12a that relative permittivity increases with filler fraction. This is due to high relative permittivity of ceramic compared to silicone rubber matrix and the increased connectivity among the filler particles. The dielectric response of the composite at lower filler loading is mainly due to the silicon rubber matrix. The connectivity among the filler particles increases at higher filler content which in turn increases the relative permittivity of the composites [David et al., 1990]. The dielectric loss decreases with increase in

volume fraction for certain composites and is due to the low loss factor of the ceramic filler compared to rubber matrix. In the case of SRAN composites, the dielectric loss increases with filler content. This is due to the high dielectric loss of the AlN than that of silicone rubber matrix.
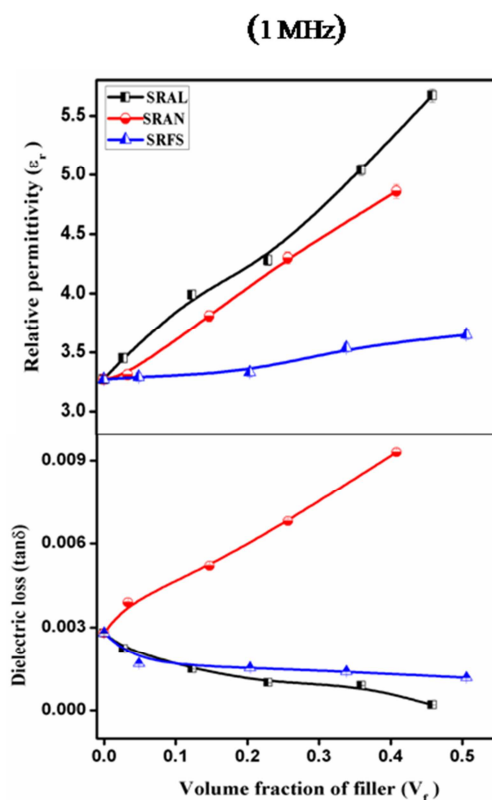
Fig.2.12 a Variations of dielectric properties of silicone rubber composites at 1 MHz

The variation of microwave dielectric properties of SR composites with varying filler fraction at 5 GHz and 15 GHz is shown in figure 2.12 b. The trend was similar to that of radio frequency region and the permittivity increases with filler loading. The addition of ceramic fillers gradually increased the relative permittivity. The increased filler loading increase the dipole-dipole interaction which in turn can also increases the permittivity [Kuo et al., 2004]. The relative permittivity of the samples at 5 GHz and 15 GHz do not show appreciable differences since there is hardly any change in the polarization mechanism [Zhou et al., 2012]. The dielectric properties of the composites depend on the loading level of the filler, size and shape of the filler particles and the interfacial properties of the composites [Battacharya et al., 2000]. The dielectric loss of a polymer – ceramic composite depends on the factors such as interface between two components in the composite, moisture

content and porosity. The effective dielectric loss of SRAL and SRFS composites decreases with increase in filler content. Similar behaviour was observed by Joseph et al. in their work of $Sr_2ZnSi_2O_7$ based polymer/ceramic composites [Joseph et al., 2012]. In the case of SRAL and SRFS composites, the major factor controlling the dielectric loss is the extremely low tan δ value of fillers compared to pure silicone rubber matrix. Here the effect of increased inhomogeneity with filler loading is underestimated by the low value of tan δ of ceramics. The tan δ values of AlN have the same order of magnitude as that of silicone rubber matrix and hence the addition of filler does not have a major role in controlling the dielectric loss of the composites. Therefore the increase in the dielectric loss of the composites is attributed to the increase in the heterogeneity of the samples with filler content. As explained the agglomeration of filler particles and hence the entrapped porosity and moisture absorption have large values for composites with high filler content. This might be the reason for the increase in tan δ values of SRAN composites.
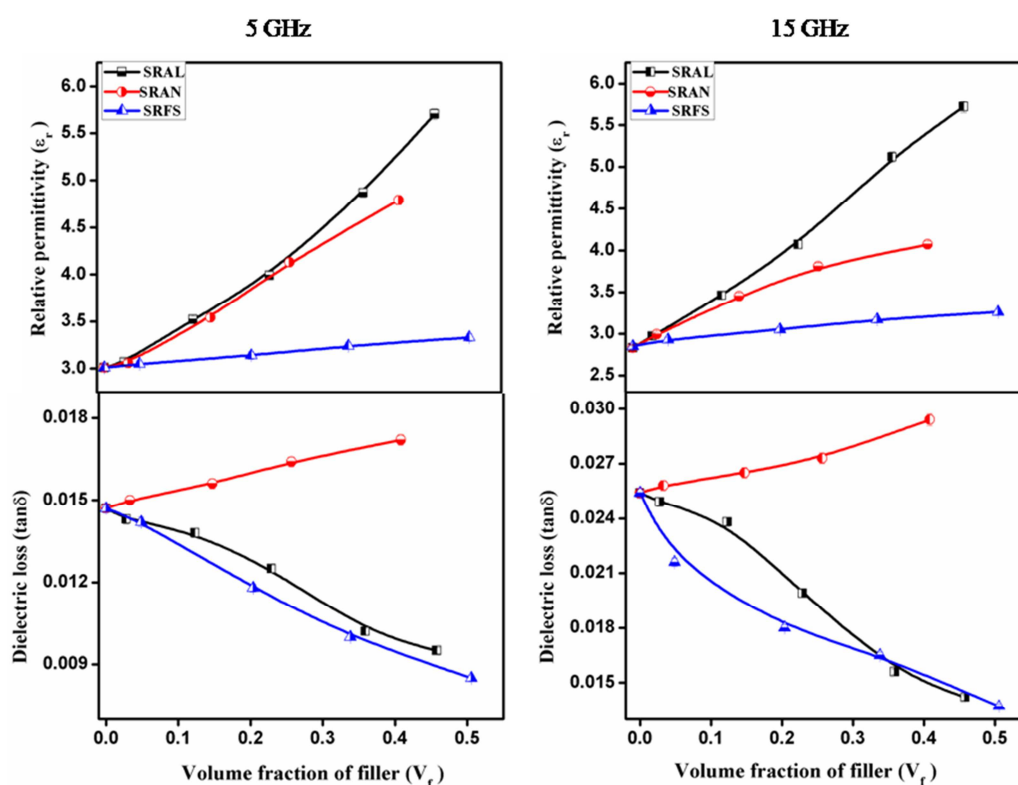
Fig.2.12 b Variations of dielectric properties of silicone rubber composites at 5 GHz and 15 GHz
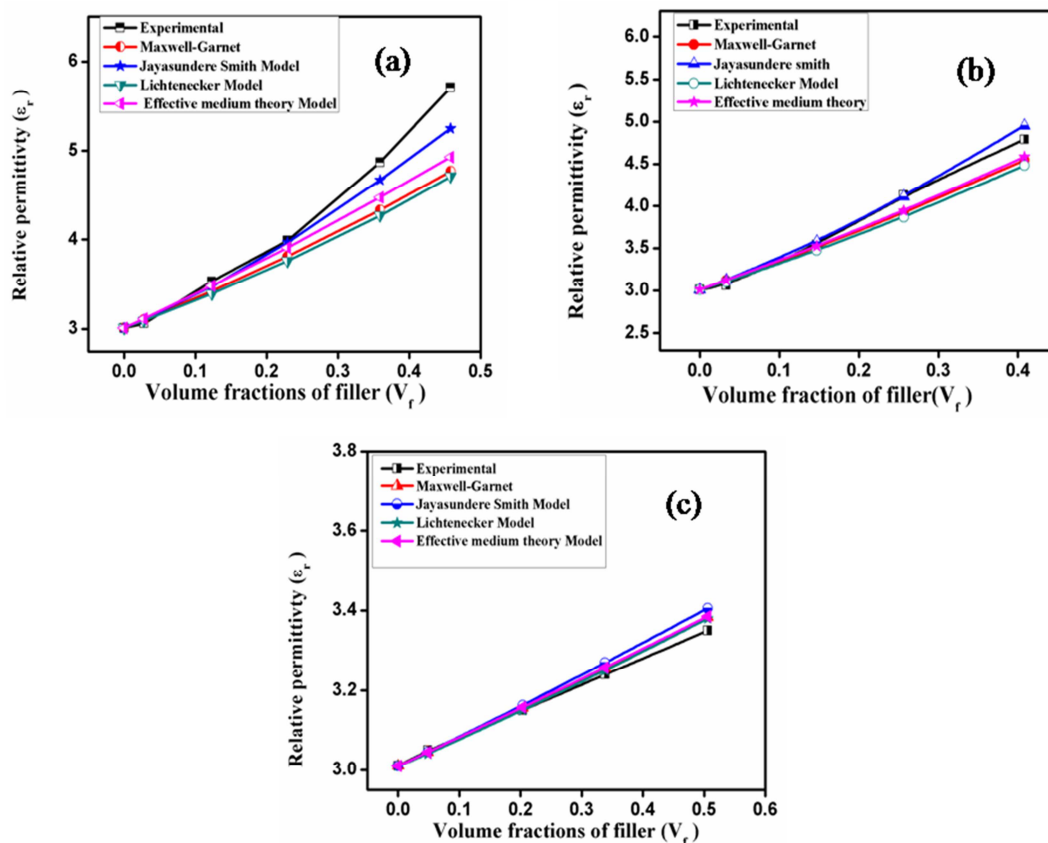
Fig.2.13 Comparison of theoretical and experimental relative permittivity of (a) SRAL (b) SRAN (c) SRFS composites at 5 GHz

The theoretical models follow certain assumptions which are related to dielectric properties of individual components, the connectivity of polymer – ceramic composites, size and shape of the filler and morphology. Figure 2.13 shows the comparison of experimentally observed relative permittivity of composites at 5 GHz in the present study with the values predicted using the equations (2.7) to (2.10). It is clear from figure 2.13 (a) that the experimental relative permittivity of SRAL composites shows slight deviations from Maxwell- Garnett and Lichtenecker equation at higher ceramic content. In Maxwell-Garnett model, only the excitation of dipolar character is considered to be important and the correlations between these excitations are not taken into account. The multipolar contributions to the local field are also neglected. But these assumptions are valid only in dilute systems [Claro et al., 1991]. Hence, Maxwell-Garnett equation shows deviation at higher filler content. The most widely used relation for the prediction of ε_r is Lichtenecker's

logarithmic law of mixing. It considers the composite system as randomly oriented spheroids that are uniformly distributed in a continuous matrix. The deviation of experimental ε_r of the composites from Lichtenecker's equation at higher filler loadings may be due to the lack of consideration of interfacial interaction between the polymer and the filler particles. The EMT model is also in agreement with experimental ε_r of the composite at lower filler loadings and shows deviation at higher filler content. The deviation of all theoretical models at higher filler loading is due to the imperfect dispersion of filler particles in the silicone rubber matrix. The Jayasundere-Smith equation considers the particulate filled composite as a binary system and is valid only when $\varepsilon_f \gg \varepsilon_m$ where ε_f and ε_m is the relative permittivity of filler and matrix respectively. The Jayasundere-Smith equation is in agreement with experimental data since this equation considers the interactions between the fields of neighbouring filler particles. Fig. 2.13 (b) shows the comparison of experimentally observed relative permittivity of SRAN composites with theoretical models. It is evident from the figure that the values of ε_r predicted by Maxwell-Garnett equation shows considerable deviation from the experimental values of SRAN composites except at very low filler loading. As the interparticle distance decreases with the increase in filler volume fraction, Maxwell-Garnett formula may not yield accurate results. Lichtenecker's equation is valid upto a volume fraction of 0.15 and shows deviation at higher AlN loading. This may be due to the lack of consideration of interfacial interaction between the polymer and the filler particles. The experimental relative permittivity of SRAN composites shows deviation with EMT model at higher filler loading. The 'n' value is determined empirically and the 'n' value for SRAN composite is 0.3. The Jayasundere-Smith equation is in agreement with experimental data since this equation considers the interactions between the fields of neighbouring filler particles. Figure 2.13(c) reveals that the experimental relative permittivity of SRFS composites are in agreement with theoretical models upto a filler loading of 0.35 V_f and shows deviation at higher silica content. Among the theoretical models, the EMT model is matching well with the experimental results. EMT model considers the composite as an effective medium in which random unit cell (RUC) is embedded. The importance of EMT model is that shape of the filler particles is taken into account through the morphology factor 'n' in calculations.

Therefore no restrictions are imposed on the shape of the particles to be used. The shape factor, 'n' for SRFS composites is 0.3, which is in agreement with earlier reports [Rao et al., 2000].
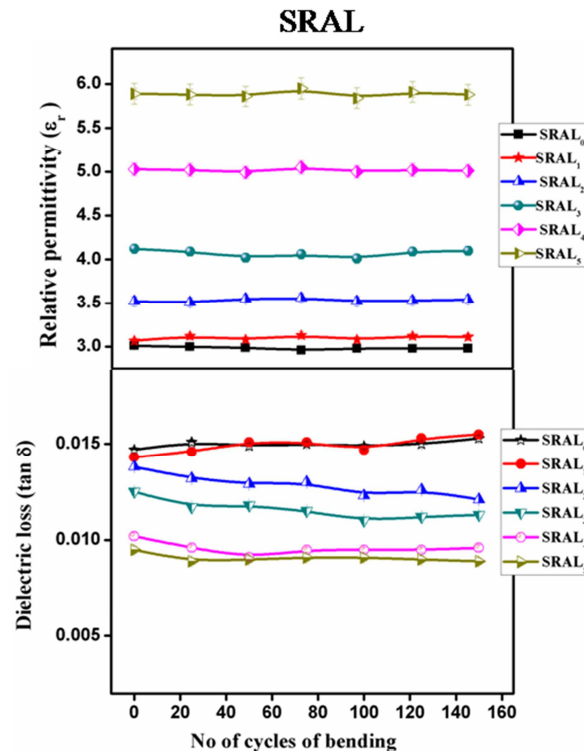
Fig.2.14 a Variation of dielectric properties of SRAL composites with bending

The bending effect on dielectric properties is important as far as flexible electronic applications concerned. The effect of bending on microwave dielectric properties of SRAL, SRAN and SRFS composites is shown in figure 2.14 a & b. It is clear from the figure that the relative permittivity of all the composites is nearly independent of bending. Also it is evident that the dielectric loss of the composites shows slight variation with bending. But the variation is only marginal. Hence, these composites are suitable for flexible electronic application [Ward et al., 2003].
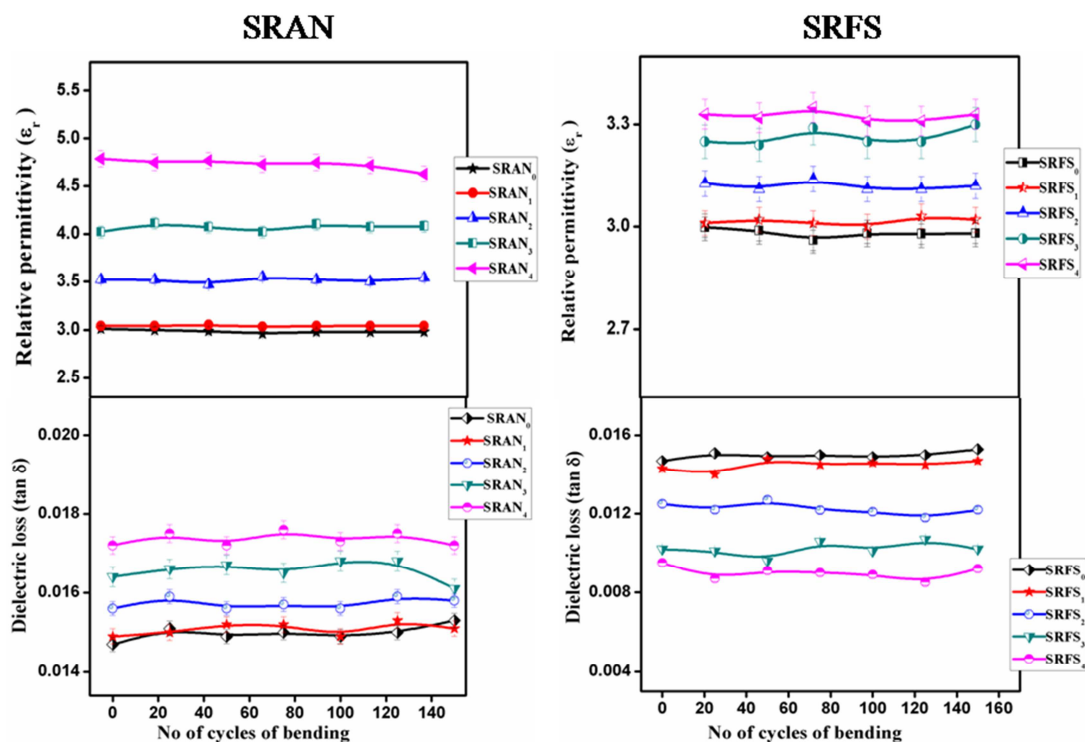
Fig.2.14 b Variation of dielectric properties of SRAN and SRFS composites with bending

The thermal stability of relative permittivity is one of the important properties of the substrate materials that control the overall performance of the materials. Figure 2.15 (a), (b) and (c) show the variation of relative permittivity of SRAL, SRAN and SRFS composites with temperature at 5GHz. From the figure it is clear that all the composites are almost thermally stable within the measured temperature range. The SRAL and SRAN composites show reasonable stability with temperature at low filler loadings but slight decrease of ε_r is observed with temperature at higher filler loading. The SRFS composite show a small decrease in relative permittivity with temperature. This may be due to the difference in the thermal expansion coefficient of the matrix and the filler and also due to the decrease in polarizability of dipoles with temperature [Xie et al., 2005; Berger et al., 1985]. The large difference in CTE may prevent the aggregation of the polar components and this might lead to a reduction in relative permittivity with increase

in temperature [Ward et al., 2003]. All the silicone rubber composites are almost thermally stable in the measured temperature range.
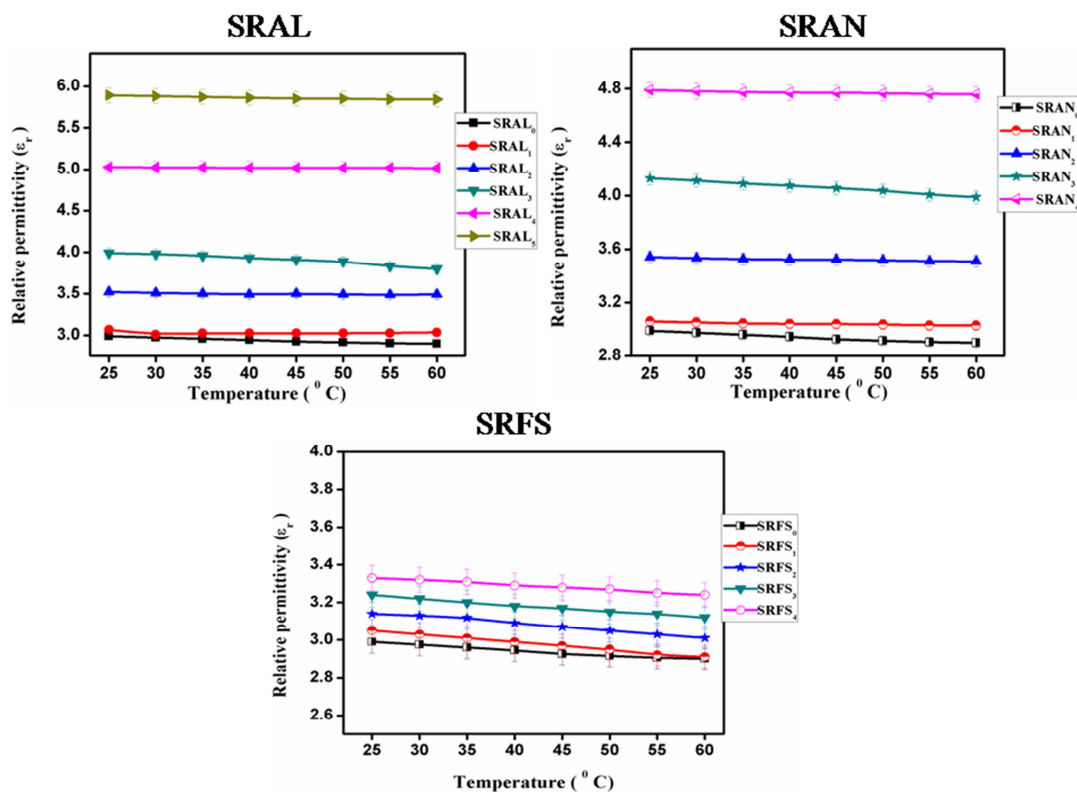
Fig.2.15 Temperature dependence of relative permittivity of (a) SRAL (b) SRAN and (c) SRFS composites at 5 GHz

The variation of coefficient of thermal expansion (CTE) of silicone rubber composites filled with Al_2O_3, AlN and fused SiO_2 are shown in figure 2.16. It is seen that the CTE of SRAL, SRAN, SRFS composites decreases with filler loading as the CTE of the fillers, alumina (7.0 ppm/°C), aluminum nitride (4.4 ppm/°C) and fused silica (0.5 ppm/°C) are lower than that of rubber matrix (266ppm/°C). In polymer-ceramic composite there exists a strong mechanical interaction between filler and matrix in the immediate vicinity of the filler particles followed by a region of loosely bound polymer chains [Goyal et al., 2007]. The filler particles will largely restrict the mobility of silicone molecule because of the entanglement of filler particles by the rubber matrix. But the thermal expansion of loosely bound polymer chains may not be that much constrained. The addition of more filler leads to the

reduction in volume of loosely bound polymer chains. Consequently the thermal expansion of the composite will get suppressed.
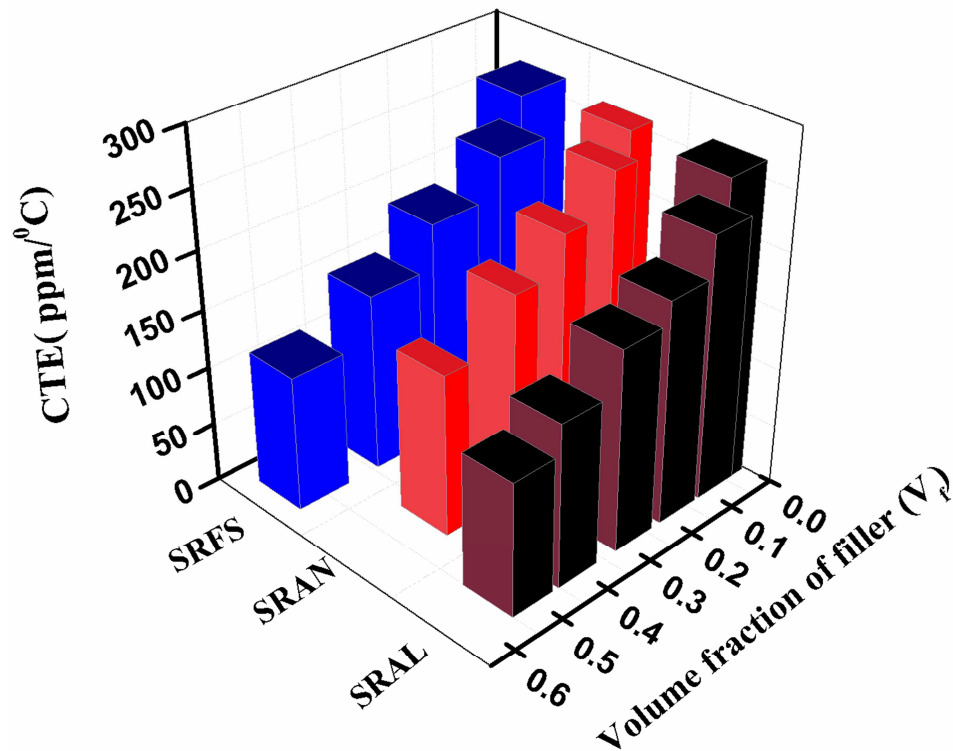
Fig.2.16 Variation of coefficient of thermal expansion of (a) SRAL (b) SRAN (c) SRFS composites with ceramic loading

Heat dissipation from integrated circuits is a crucial problem for electronic industry that affects potential miniaturization, speed and reliability. The thermal conductivity (TC) of polymers is very low, ranging from 0.14 to 0.60 $Wm^{-1}K^{-1}$ and can be improved by the addition of ceramic fillers as the TC of ceramic is higher than that of polymers [Tavman, 1998]. The thermal conductivity of silicone rubber is 0.19 $Wm^{-1}K^{-1}$. The thermal conductivity of the composites depends on the intrinsic thermal conductivities of filler and matrix, shape and size of the filler and the loading level of filler [Kemaloglue et al., 2010]. The variation of thermal conductivity of SRAL, SRAN and SRFS composites with filler content are shown in figure 2.17 a. The TC of SRAL, SRAN and SRFS composites shows increasing trend with ceramic loading. At lower filler loading the heat conductive filler

particles are surrounded by the matrix and cannot touch each other and hence thermal conductivity increases very slowly. At higher filler loading the filler particles begin to touch each other and form more compact structure. This will leads to the formation of large number of conductive channels in higher filler added composites [He et al., 2007].
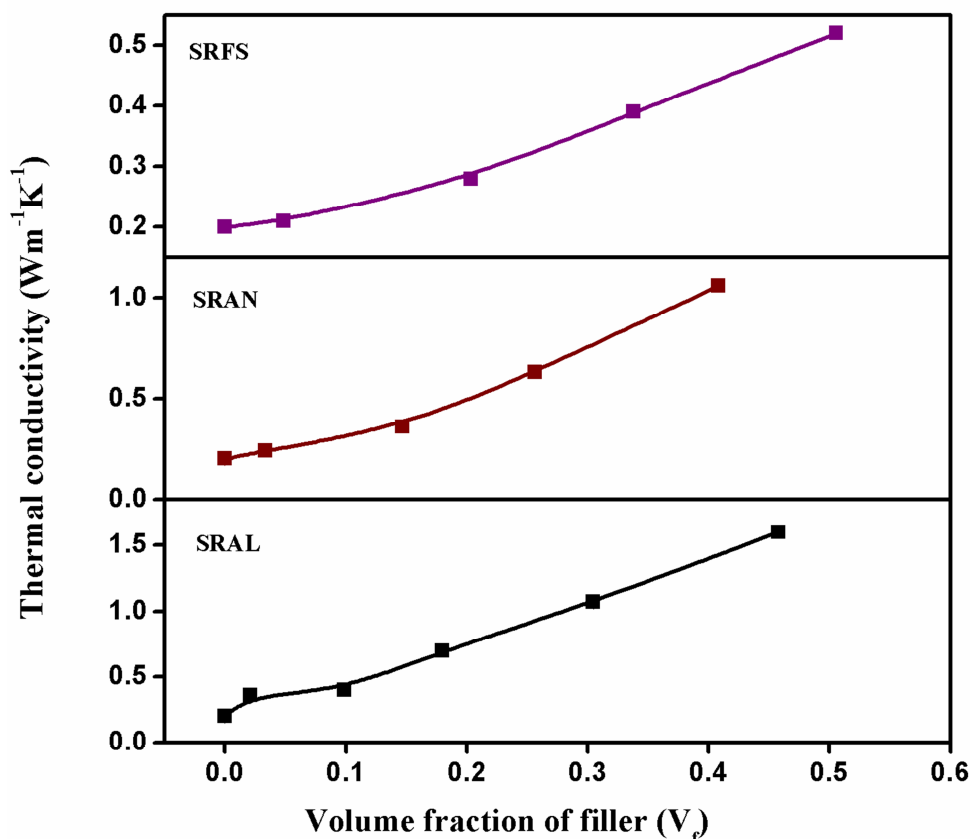
Fig.2.17 a Variation of thermal conductivity of SRAL, SRAN, SRFS composites with filler content

The variation of specific heat capacity and thermal diffusivity of SRAL, SRAN and SRFS composites with volume fraction of filler is shown in figure 2.17 b. As the ceramic content increases the specific heat capacity of the composites decreases which is due to the low specific heat capacity of the ceramic filler compared to the matrix where as the thermal diffusivity increased with filler volume fraction. Similar observation is reported in PTFE-SCT system by Subodh et al. [Subodh et al., 2008].
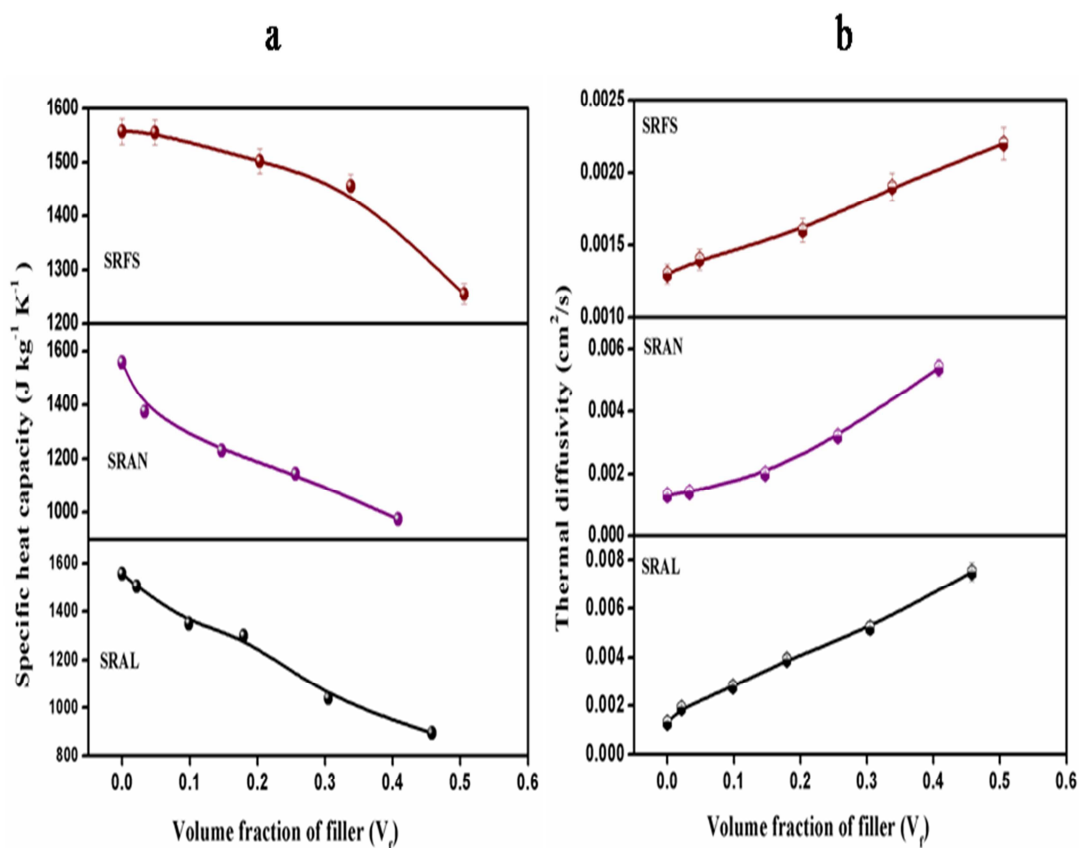
Fig.2.17 b Variation of (a) specific heat capacity and (b) thermal diffusivity of SRAL, SRAN and SRFS composites with filler content

Water absorption of the composite substrate material is very important since it adversely affects the dielectric properties of substrate for practical applications [Murali et al., 2009]. The variation in water absorption of SRAL, SRAN, SRFS composites as a function of filler loading is shown in figure 2.18. It is evident from the figure that the vol. % of water content increases with filler loading for silicone rubber composites. The increase of water absorption may be due to the increase in porosity with filler loading and the hydrophilic nature of the ceramic particles. It was reported by Laverghetta that the upper limit of moisture absorption for electronic packaging applications is 0.1 % [Laverghetta, 1984]. In the present elastomer - ceramic composites almost all the compositions lie within this limit and hence all these composites are suitable for the practical applications.
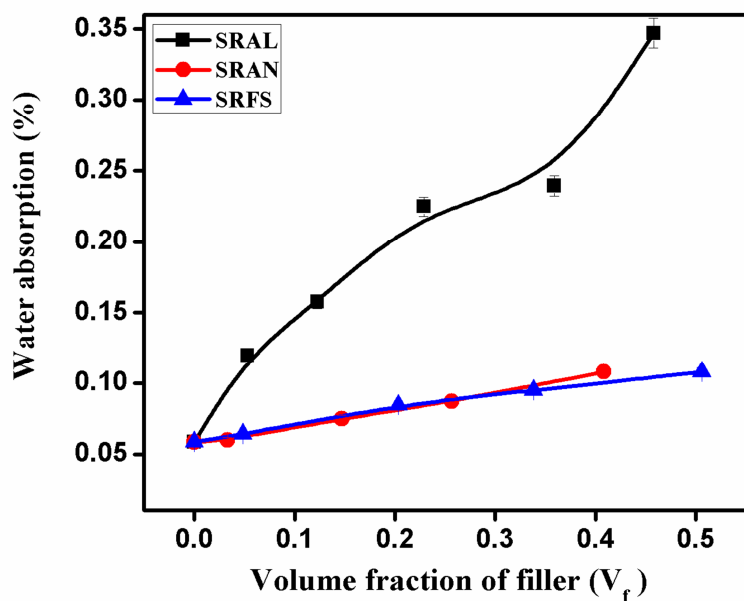
Fig.2.18 Variation of water absorption of (a) SRAL (b) SRAN (c) SRFS composites with filler loading.

2.4 Conclusions

❖ The effect of low permittivity fillers such as alumina, aluminum nitride and fused silica on the dielectric, physical, thermal and mechanical properties of silicone rubber composites is investigated.

❖ The microstructure of the composites shows uniform dispersion of filler in the matrix and also some pores are present at higher filler loading.

❖ The stress-strain curves of all composite show good mechanical flexibility of the composites. The silicone rubber - ceramic composites are bendable and stretchable.

❖ The dielectric properties of the composites are studied at radio frequency (1 MHz) as well as at microwave frequency (5 GHz and 15 GHz) and are found to be improved with ceramic loading.

❖ The SRAL composites attained ε_r = 4.87, tan δ = 0.0102 for a optimum alumina loading of 0.36 V_f, the SRAN composite have ε_r = 4.13, tan δ = 0.0164 for a optimum AlN loading of 0.26 V_f and the SRFS composite have ε_r = 3.24, tan δ = 0.0100 for a optimum alumina loading of 0.34 V_f, at 5 GHz.

❖ The composites do not show appreciable variation in microwave dielectric properties after repeated bending.

❖ The relative permittivity of the composites is found to decrease slightly with temperature.

❖ The thermal properties of the composite are also improved with filler content. The coefficient of thermal expansion decreases whereas the thermal conductivity increases with filler loading.

❖ The SRAL composites has CTE = 139 ppm/$^{\circ}$C, TC = 1.07 $Wm^{-1}K^{-1}$ and water absorption = 0.239 vol. % for an optimum loading of 0.36 V_f. The SRAN composite has CTE = 176 ppm/$^{\circ}$C, TC = 0.63 $Wm^{-1}K^{-1}$ and water absorption= 0.087 vol. % for an optimum AlN filler loading of 0.26 V_f. The SRFS composite has CTE = 153 ppm/$^{\circ}$C, TC = 0.39 $Wm^{-1}K^{-1}$ and water absorption= 0.095 vol. % for an optimum silica loading of 0.34 V_f.

❖ Various theoretical models are used to fit the experimental values of relative permittivity of all the composites.

❖ The measured properties suggest that silicone rubber - Al_2O_3, silicone rubber - AlN and silicone rubber - fused SiO_2 composites are possible candidates for flexible microwave substrate applications as well as electronic packaging applications.

CHAPTER 3

Silicone Elastomer-Medium Permittivity Ceramic Composites

This chapter deals with the synthesis and characterization of medium permittivity ceramics loaded silicone rubber composites. The fillers chosen for the current study are $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Li_2ZnTi_3O_8$. The composites possess reasonably good dielectric properties both at radio and microwave frequencies. The mechanical, thermal and dielectric properties of the composites are tailored by using ceramic fillers of medium relative permittivity by varying the filler volume fractions. The observed relative permittivity (ε_r) was compared with different theoretical models. The thermal conductivity and moisture absorption increase with filler content whereas the coefficient of thermal expansion shows a reverse trend. The study of the mechanical property showed that the silicone rubber composites are flexible and stretchable. A flexible microstrip patch antenna is designed and fabricated using suitable SR-BMT composite.

3.1 Introduction

Stretchable and flexible electronics has been one of the least exploited and hardly researched areas of the microwave electronics over the past decade. Despite its relative infancy, the field is rapidly proliferating spawning exciting and vibrant research areas, driven by new applications. Flexible electronic circuit comprises a flexible dielectric substrate on which various electronic components are assembled. Such electronic modules can be easily integrated to surfaces of any shape unlike the conventional rigid circuit boards [De Geyter et al., 2008]. Compared to flexible electronics built on non-stretchable materials, stretchable materials offer a wide range of advantages such as ability to reduce package size and weight, cost effective installation and dissipation of heat at a higher rate [Nathan et al., 2005]. Flexible electronics are increasingly being used in a number of applications which benefit from their low profile, light weight and favorable dielectric properties. The potential applications of flexible electronics are in various societal sectors, including: healthcare, the automotive industry, human – machine interfaces, mobile communications and computing platform. The flexible circuitry would be able to do many things that rigid circuits cannot. For many applications, particularly in the biomedical field and body-worn antenna, electronic circuits are to be conformally wrapped around curved surfaces. In such systems, the circuits must be not only flexible but also stretchable [Seol et al., 2008]. The current market analysis estimates that the revenue of flexible electronics can reach 30 billion USD in 2017 and over 300 billion USD in 2028 [Nathan et al., 2012]. The flexible substrates have many potential applications from neural prosthetics in the medical field to microwave devices in electronics, which provides the advantage of three-dimensional designs of conformal structures [Yang et al., 2012; Gubbels et al., 2007]. The continuous evolution of smaller, lighter and faster electronics necessitated the demand for new materials which can satisfy the requirements of today's electronics. The requirements of a material to be used as a flexible dielectric are good mechanical flexibility, high thermal conductivity and low coefficient of thermal expansion. In addition, for an ideal microwave substrate material need optimum permittivity, good

processability, low dielectric loss and low cost [Chung, 1995; Garrou et al., 1998; Tian, 2003]. Several ceramics with excellent microwave dielectric properties especially low dielectric loss (or high quality factor) and low relative permittivity have been reported in the literature [Sebastian, 2008; Oshato et al., 2006; Surendran et al., 2005, George et al., 2010]. The proper selection of individual components is very important for achieving the balanced electrical, thermal and mechanical properties of polymer – ceramic composites. Extensive research is being done in the field of microwave dielectric properties of low permittivity filler–polymer composite.

Recently elastomer-ceramic composites have been found to be most promising candidates for flexible electronic applications. Elastomers play a vital role in electronic packages as a result of their ease of processing, low cost, low relative permittivity, adhesive properties etc., but their low thermal conductivity and high coefficient of thermal expansion limit their substrate application. Ceramics are well known for their high ε_r, high thermal conductivity and low thermal expansion even though they are very brittle. Hence polymers or ceramics as such have limitations for substrate application [Sebastian, 2008]. By combining the ceramics and elastomer we can improve or alter the properties of elastomer suitable for substrate application. A key advantage of composite is its ability to prepare a significant range of relative permittivity by controlling the ceramic mixture suitable for various applications. Therefore elastomer filled with low loss ceramics is suitable for electronic packaging applications [Sebastian et al., 2010; Chameswary, 2014].

Among the available elastomers silicone rubber has a prominent position due to its unique properties such as good dielectric properties, high binding energy, high elasticity, resistant to extreme environments, biocompatibility and physiologically inert character [*http://www. Silicone.jp/*]. Silicone rubbers are quite flexible above their glass transition temperature and have excellent elasticity. The high binding energy of the silicon-oxygen bond (445 kJ /mol) makes them chemically stable even at high temperatures. The availability of medium dielectric substrates is limited. In order to

improve the microwave circuit design flexibility, there is a perceived need to develop medium dielectric composites with properties superior than the commercially available ones. To achieve this aim we use medium permittivity fillers like $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT), $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) and $Li_2ZnTi_3O_8$ (LZT) ceramics in the present study. BZT and BMT are the most widely studied materials in the perovskite family and are commercially produced for applications in wireless communication [Sebastian, 2008]. Recently Manu et al. reported the effect of BZT ceramic on dielectric, mechanical and thermal properties of high density polyethylene composites [Manu et al., 2013]. Chameswary et al recently studied the effect of BZT ceramic fillers on the microwave dielectric properties of butyl rubber composites [Chameswary et al., 2013]. Nijesh et al. reported that PTFE filled with 76wt % BMT ceramic attained a relative permittivity of 6.7 and a dielectric loss of 0.003 in the X-band [Nijesh et al., 2010].

Flexible substrate antennas play a key role in the integration and packaging of wireless communication devices and sensor networks [Kurian, et al., 2014]. Flexible antennas are robust, lightweight and can withstand mechanical strains up to a certain extent. In order to make the antenna flexible, alternative materials to replace existing substrates that are rigid have been considered. The basic idea is to lay a thin metal strip on top of a flexible substrate. The microstrip patch antennas are the best candidates for flexible antennas as they can be easily fabricated and are much reduced in size.

In the current study, we try to make an insight into the effect of medium permittivity fillers like BZT, BMT and LZT ceramic on the microwave dielectric, thermal and mechanical properties of mechanically flexible silicone rubber composites as a function of ceramic volume fraction. A flexible microstrip patch antenna is fabricated using suitable silicone rubber - BMT composites.

3.2 Experimental

3.2.1 Materials

In the present investigation silicone elastomer as matrix and ceramic fillers such as BZT, BMT and LZT were used for the composite preparation.

The rubber matrix used for the present study and their physical properties are mentioned in the section 2.2.1.1 and in Table 2.1.

3.2.1.1 Ceramic fillers

3.2.1.1.1 Synthesis

In the present work, ceramic fillers are prepared by conventional solid state ceramic route. The stoichiometrically weighed chemicals are mixed by wet ball milling using yttria-stabilized zirconia balls and dried. The mixtures are then calcined at appropriate temperatures and ground well. The resultant powders are used for composite preparation with silicone rubber. The raw materials used for the synthesis of $Ba(Zn_{1/3}Ta_{2/3})O_3$ are $BaCO_3$, ZnO (99.9 + %, Sigma Aldrich) and Ta_2O_5 (99.99%, Treibacher Industries) and for $Ba(Mg_{1/3}Ta_{2/3})O_3$, $BaCO_3$, $Mg(OH)_2$-4($MgCO_3$)-5H_2O (Sigma Aldrich, 99%) and Ta_2O_5 (99.99%, Treibacher Industries). The calcinations temperature for BZT is 1200°C for 4 h and for BMT is 1300°C for 4 h. High-purity Li_2CO_3, ZnO and TiO_2 (99.91%, Aldrich Chemical Company Inc., Milwaukee, WI) were used as the starting materials for the synthesis of $Li_2ZnTi_3O_8$. The LZT ceramic powders were calcined at 900°C for 4 h.

3.2.1.1.2 Barium zinc tantalate, $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT)

$Ba(Zn_{1/3}Ta_{2/3})O_3$ is a complex perovskite ceramic with $\varepsilon_r = 28$, low dielectric loss(tan $\delta \approx 1x\ 10^{-4}$) and a nearly zero temperature coefficient of relative permittivity (τ_ε=10 ppm/^{o}C). It is an ideal dielectric resonator at microwave frequencies [Kawashima et al., 1983]

3.2.1.1.3 Barium magnesium tantalate, Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ (BMT)

Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ is an exemplary, high quality factor material with medium relative permittivity ($\varepsilon_r \sim 25$) together with near zero temperature coefficient of resonant frequency. Due to the peculiar structural and micro structural characteristics, wide scatter exists (1×10^{-3} to 1×10^{-5}) in the reported dielectric loss of BMT ceramics [Ratheesh et al., 1999; Kolodiazhnyi et al., 2006].

3.2.1.1.4 Lithium zinc titanate, Li$_2$ZnTi$_3$O$_8$ (LZT)

Li$_2$ZnTi$_3$O$_8$ ceramics have $\varepsilon_r = 25.6$, dielectric loss, tan $\delta = 1 \times 10^{-3}$ and temperature coefficient of relative permittivity, $\tau_\varepsilon = 4$ ppm/°C. It has excellent physical and electrical properties. This material has the advantages like especially low cost of raw materials and lower preparation temperature.

The physical properties of ceramic fillers are given in Table 3.1.

Table 3.1 Physical properties of ceramic fillers

Material	Density (g/cm^3)	Avg.particle size (μm)	Relative permittivity ε_r	Dielectric loss tan δ	Coefficient of thermal expansion (ppm/°C)	Thermal conductivity (Wm^{-1}K^{-1})
Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$	7.95	0.75	28.0	10^{-4}	4.2	3.9
Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$	7.63	0.55	25.0	10^{-4}	8.0	4.5
Li$_2$ZnTi$_3$O$_8$	3.97	0.70	25.6	10^{-3}	11.7	5.4

3.2.1.2 Silicone rubber-ceramic composite preparation

The compounding of silicone rubber composites was done by sigma blend method using a kneading machine discussed in section 2.2.1.3.

3.2.2 Characterization

The phase purity of the synthesized ceramics was analyzed using XRD analysis mentioned in the section 2.2.2.1. The microstructure, dielectric, thermal and mechanical properties of developed composites were characterized using techniques explained in section 2.2 and sub sections of chapter 2.

3.2.2.1 Fabrication and characterization of microstrip patch Antenna

In the current study, the microstrip patch antenna design is done by using Ansoft HFSS (High Frequency Structure Simulator). HFSS is a commercial finite element method solver for electromagnetic structures from Ansys. It is one of several commercial tools used for antenna design and the design of complex RF electronic circuit element including filters, transmission lines and packaging. HFSS is commonly used as a software package for electromagnetic modeling and analyzing 3D structures. A microstrip patch antenna is designed and fabricated on $SRBM_3$ composite substrate having relative permittivity of 4.75 and thickness 0.0122 mm in the present study. The antenna is fabricated by screen printing technique. Commercially available silver ink is used for screen printing the antenna design. To provide a planar nature and cost effectiveness, here a microstrip feeding technique was used to feed the antenna. The reflection coefficient of fabricated antenna was characterized using HP8510C vector network analyzer and far field radiation characteristics were measured in anechoic chamber (Department of Electronics, CUSAT).

3.3 Results and discussion

Silicone rubber reinforced with medium permittivity fillers like BZT, BMT and LZT. These composites were prepared by sigma mixing in a kneading machine. The uniform mixtures thus obtained were then hot pressed at 200°C for 90 minutes under a pressure of 2 MPa with appropriate dies. The sample designation and corresponding ceramic volume fraction are given in Table 3.2. The density of LZT ($\rho \approx 3.97$ g/cm^{-3}) is lower than that of BZT ($\rho \approx 7.96$ g/cm^{-3}) and BMT ($\rho \approx 7.63$ g/cm^{-3}). Hence, the LZT

filled composites were prepared upto a loading of 0.36 V_f (200 phr) and that of SRBZ composites upto a filler loading of 0.29 V_f (300 phr) and SRBM composites up to 0.23 V_f (200 phr). The mixing became more difficult at higher loadings due to filler agglomeration [Hu et al., 2007].
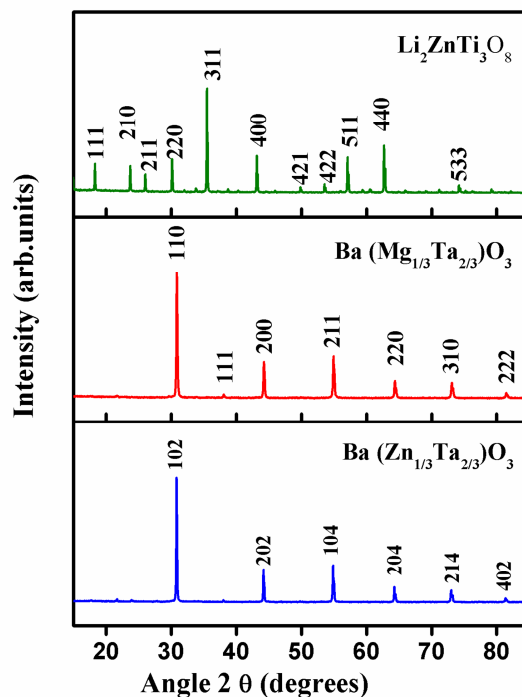
Fig.3.1 XRD patterns of (a) BZT (b) BMT and (c) LZT

The phase purity of the ceramics BZT, BMT and LZT was analyzed by XRD and is shown in figure 3.1. The peaks were indexed based on the JCPDS file 70-0197 for BZT, 18-0176 for BMT and 86-1512 for LZT respectively and the phase purity of the ceramic powders were confirmed. The diffraction peak positions exactly match with standard data without any secondary phases.
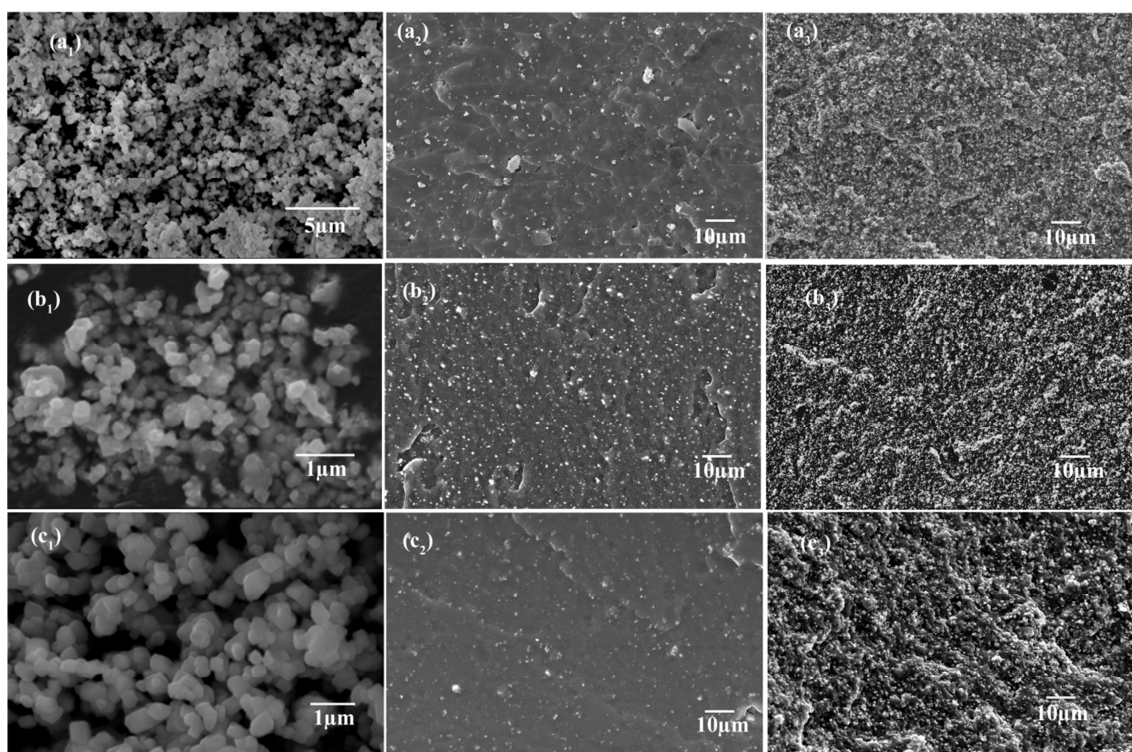
Fig.3.2 SEM images of (a$_1$) BZT (b$_1$) BMT (c$_1$) LZT ceramics, (a$_2$), (b$_2$) and (c$_2$) fractograms of low filler loaded composites and (a$_3$), (b$_3$) and (c$_3$) fractograms of higher filler loaded SRBZ, SRBM and SRLT composites respectively.

Figure 3.2 shows microstructure of BZT, BMT, LZT ceramic and their composites with silicone rubber. The SEM images of BZT, BMT and LZT ceramic powder was depicted in figure 3.2 (a$_1$), (b$_1$) and (c$_1$) respectively. Figure.3.2 (a$_2$), (b$_2$) and (c$_2$) shows the fractured surface of lower filler loaded composites whereas (a$_3$), (b$_3$) and (c$_3$) shows the fractograms of higher filler loaded composites respectively. A homogenous dispersion of filler particles in the matrix can be seen from the figures even though some pores are present at higher filler loading due to the agglomeration of filler particles.

Table 3.2 The formulations of silicone rubber composites (Ingredients in phr [a])

Composite material	Sample designation	Silicone rubber in phr[a]	Dicumyl peroxide (DCP) in phr[a]	Filler in phr[a] [][b]
Silicone rubber-Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ (SRBZ)	SRBZ$_0$	100	2	0[0]
	SRBZ$_1$	100	2	10[0.014]
	SRBZ$_2$	100	2	50[0.066]
	SRBZ$_3$	100	2	100[0.124]
	SRBZ$_4$	100	2	200[0.220]
	SRBZ$_5$	100	2	300[0.299]
Silicone rubber-Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ (SRBM)	SRBM$_0$	100	2	0[0]
	SRBM$_1$	100	2	10[0.015]
	SRBM$_2$	100	2	50[0.072]
	SRBM$_3$	100	2	100[0.134]
	SRBM$_4$	100	2	200[0.233]
Silicone rubber-Li$_2$ZnTi$_3$O$_8$ (SRLT)	SRLT$_0$	100	2	0[0]
	SRLT$_1$	100	2	10[0.028]
	SRLT$_2$	100	2	50[0.125]
	SRLT$_3$	100	2	100[0.222]
	SRLT$_4$	100	2	200[0.363]

[a]Parts per hundred of rubber [b]Volume fractions of filler given in parenthesis

The stress - strain curves of SRBZ,SRBM and SRLT composites are shown in figure 3.3. It has been reported that the stress-strain curves for particle filled rubber systems are affected by the crosslink density of the rubber matrix, the size of agglomerates and rubber - filler interactions [Yatsuyanagi et al., 2002]. Addition of large amount of filler ceramic degrades the flexibility. Todorova et al. reported that the interfacial adhesion increases with filler loading which in turn increases the effectiveness of the stress transfer from rubber chains [Todorova et al., 2008]. From the figure, it is clear that the stress for the same elongation is larger for ceramic filled composite as compared to pure silicone rubber. The uniformity in filler distribution has efficiently hinders the chain movement during deformation. This mechanism will increase the stiffness of the composites as well as tensile strength [Zhou et al., 2007].
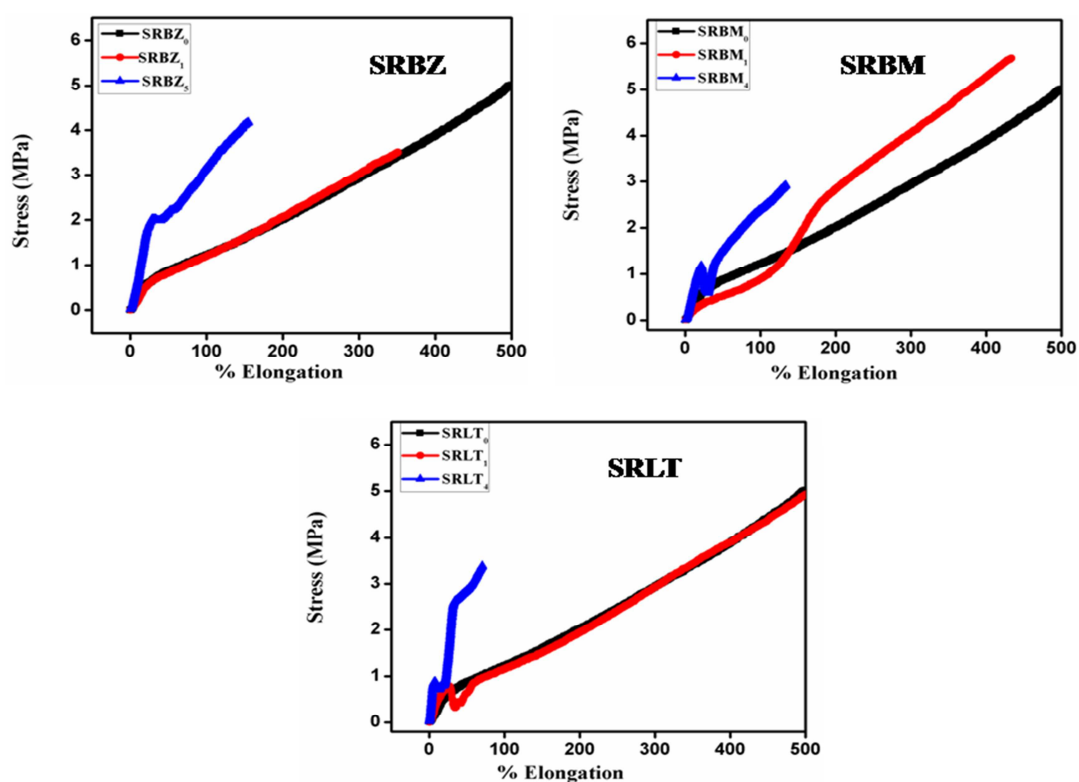
Fig.3.3 Stress-strain curves of SRBZ, SRBM and SRLT composites

Polymer – ceramic composites with low relative permittivity are needed for microwave substrate applications since low relative permittivity will increase the signal transmission speed. Figure 3.4 a shows the variation of dielectric properties of the developed composites with filler loading at radio frequency (1 MHz). From the figure it is clear that relative permittivity of the composites increases with filler loading where as the dielectric loss decreases with filler loading. The increase in the relative permittivity of composite is expected since; the particulate filler has much higher relative permittivity compared with that of the rubber matrix. The variation of relative permittivity of rubber - ceramic composite with respect to the filler concentration can be attributed to an increase in the total polarizability of the composite material. Dielectric loss decreases as the filler volume fraction increases, which is due to the lower dielectric loss of ceramic filler compared to the silicone rubber matrix.
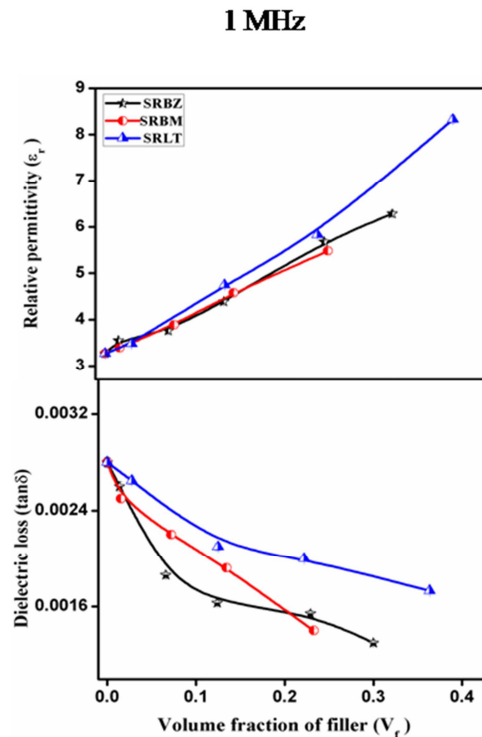
1 MHz

Fig.3.4 a Variations of dielectric properties of silicone rubber composites at 1 MHz
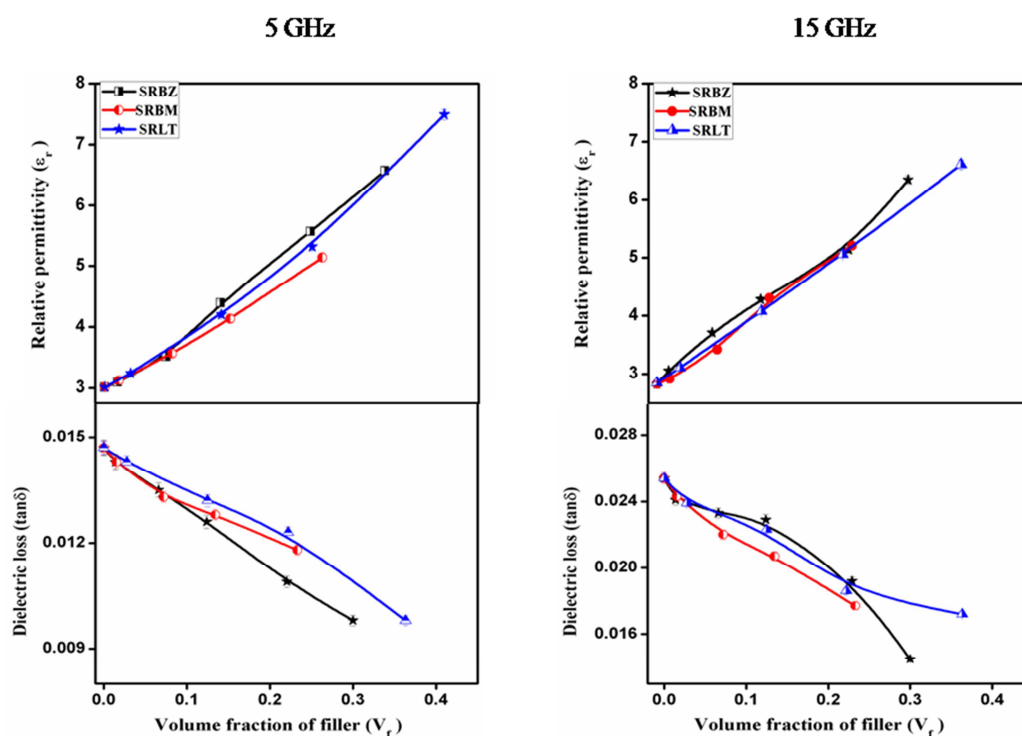
Fig.3.4 b Variations of dielectric properties of silicone rubber composites at 5 GHz and 15 GHz

Figure 3.4 b shows the variation of relative permittivity and dielectric loss of SRBZ, SRBM and SRLT composites with filler loading at 5 GHz and 15 GHz respectively. The variation of both relative permittivity and dielectric loss at microwave frequencies with the volume fraction of the filler follows asimilar trend to that observed at radio frequncey. The Maxwell–Wagner-Sillars effect appears generally in heterogeneous media due to the accumulation of charges at the interface which leads to the formation of large dipoles [Smaoui et al., 2009]. Hence the relative permittivity increases with ceramic loading. The dielectric properties of the composites do not show appreciable differences at 5 GHz and 15 GHz. since there is hardly any change in the polarization mechanism [Zhou et al., 2012]. The dielectric loss is the primary factor affecting the frequency selectivity of materials. The effect of low dielectric loss of ceramic fillers is more pronounced than the increase in inhomogeneity of the samples with increase in filler content. Hence the dielectric loss decreases with filler loading.

Subodh et al. also observed similar trend in $Sr_9Ce_2Ti_{12}O_{36}$ ceramic filled epoxy composites [Subodh et al., 2009].

One of the attractive features of the composites is that their dielectric properties can be designed by varying the volume fraction of the filler. Hence the prediction of effective dielectric behavior of the composite is important as far as its application in electronic packaging is concerned. The experimental value of relative permittivity of composites are compared with the theoretical values predicted by several equations like Maxwell - Garnet, Jayasundere – Smith, Lichtenecker and EMT model given in equations (2.7) to (2.10) in chapter 2. Figure 3.5 shows the comparison of experimentally observed effective relative permittivity with the values predicted using the equations. The variation of effective permittivity of all the composites obtained using numerical equations shows the same trend as experimentally observed results. It is found that the Maxwell-Garnet, Jayasundere-Smith and Lichtenecker models are valid for low volume fraction of filler loading whereas the EMT model is found to match with experimental values for SRBZ, SRBM and SRLT composites. The morphology factor 'n' for EMT model is found to be 0.23, 0.24 and 0.20 for SRBZ, SRBM and SRLT composites respectively. The composite morphology exhibit a homogeneous distribution of the dispersed component. Generally, the theoretical predictions are valid for lower volume fraction of filler loading. This is due the imperfect dispersion of ceramic particle in rubber matrix [Anjana et al., 2008; Rajesh et al., 2008; Subodh et al., 2009]. Many theoretical models suggest that the filler particles in a material should ideally be separated, non-interacting and roughly spherical [Stroud, 1979]. Bai et al reported that in PMN-PT-polymer composite system the failure of theoretical predictions at higher filler loading could be either due to increase in porosity or the filler particle clustering [Bai et al., 2000]. The effective permittivity of the composite depends on the permittivity of each phase in the mixture, volume fractions, shape, size, porosity, interface polarizabiliy and interface volume fractions [Todd et al., 2003].
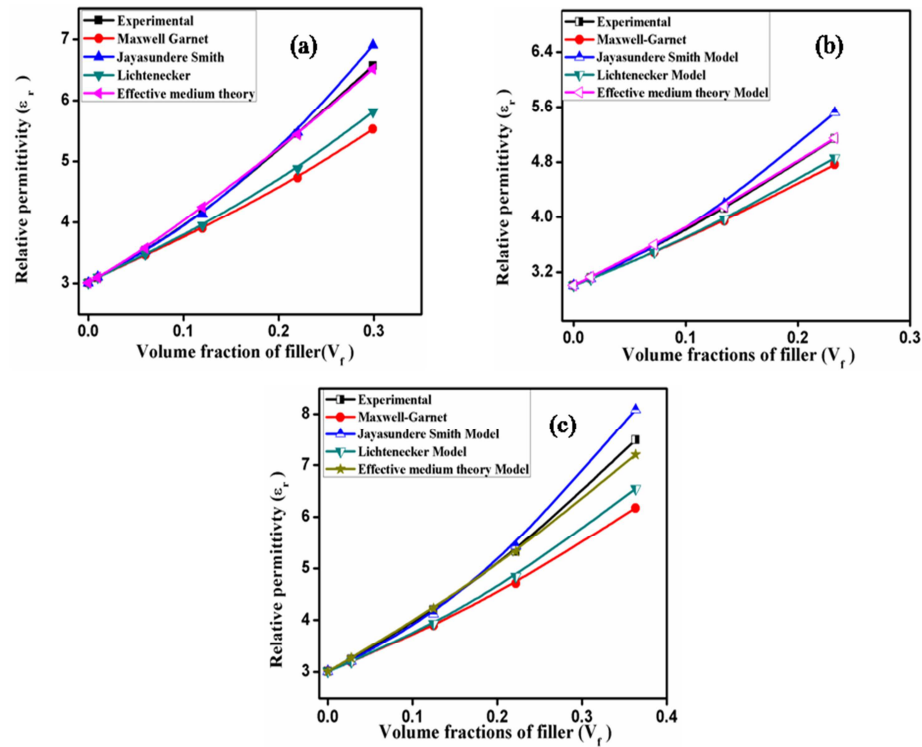
Fig.3.5 Comparison of theoretical and experimental relative permittivity of (a) SRBZ (b) SRBM (c) SRLT composites at 5 GHz

The microwave dielectric properties of all the composites after repeated bending by an angle of 180° are shown in figure 3.6. From the figure it is clear that the relative permittivity of SRBZ, SRBM and SRLT composites is independent of bending. The dielectric loss of all the composites shows only small variation with repeated bending. In an undeformed sample, there would be a small amount of rubber trapped within the filler network losing its identity as elastomer. The cyclic deformations would breakdown this trapped rubber making the matrix more homogeneous. Consequently the effective filler volume fraction would decrease [Ward et al., 2003]. At higher volume fractions of filler, since the possibility for particle agglomeration is high, this effect will be more distinguishable. Because of this effect the dielectric loss shows the slight variation but this is marginal only.
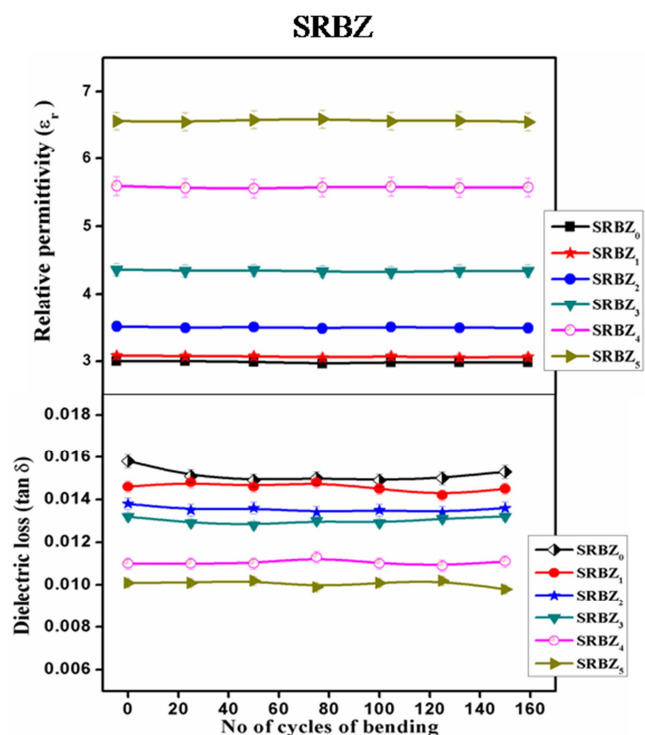
Fig.3.6 a Variation of dielectric properties of SRBZ composites with bending
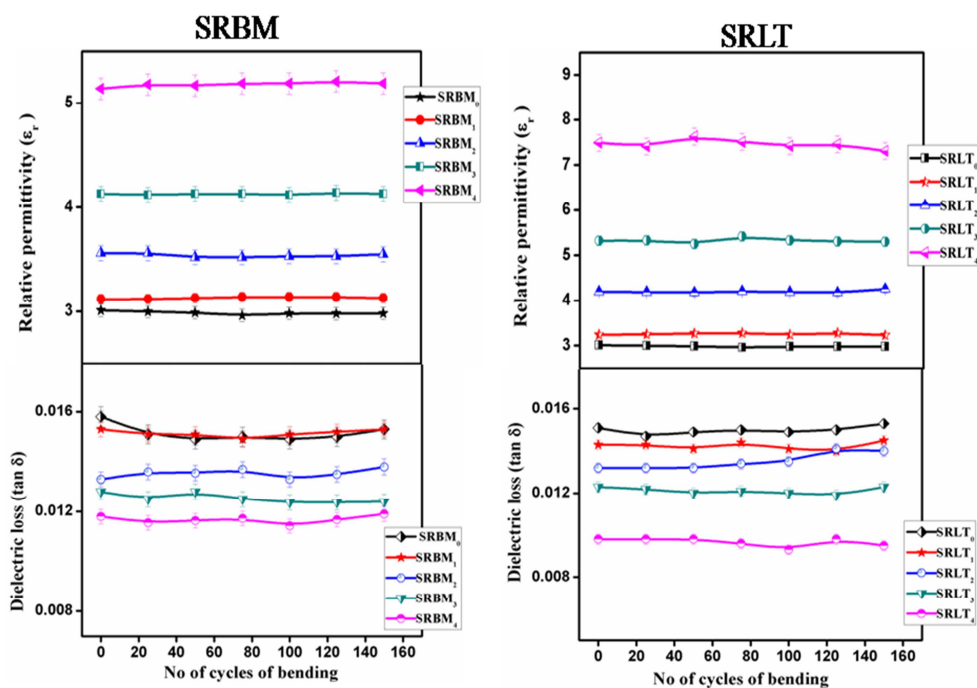
Fig.3.6 b Variation of dielectric properties of SRBM and SRLT composites with bending

Figure 3.7 illustrates the variation in relative permittivity of SRBZ, SRBM and SRLT composites as a function of temperature. The drift in relative permittivity with temperature should be small for practical applications. It is found that the relative permittivity of the composites decrease with temperature and this may be due to the decrease in polarizability of dipoles with temperature and also due to the difference in CTE of rubber and filler [Hench et al., 1990]. It is worth to be noted that all the composites were found to be almost thermally stable within the measured temperature range.
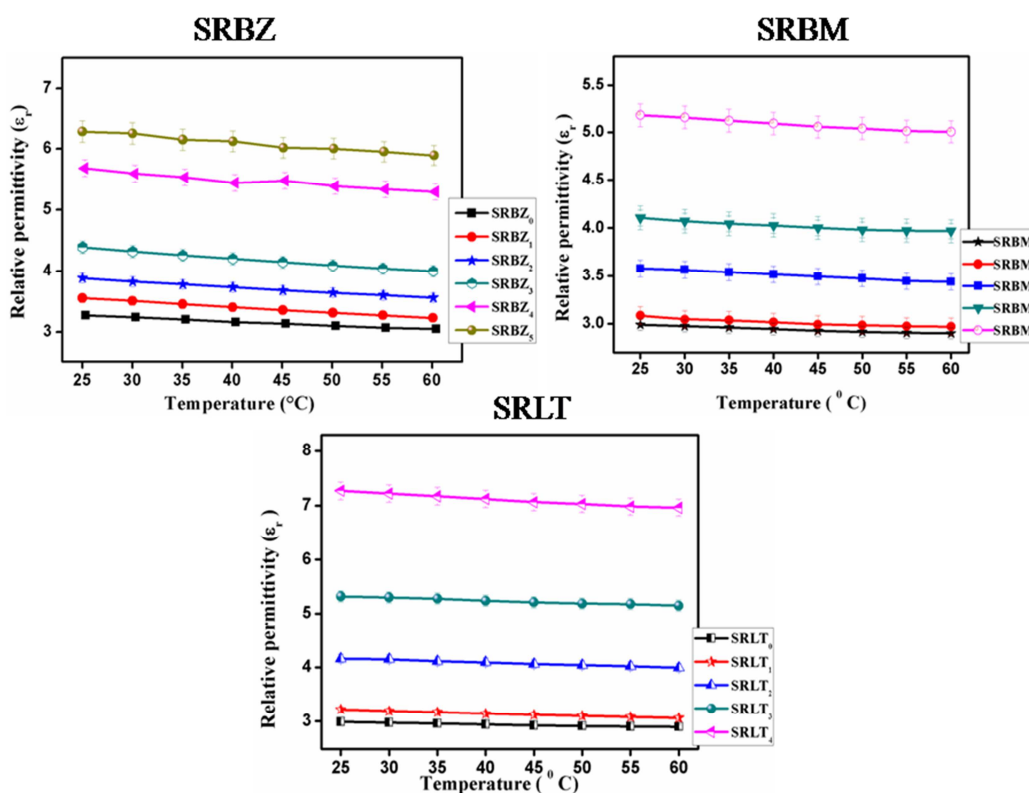
Fig.3.7 Variation of relative permittivity of (a) SRBZ (b) SRBM (c) SRLT composite as a function of temperature

The large value of CTE of polymers is caused by the low energy barrier to change the chain conformation and this high CTE precludes polymers from practical

applications [Rao et al., 2008]. The variation of coefficient of thermal expansion of silicone rubber composites with filler content is given in figure 3.8. It can be observed from figure that, the coefficient of thermal expansion (CTE) of elastomer - ceramic composite decreases with increases in the filler loading. This is due to the relatively low thermal expansion of ceramic compared to the rubber matrix. The free volume of polymer decreases as the ceramic loading increases and thereby thermal expansion of the composite is suppressed [Goyal et al., 2013].
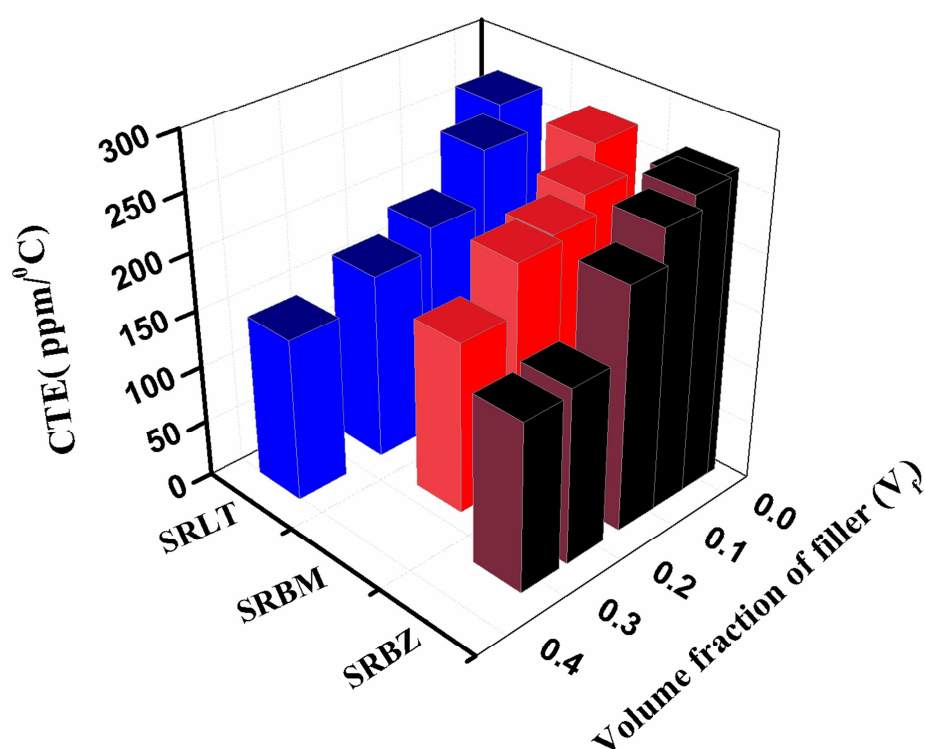
Fig.3.8 Variation of coefficient of thermal expansion of (a) SRBZ, (b) SRBM (c) SRLT composites with ceramic loading

The thermal conductivity of polymers seems to be improved by the ceramic fillers as they act as conducting channels with lower thermal resistance than the matrix. The thermal properties of the composites are influenced by dispersion and orientation of the filler particles, the filler aspect ratio, the relative ratio of thermal conductivity of the filler and the matrix etc. The variation of thermal conductivity of SRBZ, SRBM and

SRLT composites with filler content are shown in figure 3.9 a. It can be observed in the figure that the thermal conductivity of the composite increases with ceramic loading. This is due to the slightly higher conductivity of the filler ceramics compared to rubber and also due to the heterogeneity of the composites. As the filler content increases, the filler particles begin to touch each other and thermally conductive networks were formed throughout the system and this leads to the rise in thermal conductivity of the composites.
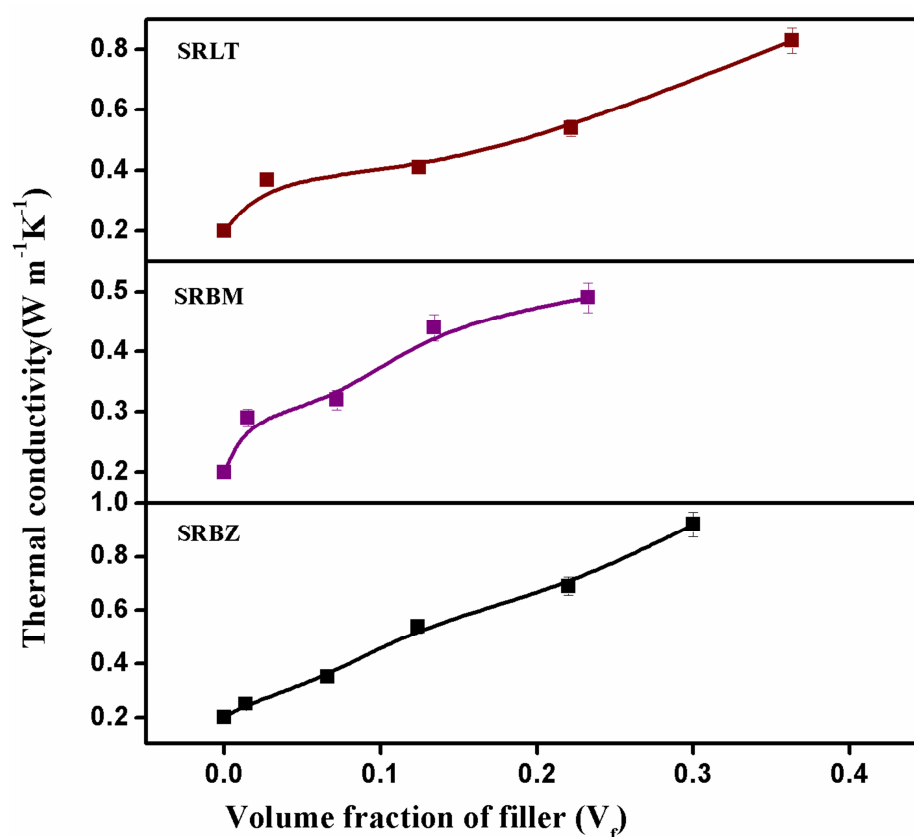
Fig.3.9 a Variation of thermal conductivity of (a) SRBZ (b) SRBM (c) SRLT composite with ceramic loading

Figure 3.9 b illustrates the variation of specific heat capacity and thermal diffusivity with ceramic loading. The specific heat capacity of the silicone rubber composites decreased with increasing ceramic content. This was due to the low specific

heat capacity of the ceramic fillers. The thermal diffusivity of the composites increases with filler volume fraction, as long as the filler's thermal diffusivity exceeds that of the matrix.
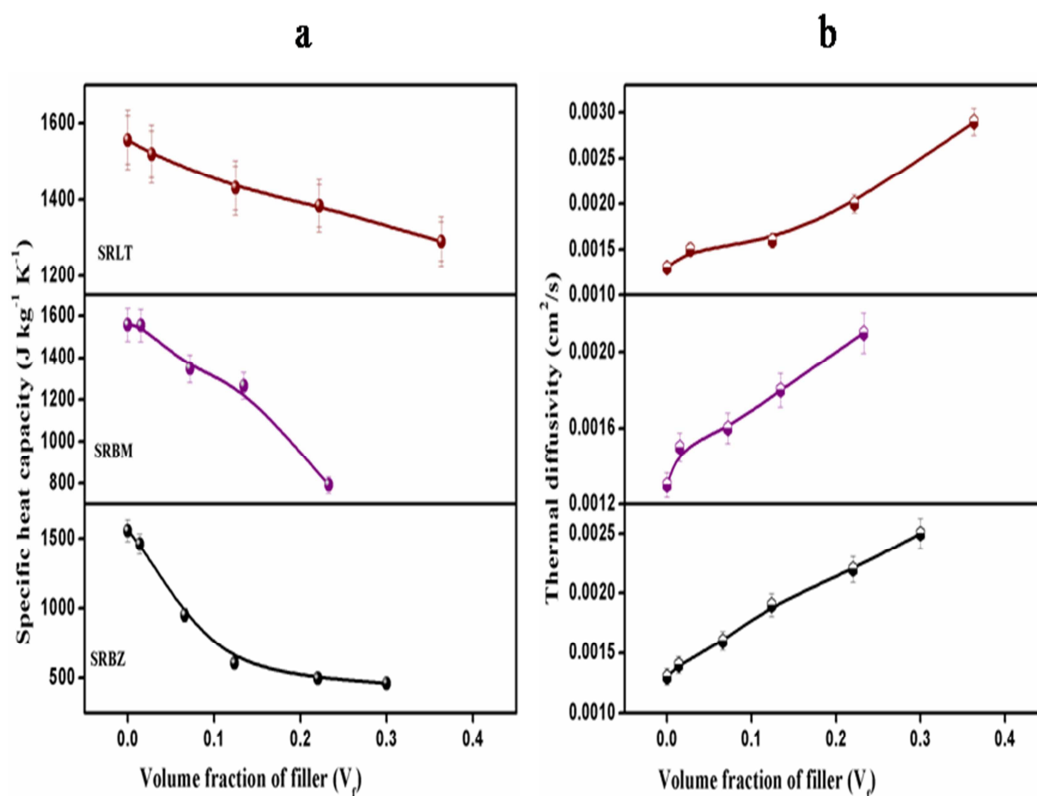
Fig.3.9 b Variation of (a) specific heat capacity (b) thermal diffusivity of SRBZ, SRBM and SRLT composite with ceramic loading

Water absorption is a major concern in polymer - ceramic composites when it comes to practical applications. The absorbed water interacts with polymer matrix and also at the filler - matrix interfaces and thus affects the dielectric properties of composites [Zhao et al., 2008]. It is evident from the figure 3.10 that as the filler content increases, the water absorption of all the composites increases gradually. This is probably due to the void formation at higher ceramic loading.
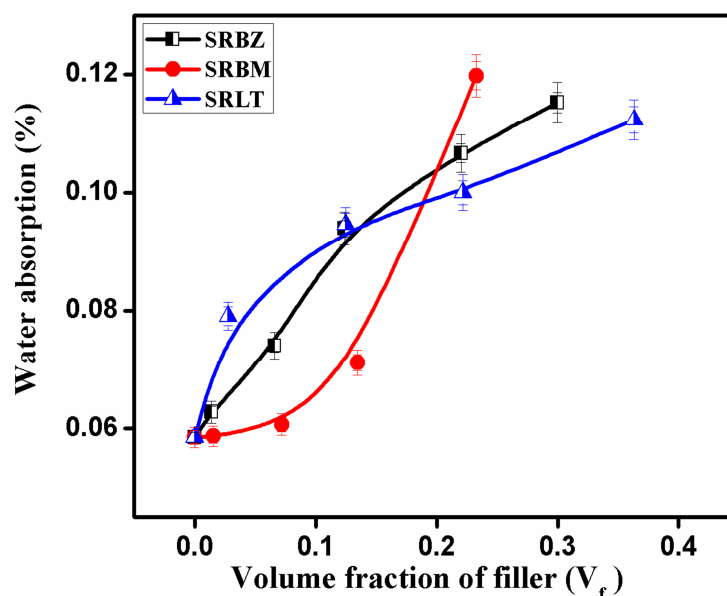
Fig.3.10 Variation of water absorption of (a) SRBZ (b) SRBM (c) SRLT composites with ceramic loading

3.4 Fabrication of flexible microstrip patch antenna using SRBM$_3$ substrate

Flexible electronics can currently be considered as a well established technology, in this context; flexible substrate antennas (FSAs) play a key role in the integration and packaging of wireless communication devices and sensor networks. Polymer-based antennas become a popular topic in the field of flexible antennas. The microstrip patch antennas are the best candidates for flexible antennas as they can be easily fabricated and are much reduced in size. The rectangular microstrip patch antenna for Wireless local area network (WLAN) was fabricated using SR-0.134 V_f BMT substrate simulated using Ansoft High Frequency Structure Simulator (HFSS). The proposed patch antenna of dimension 28 x 36 mm (see Fig.3.11) was fabricated on a cost effective and flexible SRBM$_3$ substrate with a permittivity 4.75 and thickness 0.0122 mm. The designed parameters are listed out in the Table 3.3. To provide a planar nature and cost effectiveness [Varshney et al., 2014], here a microstrip feeding technique was used to feed the antenna. The conductive patch along with feed and

ground patterns were screen printed on either sides of substrate using metalon silver ink with the aid of a screen printer. The reflection coefficient of fabricated antenna is characterized using HP8510C vector network analyzer and far field radiation characteristics were measured in anechoic chamber. The photograph of developed flexible antenna is given in figure 3.12.
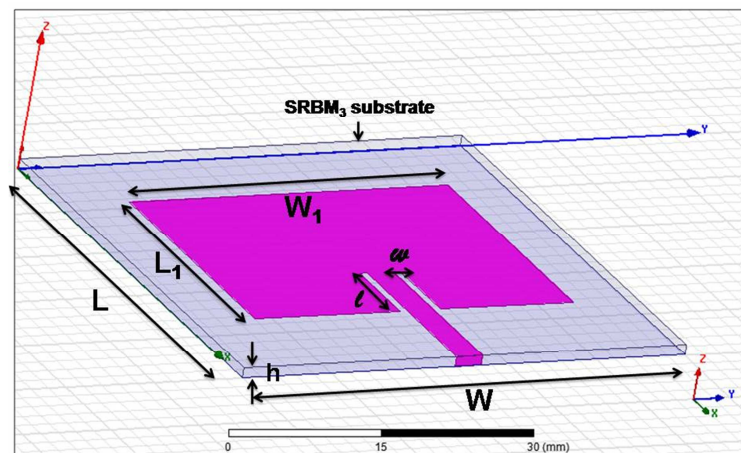
Fig.3.11 Design of proposed microstrip patch antenna
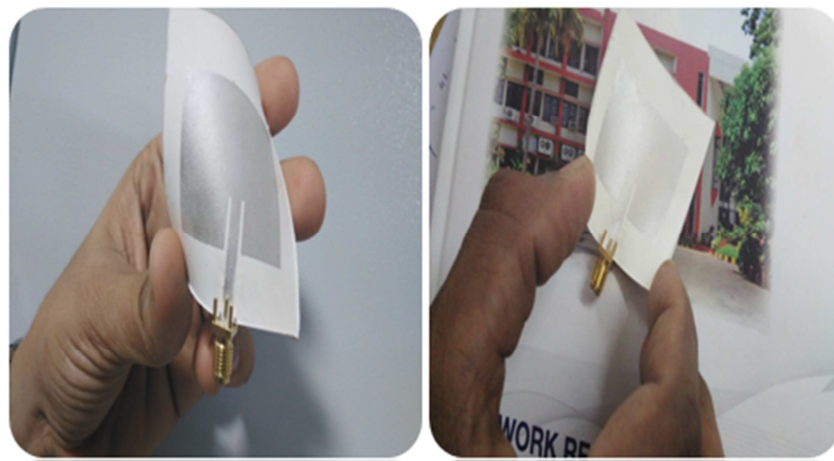
Fig.3.12 Photograph of developed flexible antenna

Table 3.3 Rectangular Microstrip Patch Antenna Specifications

Design Parameters		Dimensions
SRBM₃ substrate	Relative permittivity (ε_r)	4.75
	Dielectric Loss (tan δ)	0.0122
	Thickness (h)	1.092 mm
	Length (L)	50 mm
	Width (W)	50 mm
Rectangular patch	Length (L_1)	28 mm
	Width (W_1)	36 mm
	Inset cut depth (l)	9 mm
	Inset cut width (w)	0.8 mm
Ground	Length (L_2)	50 mm
	Width (W_2)	50 mm

Figure 3.13 a depicts the simulated and measured return loss against frequency of microstrip patch antenna on SRBM₃ flexible substrate. The fabricated microstrip patch antenna prototype is shown in the inset of figure. The fabricated antenna successfully operates at 2.48 GHz with a return loss of -12.96 dB. Although, the measured results shows reasonably fair agreement with the simulated results of microstrip patch antenna using Ansoft HFSS software. A gain of about 3.89 dB is obtained from the 3D radiation pattern of proposed patch antenna as shown in figure 3.13 b.
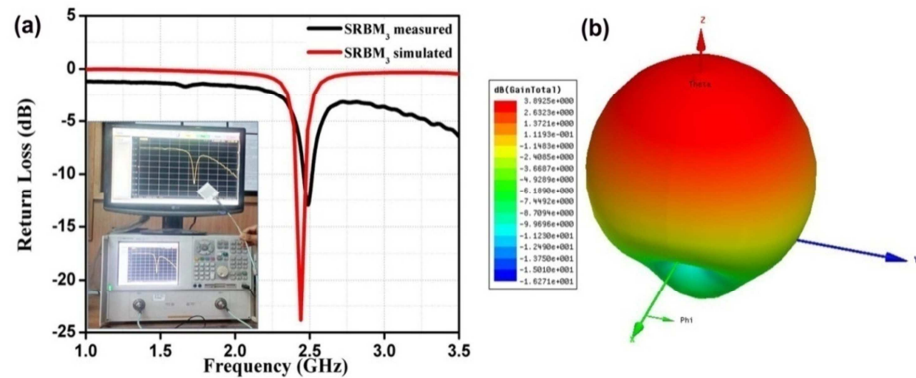
Fig.3.13 (a) Simulated and measured return loss and (b) 3D radiation pattern of microstrip patch antenna on SRBM$_3$ substrate

The figure shows measured two dimensional radiation patterns of proposed microstrip antenna. Here cross polarization and co polarization of both E plane and H plane patterns are plotted. The proposed antenna is nearly omnidirectional. The fabricated antenna exhibits linear polarization characteristics as its cross polarization level is lower than the co polarization in the radiation pattern and indicates the characteristics of standard radiation pattern [Islam et al., 2015].
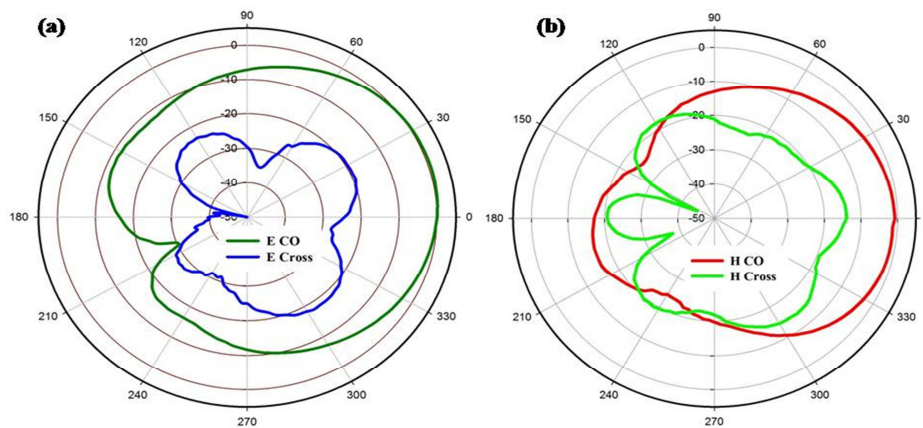
Fig.3.14 (a) E-plane and (b) H-plane radiation pattern of microstrip patch antenna based on SRBM$_3$ substrate

3.5 Conclusions

➢ The silicone rubber reinforced with medium permittivity fillers such as $Ba(Zn_{1/3}Ta_{2/3})O_3(BZT)$, $Ba(Mg_{1/3}Ta_{2/3})O_3(BMT)$ and $Li_2ZnTi_3O_8(LZT)$ ceramics and composites are prepared by sigma mixing followed by hot pressing.

➢ The dielectric, thermal and mechanical properties of these composites is investigated as a function of filler loading.

➢ The homogenous dispersion of filler particles in the rubber matrix is confirmed from the microstructural analysis of the composites.

➢ Stress-strain curves show the flexibility of the developed composites.

➢ The experimental relative permittivity of all the composites as compared with theoretical models.

➢ As the volume fraction of filler increases, the relative permittivity, thermal conductivity and water absorption increases whereas, dielectric loss and the coefficient of linear thermal expansion decrease in ceramic reinforced silicone rubber composites.

➢ For 0. 299 V_f of BZT loading, SRBZ composite has ε_r = 6.57 and tan δ = 0.0098 (at 5 GHz), CTE = 149 ppm/°C, TC = 0.92 $Wm^{-1}K^{-1}$ and water absorption = 0.115 vol %. The SRBM composites have ε_r = 5.14 and tan δ = 0.0118 (at 5 GHz), CTE = 152 ppm/°C and TC = 0.49 $Wm^{-1}K^{-1}$ and water absorption of 0.119 vol % for 0.23 V_f of BMT content and SRLT composites achieved a ε_r of 7.49 and tan δ of 0.0098 (at 5 GHz), CTE and TC of

144 ppm/°C and 0.83 $Wm^{-1}K^{-1}$ respectively and water absorption of 0.112 vol % for 0.36 V_f of LZT.

➢ A microstrip patch antenna is fabricated using $SRBM_3$ substrate and is found to be a suitable candidate for flexible microwave antenna substrate application.

➢ The maximum filler loaded composites can find applications as cladding of flexible dielectric waveguide and all other compositions can be used for microwave substrate and electronic packaging applications.

CHAPTER 4

Silicone Elastomer-High Permittivity Ceramic Composites

Rapid growth of electronic industry requires development of new materials that combine the high relative permittivity intrinsic to ferroelectric ceramic materials with easy processing characteristics of elastomer. The current chapter discuss the preparation and characterization of high permittivity fillers like $BaTiO_3$, $SrTiO_3$ and $Ca_{(1-x)}Nd_{(2x/3)}TiO_3$ filled silicone elastomer composites for flexible dielectric waveguide as well as microwave substrate applications. The dielectric properties both at radio and microwave frequencies, mechanical and thermal properties were investigated in terms of filler loading. The composites possess reasonably high permittivity values with low dielectric loss. Different theoretical approaches have been used to model the effective permittivity of elastomer - ceramic composites. The coefficient of linear thermal expansion of the composites has been observed to decrease with filler loading where as the thermal conductivity and water absorption increases. The composites show good flexibility and stretchability.

4.1 Introduction

Flexible electronics is an important research area for the next generation consumer electronics and is becoming a part of our day today life [Agnihotri et al., 2013]. The development of flexible electronic devices continues to advance at great speeds. It is increasingly being used in a number of applications which benefit from their low profile, light weight and favorable dielectric properties. Electronics on flexible substrates are becoming more useful for various devices including sensor arrays/ skins, curved circuits and other large area electronics such as flexible displays, capacitors for energy storage, EMI shielding, flexible antenna, electronic paper, low-cost radio frequency identification tags and electronic textiles [Ryu et al., 2009 ; Siegel et al., 2010; Rogers et al., 2008]. Compared to flexible electronics built on non-stretchable materials, stretchable materials offer a wide range of advantages such as ability to reduce package size and weight, cost effective installation and dissipation of heat at a higher rate. By replacing the rigid substrate with one that is mechanically flexible will enable a number of unique applications for displays, imagers and large circuits that can be conformably fitted on curved objects and surfaces as needed in biomedical imaging and structural monitoring [Nathan et al., 2005]. In addition to this the flexible materials can cover curved surfaces and movable parts [Siegel et al., 2010]. The stretchable circuits have the ability to withstand large levels of strain without fracture and also no deterioration in the electronic properties [Rogers et al., 2008].

The current market analysis estimates that the revenue of flexible electronics can reach 30 billion USD in 2017 and over 300 billion USD in 2028 [Nathan et al., 2012]. The continuous evolution of smaller, lighter and faster electronics necessitated the demand for new materials which can satisfy the requirements of today's electronic world. A flexible dielectric waveguide consists of a flexible core and a flexible cladding. For an ideal flexible waveguide, the core and cladding must be low loss flexible dielectrics with the relative permittivity of the core being large [Burno et al., 1988]. Then only the fields of the guided mode would decrease rapidly with distance in

the cladding. The requirements for a material to be used as a core of flexible dielectric waveguide are mechanical flexibility, high relative permittivity, low dielectric loss, low coefficient of thermal expansion (CTE), high thermal conductivity etc. It is difficult to obtain a single-phase material with all the above mentioned properties. The research on the development of low loss millimeter wave guiding structures has attained much attention a little while back. Recently ceramic - polymer composites have been investigated extensively because of the need for flexible materials with high dielectric permittivity and low cost processing in the rapidly developing electronic industry [Dang et al., 2005]. However, through the composite approach the permittivity of the polymer can be tailored to a greater extent by using high permittivity low loss fillers. Several polymer based dielectric waveguide was developed for flexible electronic applications [Shindo et al., 1975; Obrzut et al., 1990]. The conventional ceramic polymer composites are flexible to a limited extent but they can't be bend or stretch. Accordingly the importance of the elastomer - ceramic composites, which is receiving wide attention due to its flexibility and stretchability.

The majority of microwave applications are related to high speed microelectronics, radar and communication systems and they need low loss high permittivity materials. High relative permittivity (High-k) ferroelectric ceramic-polymer composites have become potential candidate materials for integration into high frequency electronics due to their tailored dielectric, thermal, mechanical properties and ease of processing [Das gupta et al., 1996; Popielarz et al., 2001]. The future of electronics is expected to be soft and rubbery. Recently elastomer - ceramic composites have been found to be most promising candidates for flexible electronic applications. These composite combines the stretchability and light weight of elastomer with good dielectric and thermal properties of ceramics. Xiang et al. studied the microwave dielectric properties of polyolefin elastomer (POE)–$SrTiO_3$ composites, which can be used as the core of flexible waveguide [Xiang et al., 2007]. Latterly Thomas et al and Chameswary reported the high permittivity filler loaded butyl rubber composites for dielectric applications in flexible electronics at microwave frequencies [Thomas et al.,

2011; Chameswary, 2014]. Volakis and co-workers studied the ceramic ($BaTiO_3$, Mg-Ca-Ti and Bi-Ba-Nd-Titanate) reinforced polydimethyl siloxane (PDMS) composite substrates for conformal microwave applications in the frequency range, 100 MHz–20 GHz. Recently Salaeh et al. prepared flexible epoxidized natural rubber-$BaTiO_3$ composites and the influence of $BaTiO_3$ concentration on cure characteristics, mechanical, dielectric and morphological properties of the composites was investigated [Salaeh et al., 2011]. High permittivity ceramic materials can be used to make elastomer composites for flexible dielectric waveguide and capacitor applications.

Silicone rubber is a well-known dielectric elastomer which is widely used in various industries due to its features like favorable dielectric properties, elasticity, biocompatibility, optical transparency, permeability, UV transmission and availability. The Si-O back bone makes them chemically stable even at high temperatures. The molecular structure gives silicones their unique properties, including water-repellency, cold-resistance etc. In the current study we choose silicone elastomer as the matrix. High relative permittivity materials are used for the manufacture of embedded capacitor as well as dielectric wave guide applications. In order to develop flexible composites of low loss and high relative permittivity the ceramic used should have permittivity much higher than that of rubber matrix. Ceramics such as $BaTiO_3$ (BT), $SrTiO_3$ (ST) and $Ca_{(1-x)}Nd_{(2x/3)}TiO_3$ (CT) having high permittivity are chosen for the present study. $BaTiO_3$ and $SrTiO_3$ are well studied systems having perovskite structure. The perovskite titanates like $CaTiO_3$ and $BaTiO_3$ having high relative permittivity but rather high dielectric loss. In order to obtain compounds with high relative permittivity and low dielectric loss, the substitution of various elements in perovskite titanates is tried like $Ca_{(1-x)}Nd_{(2x/3)}TiO_3$ where x=0.39.

In this chapter we discuss the detailed investigation of silicone elastomer-high permittivity ceramic fillers like $BaTiO_3$, $SrTiO_3$ and $Ca_{(1-x)}Nd_{(2x/3)}TiO_3$ filled composites to understand their dielectric, thermal and mechanical performance for flexible electronic applications.

4.2 Experimental

4.2.1 Materials

In the current work dimethyl end blocked silicone elastomer is used as the matrix and high permittivity fillers like as $BaTiO_3$, $SrTiO_3$ and $Ca_{(1-x)}Nd_{(2x/3)}TiO_3$ used for the composite preparation.

Section 2.2.1.1 and Table 2.1 in the chapter 2 gives the details and physical properties of the rubber matrix used in the present study.

4.2.1.1 Ceramic fillers

4.2.1.1.1 Synthesis

Ceramic fillers used for the present work was prepared by the solid state ceramic route. The stoichiometric proportion of starting materials were weighed and mixed by wet ball milling using yttria-stabilized zirconia balls and dried. The powder thus obtained were then calcined at appropriate temperatures and ground well. Then it is used for composite preparation with silicone rubber. The raw materials used for the synthesis of $BaTiO_3$ and $SrTiO_3$ are $BaCO_3$, $SrCO_3$ and TiO_2 (99.9 + %, Sigma-Aldrich). The calcinations temperature for BT is 1100°C for 4 h and for ST it is 1200°C for 4 h. $Ca_{(1-x)}Nd_{(2x/3)}TiO_3$ were synthesized using $CaCO_3$, Nd_2O_3 and TiO_2 (99.91%, Aldrich Chemical Company Inc., Milwaukee, WI) of high purity. The CT ceramic powders were calcined at 1100°C for 3 h.

4.2.1.1.2 Barium titanate, $BaTiO_3$ (BT)

Barium titanate ($BaTiO_3$) is the first ferroelectric ceramic and a good candidate for a variety of applications due to its excellent dielectric, ferroelectric and piezoelectric properties [Vijatović et al., 2008]. It has a perovskite type structure with high relative permittivity ($\approx$1000 to 2000), dielectric loss ($\approx 10^{-2}$) and high breakdown strength [Wang et al., 2009]. $BaTiO_3$ is widely studied for its numerous scientific and industrial

applications, such as in dielectric capacitors, transducers and tunable phase shifters [Agoudjil et al., 2008].

4.2.1.1.3 Strontium titanate, SrTiO₃ (ST)

Strontium titanate (SrTiO₃) is a well known ceramic; which exists as a centrosymmetric paraelectric material with a perovskite structure at room temperature. It has very large value of ε_r (290) and low value (~ 10^{-3}) of tan δ [Wise et al., 2001]. SrTiO₃ has mixed ionic-covalent bonding properties. This nature of chemical bonding leads to a unique structure, which make it a model electronic material. Ratheesh and co workers studied the dielectric and mechanical properties of SrTiO₃ based PTFE and PEEK composites and found that these composites are suitable for microwave substrate applications [Nisa et al., 2008; Rajesh et al., 2009].

4.2.1.1.4 Calcium neodymium titanate, Ca$_{(1-x)}$Nd$_{(2x/3)}$TiO₃ (CT)

CaTiO₃ is a perovskite titanate having high relative permittivity of ~ 170. However, the high dielectric loss and the large τ_ε value (~ -400 ppm/°C) limits its use in many practical applications [Liang chen et al., 2002]. In order to tune the dielectric loss and τ_f the perovskite titanates were substituted with various elements. A significant modification in the properties of this material can be made through rare earth doping, which has attracted immense attention. Yoshida et al made substation of Ca by trivalent Nd in CaTiO₃ in the range of $0 \leq x \leq 1$ [Yoshida et al., 1997]. The value of dielectric loss decreased with increasing x value. After reaching a minimum value at x = 0:39, it increased with a further increase in x value. In the present study we made quaternary compound Ca$_{(1-x)}$Nd$_{(2x/3)}$TiO₃ where x=0.39 due to its appreciable dielectric properties. The ε_r and τ_ε values were 98 and -130 ppm/°C respectively at x = 0.39. Even though, the microwave dielectric properties of Ca$_{(1-x)}$Nd$_{(2x/3)}$TiO₃ are studied the Ca$_{(1-x)}$Nd$_{(2x/3)}$TiO₃ filled polymer or elastomer composites are investigated for the first time.

The physical properties of ceramic fillers are given in Table 4.1.

Table 4.1 Physical properties of ceramic fillers

Material	Density (g/cm^3)	Avg. particle size (µm)	Relative permittivity ε_r	Dielectric loss tan δ	Coefficient of thermal expansion (ppm/°C)	Thermal conductivity (Wm^{-1}K^{-1})
BaTiO$_3$	6.01	0.90	1250	10^{-2}	5.4	2.6
SrTiO$_3$	5.12	0.80	290.0	10^{-3}	9.4	12.0
Ca$_{(1-x)}$Nd$_{(2x/3)}$TiO$_3$	4.57	0.90	98.0	10^{-3}	10.3	2.4

4.2.1.2 Silicone elastomer-ceramic composite preparation

The detailed description of sigma mixing of silicone rubber composites using a kneading machine was given in section 2.2.1.3 of chapter 2.

4.2.2 Characterization techniques

The crystallinity of the prepared ceramics was confirmed using XRD technique mentioned in the section 2.2.2.1. The microstructure, dielectric, thermal and mechanical properties of developed composites were characterized using methods described in section 2.2 and sub sections of chapter 2.

4.3 Results and discussion

Silicone rubber – high permittivity ceramic fillers like BaTiO$_3$, SrTiO$_3$ and Ca$_{(1-x)}$Nd$_{(2x/3)}$TiO$_3$ loaded composites were prepared as per the recipe given in Table 4.2. These composites were prepared by sigma mixing in a kneading machine. Maximum filler loading of about 0.28 V_f can be attained for SRBT composites where as 0.3 V_f for

SRST composites. Since the density of $BaTiO_3$ is higher than that of $SrTiO_3$. In the case of SRCT composites we can mix up to 0.43 V_f this is also due to the low density of $Ca_{(1-x)}Nd_{(2x/3)}TiO_3$ particles. Larger amount of filler leads to inhomogeneous mixing, hardening and difficulty in mixing and also degradation of the mechanical properties [Zhou et al., 2007]. However, the processing step is more difficult when high filler amounts are incorporated. The optimum filler loading also depends on the particle size, distribution and morphology of the filler.

The phase formation was studied using powder X-ray diffraction technique. The X-ray diffraction peaks were compared with standard JCPDS patterns 83-1880 for $BaTiO_3$, 35-0734 for $SrTiO_3$ and 88-0082 for $Ca_{(1-x)}Nd_{(2x/3)}TiO_3$ and are shown in figure 4.1. No additional peaks are observed in the powder X-ray diffraction patterns, which indicate that phase purity of the powders of $BaTiO_3$, $SrTiO_3$ and $Ca_{(1-x)}Nd_{(2x/3)}TiO_3$.
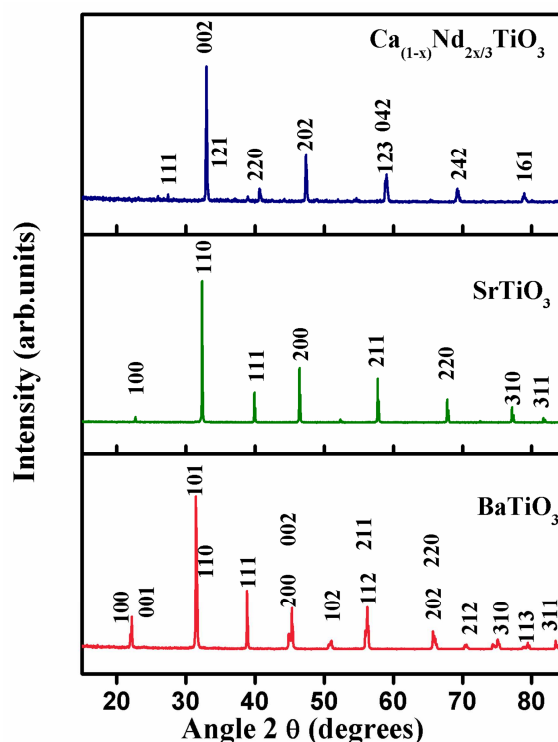
Fig.4.1 XRD patterns of (a) BT (b) ST and (c) CT

The formulation recipes of high permittivity ceramic reinforced silicone rubber composites are given in Table 4.2. The sample designation and corresponding ceramic volume fraction are given in this.

Table 4.2 The formulations of silicone rubber composites (Ingredients in phr [a])

Composite material	Sample designation	Silicone rubber in phr[a]	Dicumyl peroxide (DCP) in phr[a]	Filler in phr[a] [][b]
Silicone rubber-$BaTiO_3$ (SRBT)	$SRBT_0$	100	2	0[0]
	$SRBT_1$	100	2	10[0.04]
	$SRBT_2$	100	2	50[0.09]
	$SRBT_3$	100	2	100[0.16]
	$SRBT_4$	100	2	200[0.28]
Silicone rubber-$SrTiO_3$ (SRST)	$SRST_0$	100	2	0[0]
	$SRST_1$	100	2	10[0.02]
	$SRST_2$	100	2	50[0.09]
	$SRST_3$	100	2	100[0.18]
	$SRST_4$	100	2	200[0.30]
Silicone rubber-$Ca_{(1-x)}Nd_{(2x/3)}TiO_3$ (SRCT)	$SRCT_0$	100	2	0[0]
	$SRCT_1$	100	2	10[0.04]
	$SRCT_2$	100	2	50[0.16]
	$SRCT_3$	100	2	100[0.27]
	$SRCT_4$	100	2	200[0.43]

[a]Parts per hundred of rubber [b]Volume fractions of filler given in parenthesis
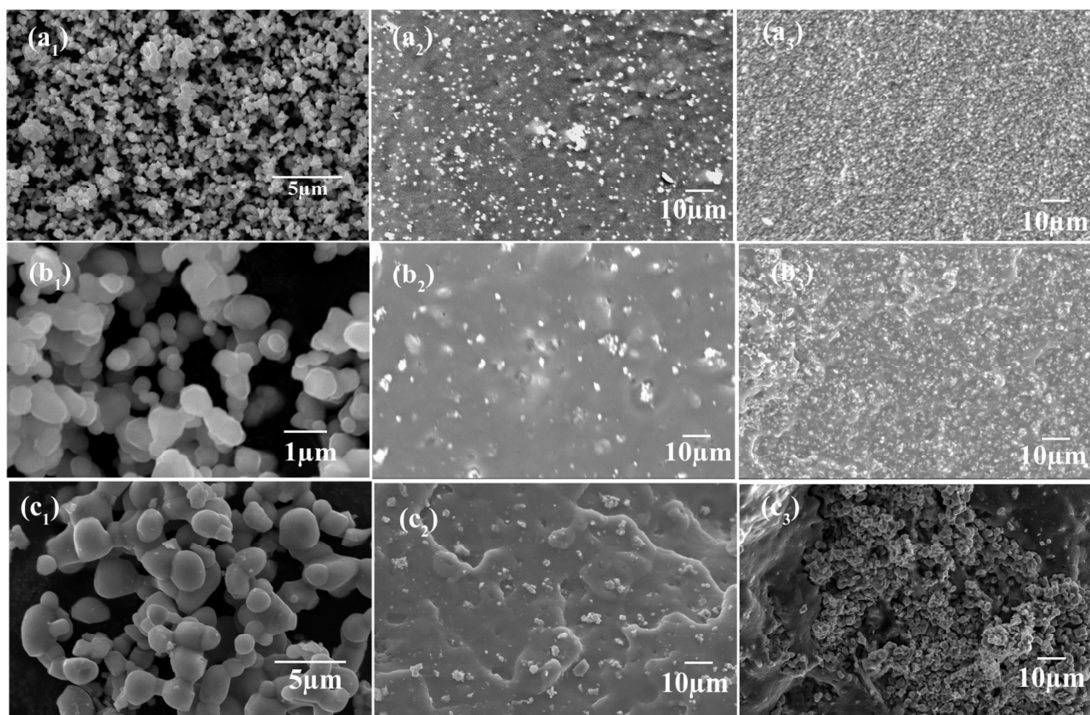
Fig.4.2 SEM images of (a$_1$) BT (b$_1$) ST (c$_1$) CT ceramics, (a$_2$), (b$_2$) and (c$_2$) fractogram of low filler loaded composites and (a$_3$), (b$_3$) and (c$_3$) fractogram of higher filler loaded SRBT, SRST and SRCT composites respectively.

Distribution of filler in the elastomer matrix and the morphology of the composite are studied using SEM. Figure 4.2 (a$_1$), (b$_1$) and (c$_1$) shows the SEM micrographs of BaTiO$_3$, SrTiO$_3$ and Ca$_{(1-x)}$Nd$_{(2x/3)}$TiO$_3$ ceramic. Figure.4.2 (a$_2$), (b$_2$) and (c$_2$) shows the fractured surface of lower volume fraction composites whereas (a$_3$), (b$_3$) and (c$_3$) show the fractogram of higher volume fraction composites respectively. The ceramic fillers are observed to be uniformly distributed throughout the elastomer matrix. In polymer - ceramic composites, as the filler loading increases the tendency for agglomeration will also increase due to the decrease in amount of polymer matrix which keeps the filler particles separated from each other. This is evident from the figure.
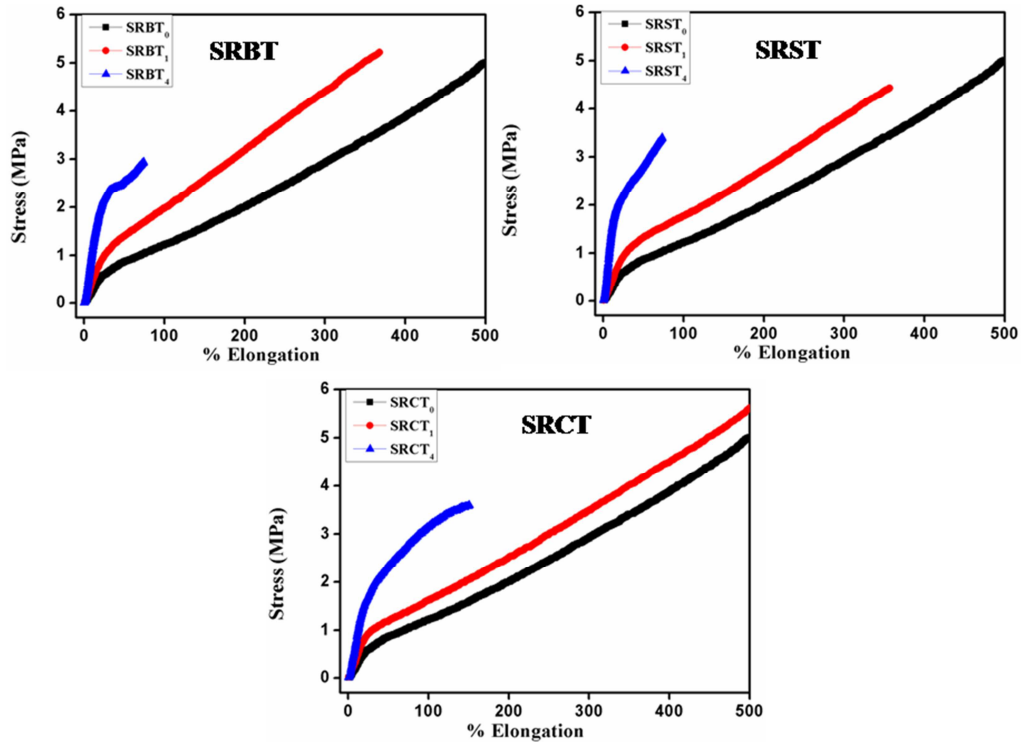
Fig.4.3 Stress-strain curves of SRBT, SRST and SRCT composites

The mechanical flexibility is a prime requirement for a material to be used for flexible applications. The stress –strain curves of pure elastomer and the composites are shown in figure 4.3. From the figure, it is clear that the stress for the same elongation is larger for ceramic filled composite as compared to unloaded elastomer matrix. As the highly brittle ceramic volume increases inside the matrix, the percentage of elongation decreases. Increased filler loading leads to increase in the stiffness of the composite and hence more stress is required for deformation. Filler parameters like size, shape and aspect ratio have a strong impact on mechanical response of the composites.

Dielectric properties of 0-3 composites as a function of the volume fraction of the ceramic were studied by many authors. The variation of relative permittivity and the dielectric loss of the composites with varying filler fraction at the radio frequency (1 MHz) as well as at microwave frequency (5 GHz &15 GHz) regions are shown in figure 4.4. The dielectric properties of a 0-3 composite using a dielectric as the filler are dependent on the dielectric properties of both the matrix and filler [Zhang et al., 2011]. Even though fillers have a very large permittivity than that of matrix, the composite cannot attain relative permittivity more than about 15, since the relative permittivity depends on the rubber matrix. The ferroelectric ceramic – polymer composites follow an exponential relationship between their relative permittivity and volume fraction of the filler. Logarithm of the relative permittivity of polymer – ferroelectric ceramic composites (ε_r composite) is linearly proportional to the volume fraction of the filler (V_f) with the slope dependent on the dielectric properties of both components [Popielarz et al., 2001]. Hence, the ferroelectric – elastomer composites follow the "loglaw" relationship, originally proposed by Lichtenecker [Lichtenecker., 1924; Frost et al., 1996].

$$\log\varepsilon'_{composite} = \phi_{filler} \ \log(\varepsilon'_{filler}/\varepsilon'_{polymer})+ \log \varepsilon'_{polymer} \qquad (4.1)$$

The relative permittivity of polymer - ferroelectric ceramic composite cannot exceed 100 even at maximum filler loading [Popielarz et al., 2007]. The effective relative permittivity of polymer - filler composite material is dependent not only on the relative permittivity of the polymer and the filler, size and shape of the filler and the volume fraction of the filler, but also on the relative permittivity of the interphase region and volume of the interphase region. As the filler content increases the interfacial area increases and influence the dielectric properties significantly. The variation of relative permittivity and the dielectric loss of the composites with varying filler fraction at the radio frequency region (1 MHz) are shown in figure 4.4 a. It is evident from the figure that relative permittivity of all the composites increases with filler fraction. The value of ε_r increases with filler loading because ε_r of fillers is relatively higher than that

of the matrix. The increased connectivity among the filler particles and between the polymer and filler can also enhance the relative permittivity. In the case of SRST and SRCT composites the dielectric loss decreases with filler loading which is due to the low dielectric loss of the filler particles. In the case of SRBT composites the dielectric loss increases with filler content. This is due to the high dielectric loss of the BT than that of silicone rubber matrix.
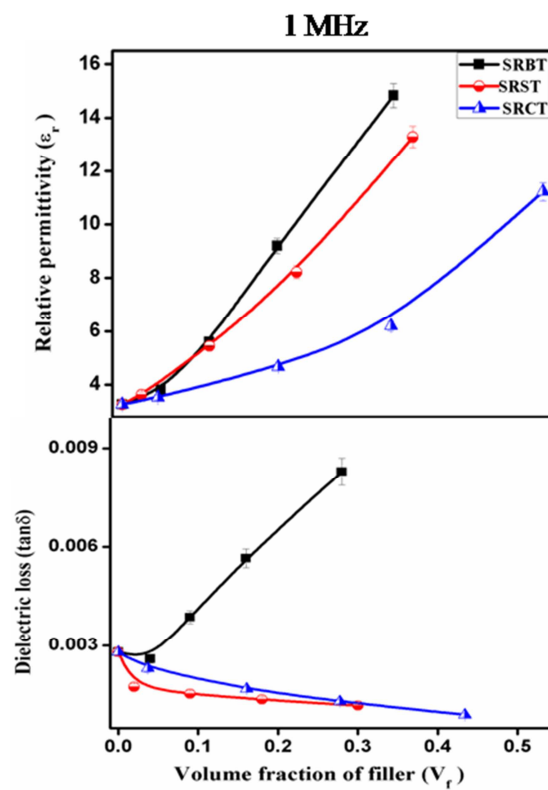
Fig.4.4 a Variations of dielectric properties of silicone rubber composites at 1 MHz
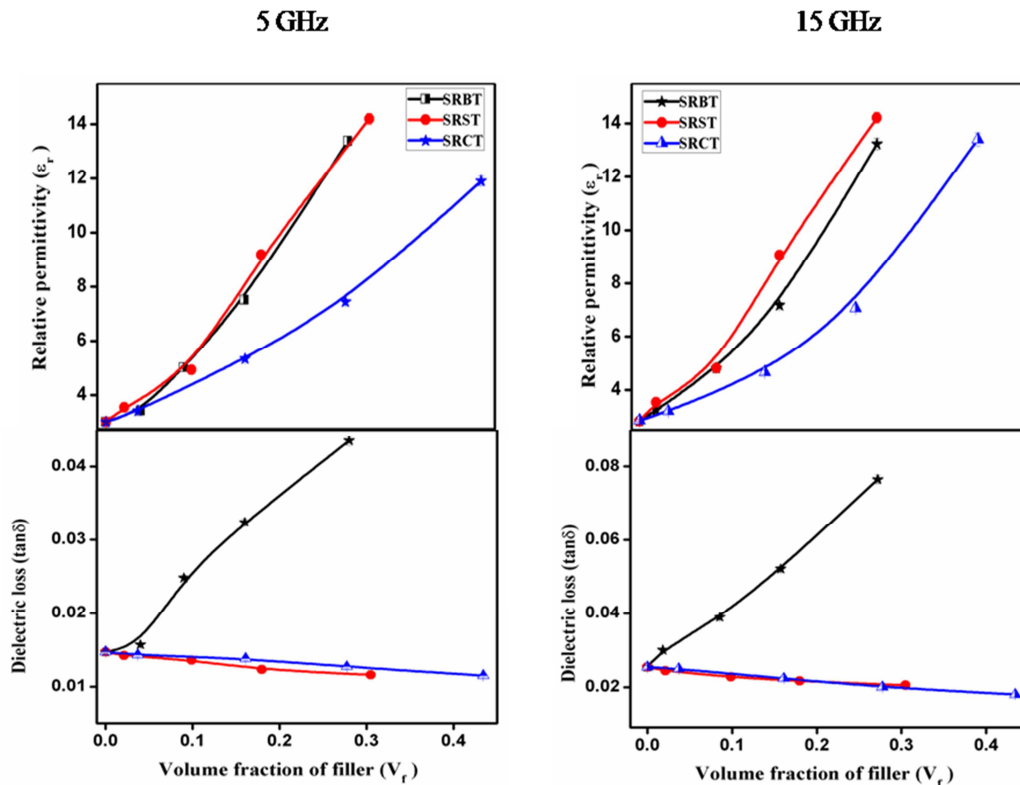
Fig.4.4 b Variations of dielectric properties of silicone rubber composites at 5 GHz and 15 GHz

Figure 4.4 b shows the variations in microwave dielectric properties of SRBT, SRST and SRCT composites with filler loading. The trend in dielectric properties is similar to that of the radio frequency region. The relative permittivity increases with filler volume fraction since the fillers have higher ε_r. At a lower concentration, the rubber matrix isolates filler particles from each other and their dielectric properties will not play a dominant role. But as the ceramic content increases, the particles will get into contact with each other leading to the formation of continuous networks. Consequently dipole-dipole interaction increases and results in increased values of ε_r [Dang et al., 2008]. The variations in complex permittivity at microwave range are mainly caused by dipolar relaxation. The effective dielectric loss of SRST and SRCT composites decreases with filler loading because here the major factor deciding the dielectric loss is

the low tan δ values of the fillers. Where as in the case of SRBT composites; a reverse trend is observed, dielectric loss increases with filler loading. The reason for this effect is the higher tan δ value of the filler and the inhomogeneous dispersion of the filler particles. Moreover, the presence of porosity and the interface between the rubber matrix and ceramics can lead to additional loss. The dielectric properties at 5 GHz and 15 GHz do not show many differences since there is hardly change in polarization mechanisms.
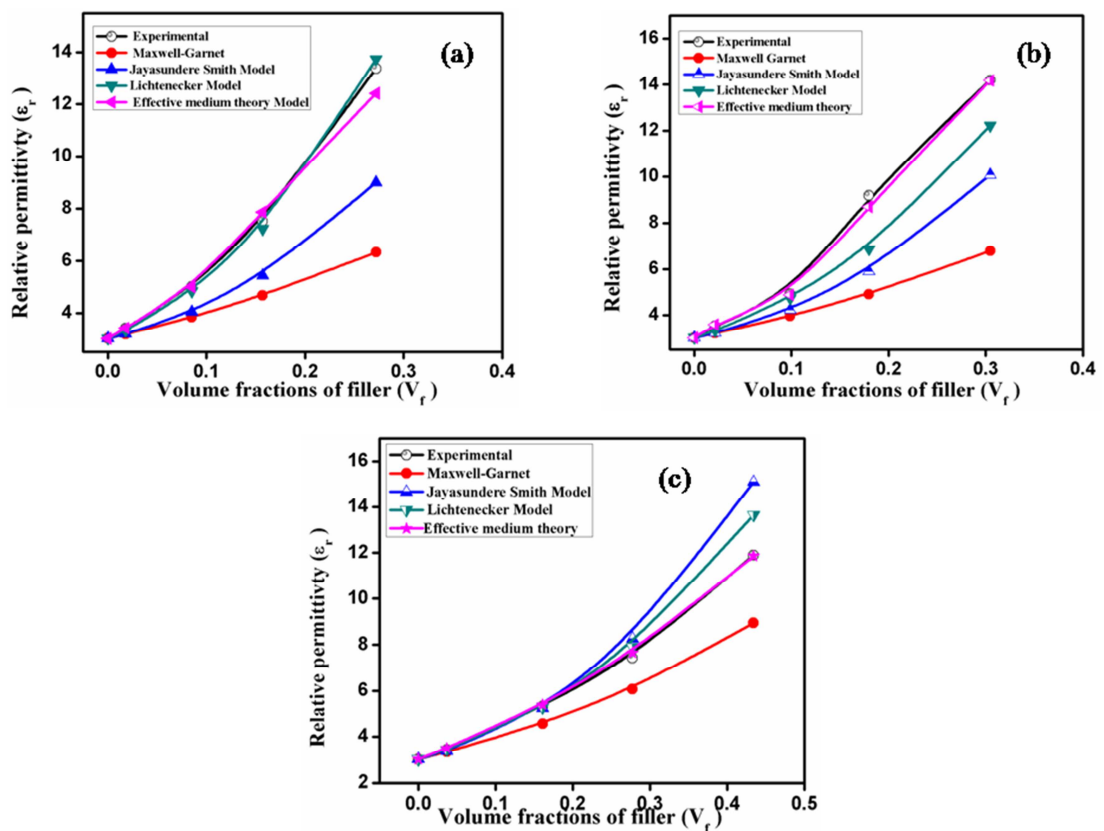
Fig.4.5 Comparison of experimental and theoretical relative permittivity of (a) SRBT (b) SRST (c) SRCT composites at 5 GHz

The theoretical models follow certain assumptions which are related to dielectric properties of individual components, the connectivity of polymer – ceramic composites, size and shape of the filler and morphology. Figure 4.5 shows the comparison between experimental and theoretical values of relative permittivity at 5 GHz for SRBT, SRST and SRCT composites. It can be seen that the theoretical values give the same trend as that of experimental curve. Maxwell - Garnet relations predict lower ε_r compared to the experimental data. Reduction in depolarization of filler and increase in relative permittivity, which are not accounted in this formula, hence shows the deviation. For SRBT composites the Lichtenecker and EMT models are matching well with experimental results. Jayasundere - Smith and Lichtenecker models are valid for low volume fraction of filler loading, the entrapped air and imperfect dispersion of filler in the composites may be the reason. Generally, the theoretical predictions are valid only for low volume fractions of filler loading [Wakino et al., 1993; Anjana et al., 2008]. This is due the imperfect dispersion of ceramic particle in polymer matrix. The EMT model is found to match with experimental values of SRST and SRCT composites. The morphology factor 'n' for EMT model is found to be 0.13, 0.103 and 0.205 SRBT, SRST and SRCT composites respectively. EMT model fits well with the experimental results. This includes morphology factor 'n' which is obtained from empirical calculations. Shape of the filler is compensated by the correction factor, n in the polymer-ceramic composite. In EMT model, composites are treated as an effective medium whose relative permittivity is the average of the relative permittivity of the constituents. The effective permittivity of a composite depends on the various factors such as relative permittivity of individual components in the system, porosity, their volume fractions, size, shape, interphase polarizability and interphase volume fractions [Rao et al., 2000]. All these parameters cannot be accounted in a single equation. So some models show slight deviations.
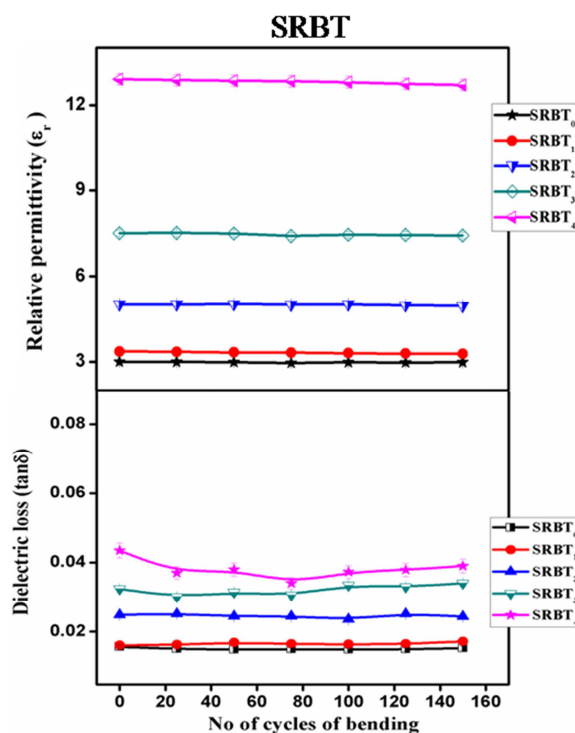
SRBT

Fig.4.6 a Variation of dielectric properties of SRBT composites with bending

Figure 4.6 a and b shows the variation of microwave dielectric properties of silicone rubber composites after repeated bending of samples by an angle of 180°. From the figure it is clear that the relative permittivity of the composites is almost independent of bending. The dielectric loss of composites shows marginal variation with bending which is clear from the figure. The prominent deviation of dielectric loss at higher filler loading may be due to the particle agglomeration at higher filler content. Similar behaviour in PFCB (perfluorocyclobutene(poly1,1,1-triphenyl ethane per-fluorocyclobutyl ether)-BaTiO$_3$ composites was observed by Vrejoiu et al. [Vrejoiu et al., 2002]. The bending of the composites does not considerably affect the microwave dielectric properties and hence, they are suitable for flexible electronic applications.
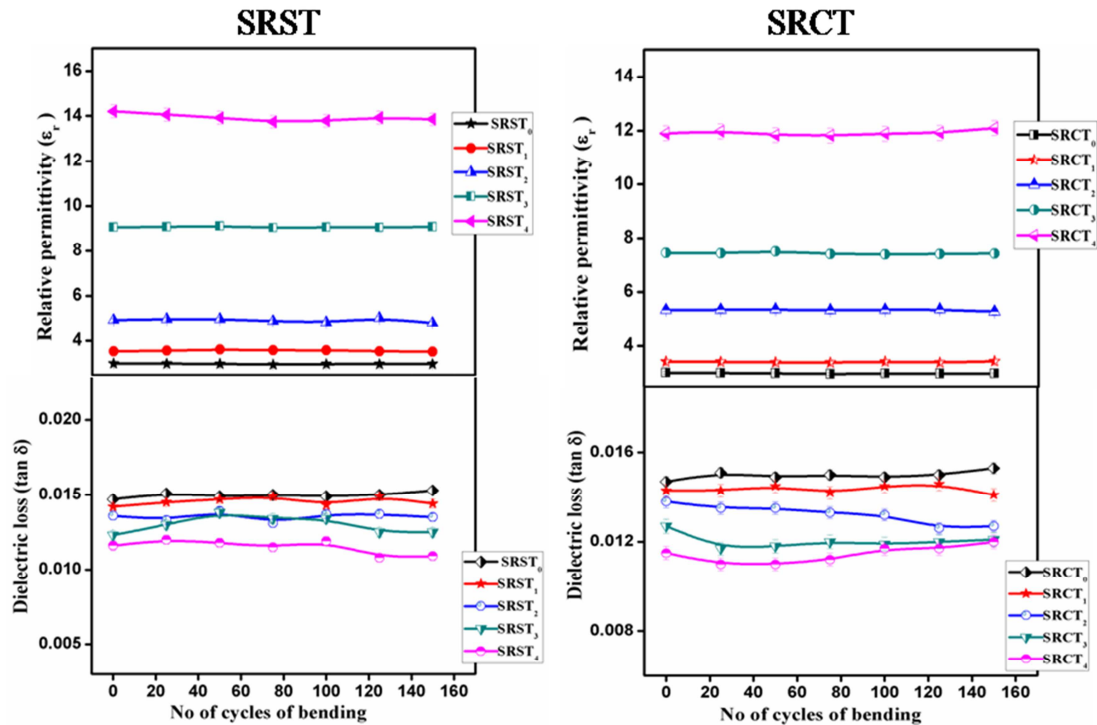
Fig.4.6 b Variation of dielectric properties of SRST and SRCT composites with bending

The relative permittivity of polymer composites should be stable within the operational temperature range of electronic devices for practical applications. From the figure it is clear that all the silicone rubber composites are almost stable within the measured temperature range. The temperature dependence of ε_r at 5 GHz of SRBT, SRST and SRCT composite is depicted in figure 4.7. It can be observed that the relative permittivity of the composites with lower filler loading is almost constant throughout the measured temperature range. As the filler loading increases there is a decrease in relative permittivity with temperature. This may be due to the disturbed polarizability of dipoles with increase in temperature. The difference in CTE of rubber and filler may be also responsible for the decrease in relative permittivity [Xie et al., 2005; Berger et al., 1985]. The incipient ferroelectric nature of both BT and ST ceramics can also affect the

temperature dependence of relative permittivity of SRBT and SRST composites. Incipient ferroelectrics are characterized by increasing permittivity on cooling due to the softening of the lowest frequency polar optical phonon [Kamba et al., 2009].
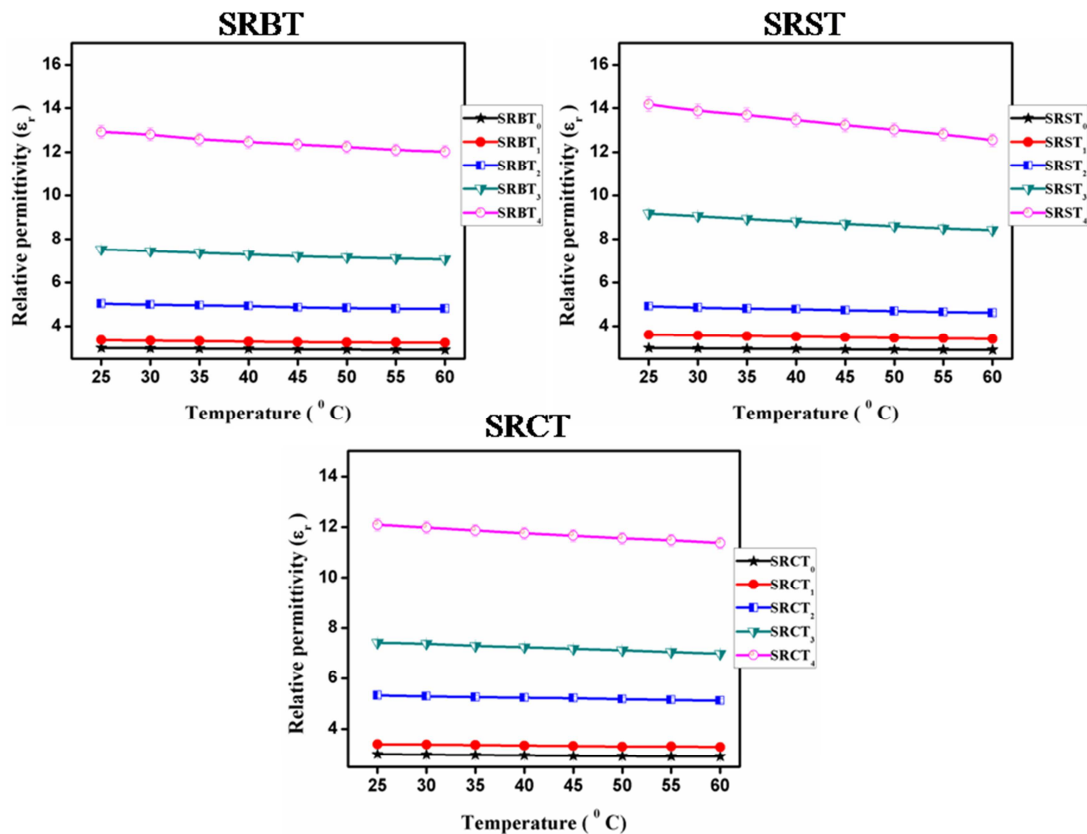
Fig.4.7 The variation of relative permittivity of (a) SRBT, (b) SRST, (c) SRCT composite as a function of temperature

The variation in coefficient of thermal expansion (CTE) is an important factor for electronic packaging applications. The variation in CTE of ceramic filled silicone rubber composites are shown in the figure 4.8. The CTE of pure rubber matrix is (266 ppm /$^\circ$C) very much reduced by the addition of ceramic fillers BT, ST and CT which are having a very low CTE of 5.4, 9.4 and 10.3 ppm/°C respectively. It is clear

from the figure that the thermal expansions of all composites are lowered with the addition of ceramic particles. When a composite is heated, the polymer matrix will expand more than that of ceramic fillers. The expansion of matrix will be reduced if the interfaces are capable of transmitting stress. The polymer chains get arrested in the presence of ceramic and unable to expand with temperature. Hence the CTE of a composite is reduced with increase in filler content and composite with strong interface exhibits an additional reduction of CTE [Holliday et al., 1973].
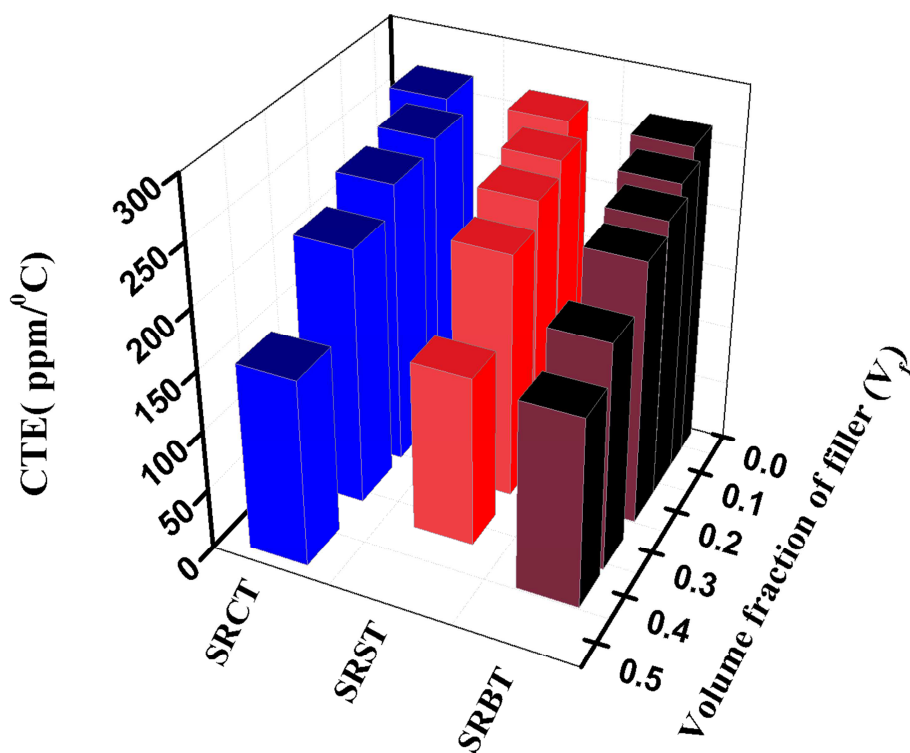
Fig.4.8 Variation of coefficient of thermal expansion of (a) SRBT, (b) SRST, (c) SRCT composites with ceramic loading

The silicone elastomer possesses a low value of thermal conductivity of about 0.19 $Wm^{-1}K^{-1}$. The thermal conductivity of the fillers are much higher than the matrix and obviously there is an expected trend of increase in the thermal conductivity value with the filler addition. The interfacial physical contact between polymer and filler is

very critical for a polymer-ceramic composite [Lee et al., 2006]. The influence of the volume fraction of filler on the thermal conductivity of SRBT, SRST and SRCT composites is shown in figure. 4.9 a. It is observed that the thermal conductivity gradually increases with increasing filler content. At low volume fractions the filler particles will disperse randomly in the rubber matrix and a little increase of thermal conductivity. For higher filler content, the particles begin to touch each other and form conductive channels in the direction of heat flow causing an exponential rise in the thermal conductivity. Ceramic fillers seem to improve the thermal conductivity of polymers as they act as conducting channels with lower thermal resistance than the matrix.
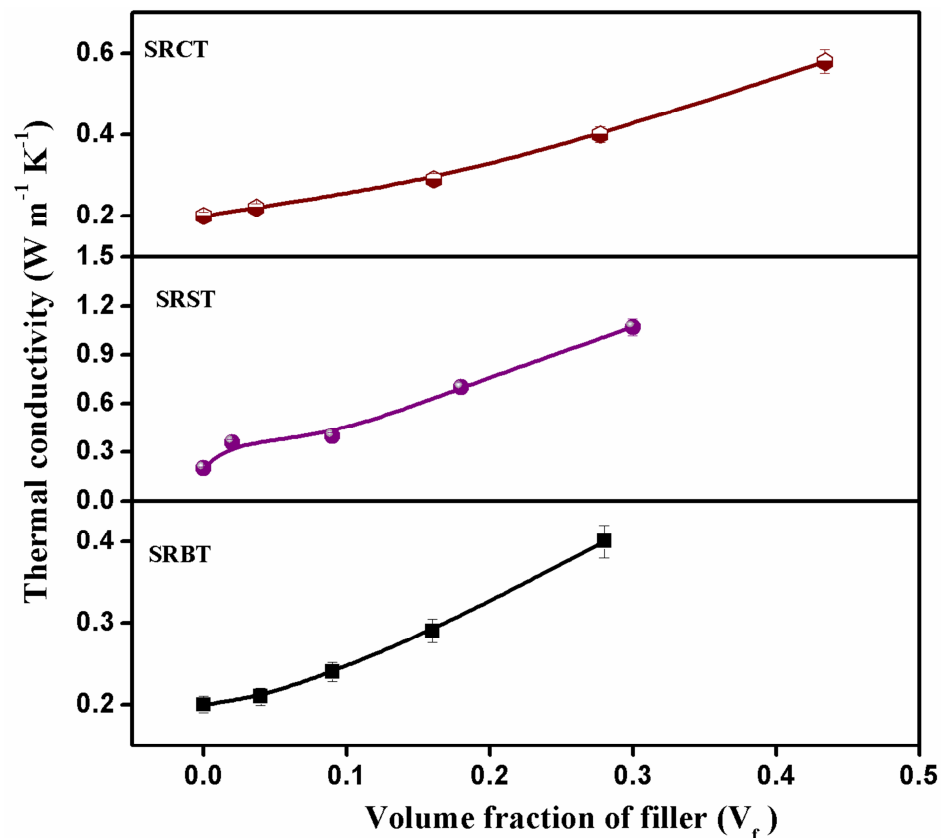
Fig.4.9 a Variation of thermal conductivity of (a) SRBT, (b) SRST, (c) SRCT composite with filler volume fraction
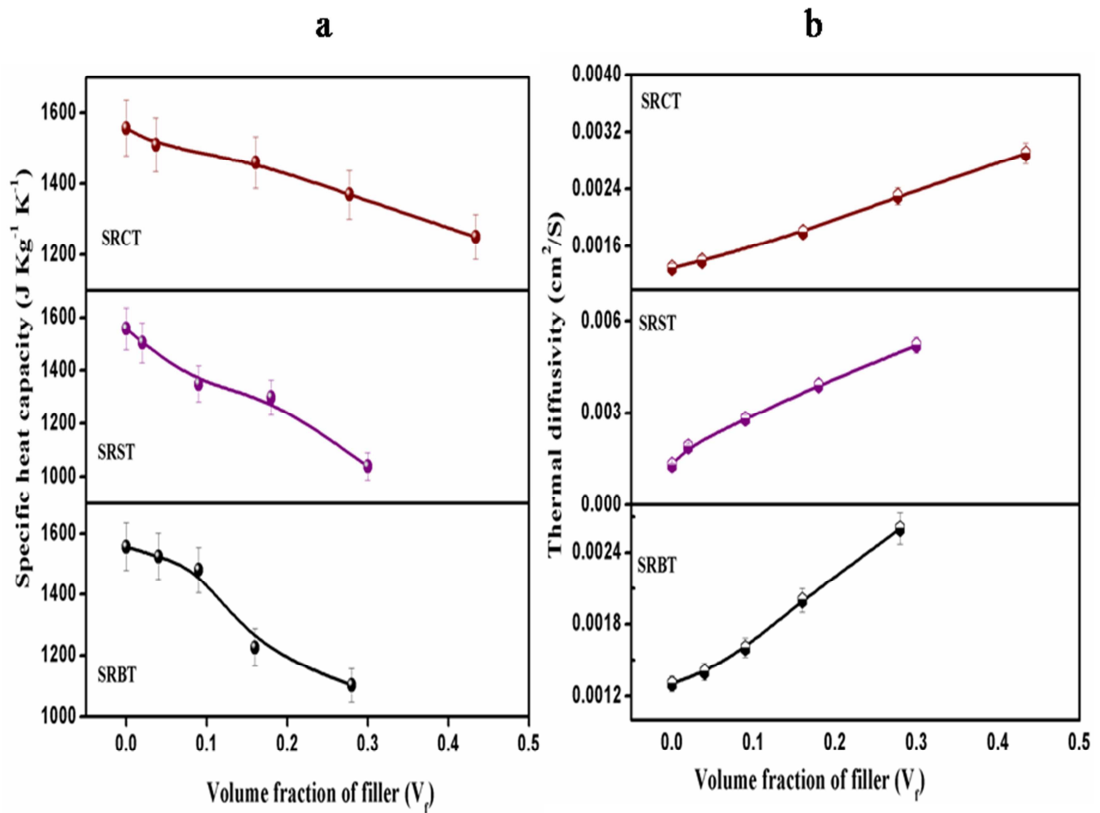
Fig.4.9 b Variation of (a) specific heat capacity and (b) thermal diffusivity of SRBT , SRST and SRCT composite with filler volume fraction

The effect of ceramic loading on specific heat capacity and thermal diffusivity of SRBT, SRST and SRCT composites are also depicted in figure 4.9 b. The specific heat capacity decreases where as thermal diffusivity increases with filler volume fraction. This is due to the effect of ceramic fillers. They have low Cp value and high thermal diffusivity compared to the rubber matrix. The result was in agreement with the earlier reports [Subodh et al., 2008].

The dielectric properties are very sensitive to humid environment. Moreover, a high value of water absorption will lead to considerable degradation of mechanical as

well as dielectric properties. The variation of water absorption of SRBT, SRST and SRCT composites as a function of filler loading is shown in figure 4.10. It is clear from the figure that the water absorption of the composites increases with filler loading. The increase of moisture absorption may be due to the increase in porosity with filler loading and the hydrophilic nature of the ceramic particles. It has been reported that the materials with moisture absorption up to about 0.1 % can be used for electronic packaging applications [Laverghetta, 2002]. In the current study all most all composites exhibit moisture absorption within this limit.
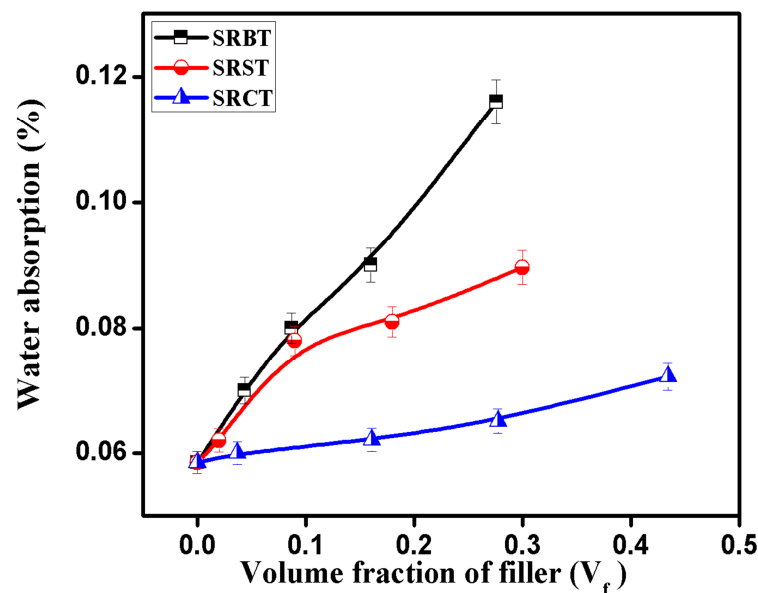
Fig.4.10 Variation of water absorption of (a) SRBT (b) SRST (c) SRCT composites with filler loading

4.4 Conclusions

● Silicone elastomer reinforced with high permittivity ceramic filler composites are prepared and their dielectric, thermal and mechanical properties are studied as a function of filler volume fractions.

- The mechanical flexibility of the composites is revealed by the stress-strain curves.

- Theoretical predictions are used for the comparison of experimental relative permittivity of all the composites.

- The relative permittivity, thermal conductivity and water absorption increases whereas, the coefficient of linear thermal expansion decreases as the volume fraction of filler increases. In the case of dielectric loss; a decreasing trend is shown by SRST and SRCT composites with filler volume fraction where as SRBT composites show a reverse trend.

- SRBT composite has ε_r = 13.38 and tan δ = 0.0435 (at 5 GHz), CTE = 188 ppm/°C, TC = 0.4 $Wm^{-1}K^{-1}$ and water absorption = 0.116 vol % for 0.272 V_f of BT loading. For 0.305 V_f of ST content, the SRST composites have ε_r = 14.21 and tan δ = 0.0116 (at 5 GHz), CTE = 142 ppm/°C and TC = 1.02 $Wm^{-1}K^{-1}$ and water absorption of 0.089 vol % and SRCT composites achieved a ε_r of 11.90 and tan δ of 0.0115 (at 5 GHz), CTE and TC of 156 ppm/°C and 0.58 $Wm^{-1}K^{-1}$ respectively and water absorption of 0.072 vol % for 0.43 V_f of CT.

- The composites with maximum filler loading are suitable candidates for core of flexible dielectric waveguide applications and embedded capacitor applications.

- The measured properties indicate that all the other compositions of SRBT, SRST and SRCT composites can be used for cladding of flexible dielectric waveguide and also for microwave substrates applications.

CHAPTER 5

Conclusions and Scope for Future Work

This chapter provides a brief summary of the thesis. The major results in the thesis is outlined as chapter wise and also highlighted in table. A comparison of the properties of some of the selected materials developed in the present study with the commercially available materials for microwave applications. The chapter also discusses the scope for extensions of the work that may be pursed in future in the field of flexible electronics.

5.1 Conclusion of the Ph. D. thesis

Flexible electronics is becoming an exciting research area drawing active participation of scientists and engineers worldwide. Flexible electronics encompasses a rather diverse range of device and materials technologies that are built on flexible and conformal substrates. Recently electronic systems that can cover large areas on flexible substrates have received increasing attention because they enable wide range of applications such as flexible displays, electronic textiles, sensory skins and active antennas etc. The potential applications of flexible electronics are in various societal sectors, including: healthcare, the automotive industry, human–machine interfaces, mobile communications and computing platform. The thesis entitled "**Ceramic Reinforced Silicone Elastomer Composites for Flexible Microwave Applications**" is divided into 5 chapters. It is the outcome of a detailed investigation carried out on the synthesis, characterization and properties of composites of silicone elastomer reinforced with low, medium and high permittivity ceramic fillers.

The chapter 1 gives a general introduction about flexible electronics, dielectrics and the importance of composite approach. The recent developments in flexible electronics and also the importance of elastomer - ceramic composites in today's electronic world are cited in this chapter. This chapter also gives a brief discussion on the selection of silicone elastomer as matrix for the present study and its characteristics.

Chapter 2 discusses the synthesis, characterization and properties of silicone rubber - low permittivity ceramic composites. A brief description of the preparation and characterization techniques of ceramic powder and their silicone elastomer composites are also included in this chapter. The low permittivity ceramic fillers used are Al_2O_3, AlN and fused SiO_2. The dielectric, thermal and mechanical properties of the composites is investigated as a function of ceramic loading. The XRD analysis of ceramics revealed that the ceramics used are phase pure. The composites are prepared by sigma mixing followed by hot pressing. The composites can be prepared upto a certain vol % after that mixing became very difficult and the properties get degraded.

The microstructure of the composites shows the uniform dispersion of filler in the matrix and also the presence of some agglomerates at higher filler loading. The dielectric properties of the composites are studied at both radio frequencies (1 MHz) as well as at microwave frequency (5 GHz and 15 GHz) and are found to be improved with ceramic loading. For maximum filler loading of about 0.46 V_f, the alumina filled silicone rubber (SRAL) composite have relative permittivity (ε_r) of 5.79 and dielectric loss (tan δ) of about 0.0095 at 5 GHz. The thermal properties of the composites also improved with filler content. The SRAL composites attained CTE = 114 ppm/^{o}C, TC = 1.60 $Wm^{-1}K^{-1}$ and water absorption = 0.347 vol % for maximum alumina loading. The AlN filled silicone rubber composite (SRAN) have attained ε_r = 4.79, tan δ = 0.0172 for filler loading of 0.41 V_f. The SRAN composites has a CTE = 138 ppm/^{o}C, TC = 1.06 $Wm^{-1}K^{-1}$ and water absorption = 0.108 vol % for a maximum AlN filler loading. The silicone rubber-fused silica composites have ε_r = 3.35, tan δ = 0.0085 for a maximum fused silica loading of about 0.51 V_f at 5 GHz. The CTE value of 116 ppm/^{o}C, TC = 0.52 $Wm^{-1}K^{-1}$ and water absorption of 0.100 vol % respectively for SRFS composites at higher filler loading. Various theoretical models were used to fit the experimental values of relative permittivity of all the composites. The silicone rubber - ceramic composites are bendable and stretchable. They are possible candidates for microwave flexible substrate applications.

The availability of medium dielectric substrates is limited, discovery of new medium dielectric composites with properties superior than the commercially available is necessary. To achieve this aim we use medium permittivity fillers like $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Li_2ZnTi_3O_8$ ceramics to make composites with silicone rubber in the present study. The effect of the fillers on dielectric, thermal and mechanical properties of silicone rubber composites are described in chapter 3. The microstructure analysis of composites reveals the filler particles dispersion in the rubber matrix. The dielectric properties of the composites both at radio frequency and microwave frequencies are investigated. As the volume fraction of filler increases, the relative permittivity, thermal conductivity and water absorption increases whereas,

dielectric loss and the coefficient of linear thermal expansion decrease in ceramic reinforced silicone rubber composites. For 0.299 V_f of BZT loading, SRBZ composite has ε_r = 6.57 and tan δ = 0.0098 (at 5 GHz), CTE = 149 ppm/°C, TC = 0.92 $Wm^{-1}K^{-1}$ and water absorption = 0.115 vol %. The SRBM composites have ε_r = 5.14 and tan δ = 0.0118 (at 5 GHz), CTE = 152 ppm/°C and TC = 0.49 $Wm^{-1}K^{-1}$ and water absorption of 0.119 vol % for 0.23 V_f of BMT content and SRLT composites achieved ε_r of 7.49 and tan δ of 0.0098 (at 5 GHz), CTE and TC of 144 ppm/°C and 0.83 $Wm^{-1}K^{-1}$ respectively and water absorption of 0.112 vol % for 0.36 V_f of LZT. Stress strain curves of all composites indicate good mechanical flexibility of composites. The experimental values of relative permittivity of all the composites are compared with theoretical models. All the measured properties suggest that maximum filler loaded composites can find applications as cladding of flexible dielectric waveguide and all other compositions can be used for microwave substrate and electronic packaging applications. A rectangular microstrip patch antenna for Wireless local area network (WLAN) was fabricated using SR-0.134 V_f BMT substrate simulated using Ansoft High Frequency Structure Simulator (HFSS).The fabricated antenna successfully operates at 2.48 GHz with a return loss of -12.96 dB. The simulated and measured reflection characteristics are in good agreement. The results indicate that the SR-0.134 V_f BMT composite based substrates can be used as a cost effective, flexible microwave antenna substrate using adequate medium of metallization.

Chapter 4 discusses the synthesis, characterization and properties of silicone rubber- high permittivity ceramic composites. The ferroelectric fillers like $BaTiO_3$ and $SrTiO_3$ along with $Ca_{(1-x)}Nd_{(2x/3)}TiO_3$ are the high permittivity ceramics used in the present study. The dielectric, thermal and mechanical properties of the composite are studied as a function of ceramic volume fraction. The relative permittivity, thermal conductivity and water absorption increases whereas, the coefficient of linear thermal expansion decreases as the volume fraction of filler increases. In the case of dielectric loss; a decreasing trend was shown by SRST and SRCT composites with filler volume fraction where as SRBT composites show a reverse trend. Several theoretical model

approaches have been employed to predict the relative permittivity of the composite systems and the results are compared with that of experimental data. The ε_r of the composites shows small temperature dependence. The effect of repeated bending on the microwave dielectric properties of all the composites has also been studied. The composites show only marginal variation in microwave dielectric properties after bending. SRBT composite has ε_r = 13.38 and tan δ = 0.0435 (at 5 GHz), CTE = 188 ppm/°C, TC = 0.4 Wm^{-1}K^{-1}and water absorption = 0.116 vol % for 0.272 V_f of BT loading. For 0.305 V_f of ST content, the SRST composites have ε_r = 14.21 and tan δ = 0.0116 (at 5 GHz), CTE = 142 ppm/°C and TC = 1.02 Wm^{-1}K^{-1}and water absorption of 0.089 vol % and SRCT composites achieved ε_r of 11.90 and tan δ of 0.0115 (at 5 GHz), CTE and TC of 156 ppm/°C and 0.58 Wm^{-1}K^{-1}respectively and water absorption of 0.072 vol % for 0.43 V_f of CT. The composites with maximum filler loading are suitable candidates for core of flexible dielectric waveguide applications and embedded capacitor applications. The measured properties indicate that all the other compositions of SRBT, SRST and SRCT composites can be used for cladding of flexible dielectric waveguide and also for microwave substrates applications.

The physical and microwave dielectric properties of the developed silicone rubber ceramic composites are summarized in the Table 5.1

The properties of the composites developed in the present study are comparable to that of similar commercial polymer based substrates. The properties of some of the selected composites developed as a part of this work are given in Table 5.2.

Table 5.1 Properties of developed silicone rubber-ceramic composites

Composite Material (phr)	V_f of filler	ε_r	tan δ	CTE (ppm/^{o}C)	TC (Wm^{-1}K^{-1})	Water absorption vol %
SR-300AL	0.458	5.79	0.0095	114	1.60	0.347
SR-200 AN	0.408	4.79	0.0172	138	1.06	0.108
SR-200 FS	0.506	3.35	0.0085	116	0.52	0.100
SR-300 BZ	0.299	6.57	0.0098	149	0.92	0.115
SR-200 BM	0.233	5.14	0.0118	152	0.49	0.119
SR-200 LT	0.363	7.49	0.0098	144	0.83	0.112
SR-200 BT	0.272	13.38	0.0435	188	0.40	0.116
SR-200 ST	0.305	14.21	0.0116	142	1.07	0.089
SR-200 CT	0.434	11.90	0.0115	156	0.58	0.072

Table 5.2 Comparison of dielectric, thermal and physical properties of silicone rubber composites with commercial product

Materials	ε_r	tan δ	CTE (ppm/^{o}C)	TC (Wm^{-1}K^{-1})	Water absorption vol %	Flexibillty & Stretchability
RT duroid^R 6006	6.3	0.0027	117	0.49	0.05	No
SR-0.299 V_f BZ	6.6	0.0098	149	0.92	0.11	Yes
FR$_4$	4.8	0.0025	11	0.25	0.15	No
SR-0.233 V_f BM	5.1	0.0118	152	0.49	0.12	Yes
Rogers Ultralam 3000	2.9	0.0025	150	0.20	0.04	No
SR-0.34 V_f FS	3.2	0.0090	153	0.40	0.09	Yes

5.2 Scope for future work

The future direction of the present thesis is mainly focusing on the development of biocompatible composites using biocompatible ceramic fillers and silicone rubber as the matrix, since it is a biocompatible polymer material. Development of silicone rubber composites in 1, 3-type connectivity and investigate the microwave dielectric properties. Fabrication of flexible waveguide using suitable silicone rubber composites developed. Development of silicone rubber composites with giant permittivity fillers like calcium copper titanate for flexible capacitor applications. Study the effect of filler particle size and hybrid fillers on dielectric and thermal properties of the composites. Investigation on various techniques to improve the gain and radiation efficiency of fabricated microstrip antenna.

Photographs of developed samples in the present study
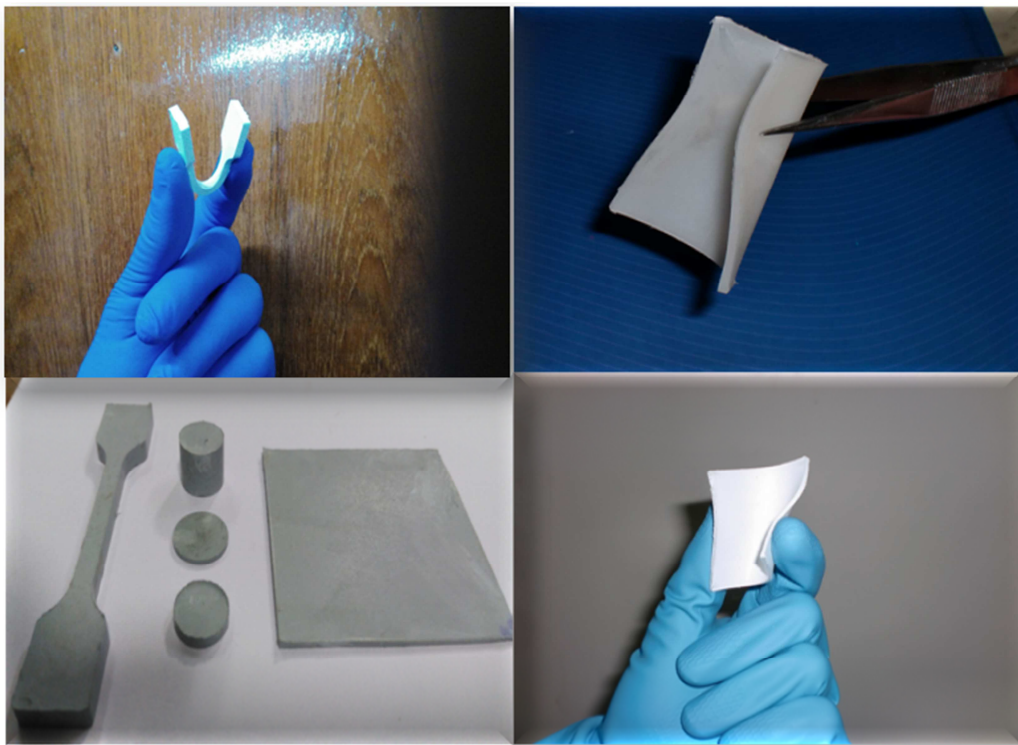
List of publications

1. **L. K. Namitha**, S. Ananthakumar and M. T. Sebastian, "Aluminum nitride filled flexible silicone rubber composites for microwave substrate applications" *J Mater Sci Mater Electr.*; 26, 891-897 (2015).

2. **L. K. Namitha** and M. T. Sebastian, "Microwave dielectric properties of flexible silicone rubber–Ba(Zn $_{1/3}$Ta $_{2/3}$)O$_3$ composite substrates", Mater. Res. Bull., 48 (11), 4911–4916 (2013).

3. **L. K. Namitha**, J. Chameswary, S. Ananthakumar and M. T. Sebastian, "Effect of micro- and nano-fillers on the properties of silicone rubber-alumina flexible microwave substrate", *Ceram. Int.,* 39 (6), 7077-7087 (2013).

4. J. Chameswary, **L. K. Namitha**, M. Brahmakumar and M. T. Sebastian, "Microwave Dielectric properties of Alumina filled Butyl rubber Composite for Microwave Substrate Application *Int. J. Appl. Ceram. Technol.*, 11 (5), 919–926 (2014).

5. **L. K. Namitha** and M. T. Sebastian, "Fused Silica filled Silicone Rubber Composites for Flexible Electronic applications" *Materials Science Forum* Vols. 830-831 ,537-540 (2015) .

6. M. V. Reshma**, L. K. Namitha**, A. Sundaresan and Challa Ravi Kiran, "Total phenol content, antioxidant activities and α -glucosidase inhibition of sesame cake extracts", *J. Food Biochem.*, 37,723-731,(2013)

7. **L. K. Namitha** and M. T. Sebastian, "Barium titanate reinforced silicone elastomer composites for flexible electronic applications" (communicated).

8. **L. K. Namitha,** Roshni.S.Babu, M.P. Jaya krishnan, P. Mohanan and M. T. Sebastian, "BMT reinfored silicone elastomer composites for microwave antenna applications" (To be communicated).

9. **L. K. Namitha** and M. T. Sebastian "Mechanically flexible silicone elastomer-SrTiO$_3$ composite substrates for microwave applications" (To be communicated).

10. **L. K. Namitha,** S. Ananthakumar and M. T. Sebastian "Effect of $Ca_{(1-x)}Nd_{(2x/3)}TiO_3$ and $Li_2Zn\ Ti_3O_8$ ceramic fillers on the microwave dielectric properties of silicone elastomer composites" (To be communicated).

Conference proceedings

1. **L. K. Namitha**, J. Chameswary, S. Ananthakumar and M. T. Sebastian, Microwave dielectric properties of flexible silicone rubber and butyl rubber composites with aluminium nitride, *2nd International Conference on Advanced Functional Materials*, ICAFM-2014. Thiruvananthapuram.

2. **L. K. Namitha,** S. Ananthakumar and M. T. Sebastian, Synthesis and microwave dielectric characterization of silicone rubber-mica flexible composites*, National Conference on "Materials; Process and applications of Novel Technologies, NMAT*-2013,Thiruvananthapuram.

3. **L. K. Namitha ,** S. Ananthakumar and M. T. Sebastian, Microwave dielectric characterization of flexible silicone rubber-fused silica composites *, National seminar on frontiers of polymer and advanced materials***,** FPAM*-2014, Thiruvananthapuram.

4. **L. K. Namitha** and M. T. Sebastian, "Fused Silica filled Silicone Rubber Composites for Flexible Electronic applications*", International conference on Advanced materials and manufacturing processes for strategic sectors, ICAMPS* 2015, Thiruvananthapuram.

5. **L. K. Namitha and** M. T. Sebastian, Preparation and characterization of $SrTiO_3$ filled silicone rubber composite for flexible electronic applications, *International conference on advanced materials for power Engineering, ICAMPE*-2015, Kottayam.

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