Chapter 3

Butyl Rubber-Low Permittivity Ceramic

[Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2} and Ba(Zn\textsubscript{1/3}Ta\textsubscript{2/3})O\textsubscript{3}] Composites

This chapter describes the synthesis, characterization and properties of butyl rubber filled with low permittivity ceramic composites. The low permittivity ceramics used for the present study were alumina, silica and barium zinc tantalate. The dielectric properties both at 1 MHz and 5 GHz, thermal and mechanical properties of these composites as a function of filler volume fraction were investigated. The effect of filler particle size on these properties was studied in butyl rubber-alumina composites. The relative permittivity and thermal conductivity of these composites were compared with theoretical models.
3.1 Introduction

The development of mechanically flexible or even stretchable electronic systems is increasing in recent years due to their attractive features [1]. Today’s citizen carries more electronic systems near or even inside the body. Hence, the systems must be light weight, must take the desirable shape of the object and should follow all complex movements of these objects [2]. The soft, stretchable and elastic electronic assemblies can take the shape of the object in which they are integrated [3]. An ideal substrate and packaging material have to satisfy diverse requirements such as low relative permittivity to reduce signal propagation delay, low loss tangent to reduce signal attenuation along with better device performance, mechanical flexibility, high dimensional stability, moisture absorption resistance, high thermal conductivity (TC) to dissipate the heat generated, low coefficient of thermal expansion (CTE) matching to that of silicon etc. [4-6]. Several low permittivity ceramics such as silicates and aluminates with excellent microwave dielectric properties have been developed for substrate and packaging applications [7-9]. Its brittle nature and high processing temperature precludes them from practical use. Polymers are also widely used in the packaging industry [10, 11]. High value of CTE and low surface energy limits their practical applications. Hence, polymers or ceramics cannot be used alone for practical applications. Button et al. proposed a composite strategy of combining the advantages of ceramic and polymer to achieve a superior property balance [12]. Polymers such as polyethylene, polytetrafluoroethylene are flexible but cannot be used for stretchable applications. Stretchability is the prime requirement for biomedical applications where circuits are to be wrapped around curved surfaces. The research on elastomer-ceramic composites has received much attention in this context. The properties of the composites are
very much dependent on the size and shape of the fillers and the interaction between the filler and the polymer matrix. Hence, by the proper design of composites, one can utilize ease of processing and low $\varepsilon_r$ of polymers with high thermal conductivity and low CTE of ceramics. Recently, the addition of nanofillers to polymers has attained much attention. An extensive research is going in the field of polymer-nano composites by incorporating nano scale fillers into polymers [13-15]. However, a few reports are available which explores the microwave dielectric properties of polymer-nanocomposites [16, 17]. In order to enhance the compatibility between the polymer phase and filler phase of composite systems chemical coupling agents such as functional silanes, organotitanates etc. are used. The coupling agents will act as a bridge between polymer matrix and filler particles. Studies were reported on the effect of coupling agents on dielectric properties of polymer ceramic composites [18, 19].

The elastomer used for the present study was butyl rubber. Butyl rubber is a synthetic elastomer with excellent dielectric properties in the microwave frequencies ($\varepsilon_r = 2.4$, $\tan\delta \approx 10^{-3}$), good mechanical flexibility, ageing resistance, weathering resistance [20] etc. In order to develop low permittivity composites, the relative permittivity of the ceramic should be as low as possible. Numerous low relative permittivity ceramic materials are available. Among the available low permittivity ceramics, Al$_2$O$_3$, SiO$_2$ and Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ (BZT) are used for the preparation of low permittivity butyl rubber-ceramic composites in the present study since they have relatively low loss factor.

Among the low permittivity ceramics, alumina is a well known low loss ceramic packaging material. The quality factor of alumina depends on the purity and density of the sintered ceramics. The quality factor (Q$_{xf}$) of alumina is about 1 million with $\varepsilon_r = 9.8$ and $\tau_f = -60$ ppm/$^\circ$C at room temperature [21]. The very high thermal conductivity (30 Wm$^{-1}$K$^{-1}$)
and low CTE (6-7 ppm/°C) of alumina makes it a suitable electronic packaging material. Elastomer-alumina composites were well studied for its mechanical and curing characteristics [22, 23]. Recently, the effect of nano alumina loading on the electrical and mechanical properties of polyvinyl alcohol composites was investigated by Nigrawal et al. [24]. Ratheesh et al. investigated the dielectric properties of alumina and magnesia filled PTFE composites and found that PTFE-alumina composites are excellent candidates for microwave substrate applications [25]. Recently the effect of particle size on dielectric, thermal and mechanical properties of silicone rubber-alumina composites was investigated by Namitha et al. [26]. Zhou et al. synthesized silicone rubber-alumina composites and investigated the effect of alumina filler on the thermal and mechanical properties of silicone rubber composites [27]. Zhou et al. also reported the effect of alumina particle size on the mechanical and physical properties of silicone rubber composites [28]. Even though studies were reported on the alumina filled polymer composites, only a few reports are available on the evaluation of microwave dielectric properties of elastomer-alumina composites.

Silica is another low permittivity ceramic with excellent dielectric properties (\(\varepsilon_r = 4\), \(\tan\delta \approx 10^{-3}\)) and thermal properties such as thermal conductivity = 1.4 Wm\(^{-1}\)K\(^{-1}\) and CTE = 0.5 ppm/°C [29]. Silica is an important reinforcing filler of elastomer for industrial applications. Silica loaded polymer composites were also reported for microwave electronic applications [30-32]. Chen et al. studied the effect of filler loading and particle size on the dielectric, mechanical and thermal properties of PTFE-SiO\(_2\) composites [33]. 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 [34].
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Ba(Zn_{1/3}Ta_{2/3})O_{3} is a complex perovskite ceramic with $\varepsilon_r = 28$, $\tan\delta \approx 10^{-3}$ and a nearly zero temperature coefficient of resonant frequency ($\tau_f = 1$ ppm/°C) [35]. It is an ideal dielectric resonator at microwave frequencies. Recently, Manu et al. reported the effect of Ba(Zn_{1/3}Ta_{2/3})O_{3} ceramic on the dielectric, mechanical and thermal properties of high density polyethylene composites [36]. The microwave dielectric properties of PTFE-Ba(Mg_{1/3}Ta_{2/3})O_{3} composite were studied by Nijesh et al. and found that PTFE filled with 76 wt% Ba(Mg_{1/3}Ta_{2/3})O_{3} attained a relative permittivity of 6.7 and a loss tangent of 0.003 in the X-band [37]. Namitha et al. studied the microwave dielectric properties of silicone rubber-BZT composites and found that the dielectric properties of silicone rubber were improved with the addition of BZT [38]. However, a very little attempt has been made to explore the microwave dielectric properties of BZT filled polymer composites.

The present chapter deals with the investigation of the effect of low permittivity ceramic fillers such as Al_{2}O_{3}, SiO_{2} and Ba(Zn_{1/3}Ta_{2/3})O_{3} on dielectric, thermal and mechanical properties of butyl rubber-ceramic composites. The effect of filler particle size on properties of the composites was studied by incorporating nano alumina in the butyl rubber matrix. The experimental values of relative permittivity and thermal conductivity of composites were compared with various theoretical models.

3.2 Butyl rubber-Al_{2}O_{3} composites

Since alumina is a widely used ceramic packaging material, the effect of filler particle size on dielectric, thermal and mechanical properties of butyl rubber-ceramic composites was studied in butyl rubber-alumina composites. The alumina (micron and nano) powder was procured from Sigma Aldrich. The powder was dried at 100°C for 24 hours before using for
composite preparation. The butyl rubber-micron alumina (BR/AL) and butyl rubber-nano alumina (BR/nAL) composites were prepared as described in section 2.1.4.1. The sample designation and the corresponding ceramic volume fraction ($v_f$) are given in Table 3.1. The BR/AL composites were prepared with a micron alumina loading from 0-0.42 $v_f$. The nano alumina has high surface area and large ceramic volume. Hence the possibility of agglomeration of nano particles increases with filler loading. This makes the processing of butyl rubber-nano alumina composites difficult at higher filler loading [39]. Hence, a maximum loading of 0.1 volume fraction of nano alumina is possible in the case of BR/nAL composites. The composites thus prepared were characterized for microstructure, dielectric, thermal and mechanical properties using techniques explained in section 2.2.

Figure 3.1 shows the powder XRD pattern of micron alumina and nano alumina. All the peaks are indexed based JCPDS file no. 46-1212. The phase purity of the ceramics was clear from Fig. 3.1.

![Fig. 3.1 XRD patterns of micron alumina and nano alumina](image-url)
Figure 3.2 shows the SEM images of micron alumina, nano alumina powder and their composites with butyl rubber. Fig. 3.2 (a) and (b) depicts the morphology of micron alumina and nano alumina powder respectively. Fig. 3.2 (c) is the fractured surface of the BR+0.1 $v_f$ of micron alumina composite which shows a homogeneous dispersion of ceramic particles in the rubber matrix. Some agglomerations are observed for the composites with nano alumina and are clear from the fractured surface of the BR+0.1 $v_f$ of nano alumina composite (Fig. 3.2 (d)).

Table 3.1 gives the dielectric properties at 1 MHz and moisture absorption of BR/AL and BR/nAL composites. The relative permittivity of both composites increases with filler loading. This is due to the high relative permittivity of alumina compared to butyl rubber matrix. From the Table 3.1 it is clear that the BR/nAL composite have high relative
permittivity than that of BR/AL composites. The composites filled with nano particles have large interfacial area for the same filler loading which promotes interfacial polarization mechanism leads to increase in relative permittivity of BR/nAL composites. The loss tangent is the main factor affecting the frequency selectivity of a material and is influenced by many factors such as porosity, microstructure and defects [40]. The loss tangent of both composites shows same trend as that of relative permittivity. The moisture content is an important parameter for materials used for packaging applications. Absorption of moisture from the working atmosphere will degrade the dielectric properties since water is a polar molecule. It is clear from Table 3.1 that as the filler content increases, the volume % (vol%) of water content increases for both composites since the ceramic is hydrophilic in nature. Compared to micron composite, nano composites have a high tendency to absorb moisture due to the large surface area of the nano alumina and also for higher nano filler loading pores are present in the composites due to the agglomeration of the particles. This is evident from the SEM image 3.2 (d). The loss tangent and moisture absorption of butyl rubber-nano alumina composites are much higher as compared to the composites based on micron alumina.

Figure 3.3 (a) and (b) shows the variation of relative permittivity and loss tangent of BR/AL and BR/nAL composites at 5 GHz. As the relative permittivity of alumina is higher than the butyl rubber, the $\varepsilon_r$ of BR/AL and BR/nAL composite shows an increasing trend with filler content. The relative permittivity of both composites at microwave frequency is slightly higher than that at 1 MHz. Further studies are needed to understand the increase in $\varepsilon_r$ in the microwave frequency range as compared to at low frequency in butyl rubber-alumina composites. The nano alumina filled butyl rubber composites have higher relative permittivity than micron
Table 3.1 Dielectric properties at 1 MHz and moisture absorption of BR/AL and BR/nAL composites

<table>
<thead>
<tr>
<th>Composite material</th>
<th>Sample Designation</th>
<th>Filler in phr&lt;sup&gt;#&lt;/sup&gt; (1&lt;sup&gt;st&lt;/sup&gt;)</th>
<th>$\varepsilon_r$&lt;sup&gt;(1 MHz)&lt;/sup&gt;</th>
<th>$\tan \delta$&lt;sup&gt;(1 MHz)&lt;/sup&gt;</th>
<th>Water absorption&lt;sup&gt;(vol%)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyl rubber-</td>
<td>BR-0</td>
<td>0 (0.00)</td>
<td>2.44</td>
<td>0.0003</td>
<td>0.039</td>
</tr>
<tr>
<td>micron alumina</td>
<td>BR/AL-1</td>
<td>10 (0.02)</td>
<td>2.48</td>
<td>0.0011</td>
<td>0.045</td>
</tr>
<tr>
<td>composite</td>
<td>BR/AL-2</td>
<td>20 (0.04)</td>
<td>2.54</td>
<td>0.0012</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>BR/AL-3</td>
<td>30 (0.06)</td>
<td>2.65</td>
<td>0.0021</td>
<td>0.056</td>
</tr>
<tr>
<td></td>
<td>BR/AL-4</td>
<td>40 (0.08)</td>
<td>2.73</td>
<td>0.0032</td>
<td>0.057</td>
</tr>
<tr>
<td></td>
<td>BR/AL-5</td>
<td>50 (0.10)</td>
<td>2.78</td>
<td>0.0046</td>
<td>0.065</td>
</tr>
<tr>
<td></td>
<td>BR/AL-6</td>
<td>100 (0.26)</td>
<td>3.01</td>
<td>0.0051</td>
<td>0.067</td>
</tr>
<tr>
<td></td>
<td>BR/AL-7</td>
<td>200 (0.33)</td>
<td>3.80</td>
<td>0.0063</td>
<td>0.071</td>
</tr>
<tr>
<td></td>
<td>BR/AL-8</td>
<td>300 (0.42)</td>
<td>4.61</td>
<td>0.0083</td>
<td>0.082</td>
</tr>
<tr>
<td>Butyl rubber-</td>
<td>BR/nAL-1</td>
<td>10 (0.02)</td>
<td>2.49</td>
<td>0.0090</td>
<td>0.150</td>
</tr>
<tr>
<td>nano alumina</td>
<td>BR/nAL-2</td>
<td>20 (0.04)</td>
<td>2.55</td>
<td>0.0110</td>
<td>0.220</td>
</tr>
<tr>
<td>composite</td>
<td>BR/nAL-3</td>
<td>30 (0.06)</td>
<td>2.67</td>
<td>0.0160</td>
<td>0.490</td>
</tr>
<tr>
<td></td>
<td>BR/nAL-4</td>
<td>40 (0.08)</td>
<td>2.79</td>
<td>0.0270</td>
<td>0.620</td>
</tr>
<tr>
<td></td>
<td>BR/nAL-5</td>
<td>50 (0.10)</td>
<td>2.81</td>
<td>0.0470</td>
<td>0.700</td>
</tr>
</tbody>
</table>

<sup>#</sup> parts per hundred rubber.

<sup>st</sup>The corresponding ceramic volume fraction is given in parenthesis.
Fig. 3.3 Variation of (a) relative permittivity and (b) loss tangent of BR/AL and BR/nAL composites at 5 GHz

composite. Similar behaviour was observed by Ratheesh et al. in their work on PTFE-rutile, PTFE-silica and PEEK-SrTiO$_3$ composites [14, 30, 41]. They have reported that the nano filler has more polarization at interface region due to its high surface area and also due to large interface region between the filler and matrix. The nano composite also have high moisture content due to its large surface area. These factors will contribute to the high relative permittivity of nano composites. The relative permittivity of BR/AL composite increases from 2.40 to 4.68 as the micron alumina content increases from 0-0.42 $v_f$ and that of BR/nAL composite from 2.40 to 3.15 when the nano alumina loading increases from 0-0.1 $v_f$. It is also noted that the loss tangent increases with the increase in filler content of both
micron and nano size alumina and a high loss tangent is exhibited by the nano alumina filled composites. The main reason for the higher loss tangent of nano composite is due to its high moisture content. The lattice strain is also higher for nano fillers due to its high surface area. Similar observation is reported in PTFE/rutile, epoxy/SiO$_2$ and PTFE/alumina composites [14, 31, 42]. The loss tangent of BR/AL composite increases from 0.0017 to 0.0027 as the micron alumina loading increases from 0-0.42 $v_f$ and that of BRnAL composite increases from 0.0017 to 0.0140 as the nano alumina content increases from 0-0.1 $v_f$ at 5 GHz.

![Fig. 3.4 Comparison of theoretical and experimental relative permittivity of BR/AL and BR/nAL composites at 5 GHz](image)

Modeling techniques give relative permittivity of a composite system in terms of the relative permittivity of every constituting component and their volume fractions. Fig. 3.4 shows the comparison between the experimental and theoretical values of relative permittivity of BR/AL and BR/nAL composites at 5 GHz. All the equations are matching with the experimental $\varepsilon_r$ of both BR/AL and BR/nAL composites upto 0.1 $v_f$. Maxwell-
Garnett and Lichtenecker equation shows slight deviation 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 [43]. Hence, Maxwell-Garnett equation shows deviation at higher filler content. The most widely used relation for the prediction of $\varepsilon_r$ is Lichtenecker’s logarithmic law of mixing. It considers the composite system as randomly oriented spheroids that are uniformly distributed in a continuous matrix [44]. The deviation of experimental $\varepsilon_r$ of both 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 experimental values of $\varepsilon_r$ of both composites are matching with those values calculated from Jayasundere-Smith equation and shows deviation only at 0.42 $v_f$ of micron alumina content and at 0.1 $v_f$ of nano alumina content. The Jayasundere-Smith equation considers the particulate filled composite as a binary system and is valid only when $\varepsilon_f >> \varepsilon_m$ where $\varepsilon_f$ and $\varepsilon_m$ is the relative permittivity of filler and matrix respectively [45]. The EMT model is also in agreement with experimental $\varepsilon_r$ of both composites 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 butyl rubber matrix. The effective permittivity of a composite depends on the various factors such as relative permittivity of individual components in the system, their volume fractions, shape, size, porosity, interphase polarizability and interphase volume fractions. All these parameters cannot be accounted in a single equation. Hence, the experimental results show deviation from the theoretical values at higher filler content.
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The bending effect on dielectric properties is important as far as flexible electronic applications concerned. Figures 3.5 and 3.6 show the variation of dielectric properties of butyl rubber-micron alumina and butyl rubber-nano alumina composites with bending. It is clear from the Fig. 3.5 (a) and (b) that the relative permittivity of all the composites is nearly independent of bending. It is evident from the Fig. 3.6 (a) and (b) that the loss tangent of the nano composites is almost independent of bending and that of micron composite shows slight variation with bending. Hence, these are suitable for flexible electronic applications.

![Fig. 3.5 Variation of relative permittivity of (a) BR/nAL and (b) BR/AL composites with bending](image1)

![Fig. 3.6 Variation of loss tangent of (a) BR/nAL and (b) BR/AL composites with bending](image2)
Figure 3.7 (a) and (b) shows the temperature dependence of butyl rubber-nano alumina and butyl rubber-micron alumina composite respectively. The thermal stability of relative permittivity is one of the important properties of the substrate materials that control the overall performance of the materials. From the figure it is clear that all the composites are almost thermally stable within the measured temperature range. The small decrease in relative permittivity with temperature may be due to the large difference in thermal expansion coefficient of butyl rubber and the alumina [46, 47].

![Graph showing the variation of relative permittivity of BR/nAL and BR/AL composites with temperature](image)

**Fig. 3.7 Variation of relative permittivity of (a) BR/nAL and (b) BR/AL composites with temperature**
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\(^{-1}\) [48] and can be improved by the addition of ceramic fillers as the TC of ceramic is higher than that of polymers. 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 [49]. The variation of thermal conductivity of both BR/AL and BR/nAL composites with filler content is shown in Fig. 3.8. The TC of both composites shows increasing trend with ceramic loading. This is quite expected since the thermal conductivity of alumina (30 Wm\(^{-1}\)K\(^{-1}\)) is higher than that of butyl rubber matrix (0.13 Wm\(^{-1}\)K\(^{-1}\)). From the inset plot in Fig. 3.8 it is clear that the TC of nano alumina loaded composites is slightly higher than that of micron composite. The matrix/filler interface plays a critical role in nano composites due to its large surface area.
The number of particles increases with decreasing particle size for the same filler content [50]. This will lead to the formation of a large number of conductive channels in nano filler added composites. Hence, the BR/nAL composites show high thermal conductivity than that of BR/AL composites. Many theoretical models have been published for predicting the thermal conductivity of composites [51]. The experimental thermal conductivity of present composites was compared with that values calculated using equations (2.13)-(2.17). Fig. 3.8 also compares the experimental thermal conductivity of both micron and nano composite with theoretical models. The physical structures assumed in the series and parallel models are of layers of the phases aligned either perpendicular or parallel to the heat flow respectively. The series and parallel model of TC gives only lower and upper limits of thermal conductivity values of composites respectively [52]. The experimental TC values of both composites are within the range of series and parallel model. The geometric mean model is in good agreement with experimental thermal conductivity of both composites upto a volume fraction of 0.1 and has a lower value than predicted thermal conductivity at higher micron alumina loading. This may be due to the agglomeration of filler particles at higher filler loadings. The other two models such as Cheng-Vachon and Maxwell-Eucken model are matching with experimental TC of both composites. Cheng and Vachon assumed a parabolic distribution of the discontinuous phase in the continuous phase based on Tsao’s model [53]. The constants of this parabolic distribution were determined by analysis and presented as a function of the discontinuous phase volume fraction. Maxwell-Eucken model considers the composite system as randomly distributed and non-interacting homogeneous spheres in a homogeneous medium.
Figure 3.9 shows the variation of coefficient of thermal expansion of butyl rubber-micron alumina and butyl rubber-nano alumina composites with filler content. The CTE of both the composites decreases with ceramic loading since the CTE value of alumina is smaller than that of rubber matrix and also the mobility of loose molecular bonds in the polymer chains are restrained by the ceramic loading [54]. The BR/nAL composites show much lower CTE value compared to that of BR/AL composites. The physical cross linking points are more in the case of nano particles because of its high specific surface area and this will increase the mechanical interaction between the filler and rubber matrix [27]. Hence the nano composites have lower CTE than that of micron composites.
Figure 3.10 shows the stress-strain curve of BR/AL and BR/nAL composites. The mechanical properties of a particulate composite depend on the strength of the adhesive bond between the different phases, the type of dispersion and the amount of particle agglomeration. From the figure it is clear that the stress needed for ceramic filled butyl rubber composite is greater than that of unfilled sample. Among BR-0, BR/AL-5 and BR/nAL-5, the stress required for BR/nAL-5 composite is high. This may be due to more homogeneous dispersion of nano particles in the rubber matrix. Chee et al. reported that at lower filler loading the nano alumina particle orient along the direction of stress and this would reinforce and increase the stiffness of the nano composite [55].

### 3.3 Butyl rubber-SiO₂ and butyl rubber-Ba(Zn₁/₃Ta₂/₃)O₃ composites

Silica was procured from Sigma Aldrich. Ba(Zn₁/₃Ta₂/₃)O₃ ceramic was prepared by conventional solid state route as described in section 2.1.2.3. The butyl rubber-silica (BR/S) and butyl rubber-BZT (BR/BZT) composites were prepared as described in section no.
2.1.4.1. The density of silica ($\rho \approx 2.6 \text{ g/cm}^3$) is lower than that of BZT ($\rho \approx 7.96 \text{ g/cm}^3$). Hence, the silica filled composites were prepared up to a loading of 0.42 vol% (200 phr) and that of BR/BZT composites up to a filler loading of 0.32 vol% (400 phr). The sample designation and the corresponding ceramic volume fraction are given in Table 3.2. The composites were then hot pressed at 200$^\circ$C for 90 minutes under a pressure of 2 MPa. The phase purity of silica and BZT were confirmed by XRD analysis. The composites were characterized for microstructure, dielectric, thermal and mechanical properties using techniques explained in section 2.2.

![XRD Patterns](image)

**Fig. 3.11** XRD patterns of (a) SiO$_2$ and (b) Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$
Figure 3.11 shows the XRD patterns of silica heat treated at 100°C for 24 hours and BZT sintered at 1500°C for 4 hours. The peaks were indexed based on the JCPDS file no. 89-8934 and 18-0201 for silica and BZT respectively. The phase purity of both the ceramics were obvious from the XRD patterns.

Figure 3.12 (a) and (b) shows the SEM images of silica and BZT powder respectively. Both silica and BZT particles are irregularly shaped and are less than 1μm in size. Fig. 3.12 (c) and (d) represents fractured SEM images of BR+0.42 v/ of SiO₂ and BR+0.32 v/ of Ba(Zn₁/₃Ta₂/₃)O₃ respectively. From the figure it is clear that the filler particles are uniformly distributed in the rubber matrix of both composites.
Table 3.2. Dielectric and water absorption properties of butyl rubber-silica and butyl rubber-BZT composites

<table>
<thead>
<tr>
<th>Composite material</th>
<th>Sample designation</th>
<th>Filler in phr</th>
<th>$\varepsilon_r$ (1 MHz)</th>
<th>tan $\delta$ (1 MHz)</th>
<th>Water absorption (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyl rubber-silica composites</td>
<td>BR-0</td>
<td>0 (0.00)</td>
<td>2.44</td>
<td>0.0003</td>
<td>0.039</td>
</tr>
<tr>
<td></td>
<td>BR/S-1</td>
<td>10 (0.03)</td>
<td>2.51</td>
<td>0.0020</td>
<td>0.048</td>
</tr>
<tr>
<td></td>
<td>BR/S-2</td>
<td>25 (0.08)</td>
<td>2.75</td>
<td>0.0050</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>BR/S-3</td>
<td>50 (0.15)</td>
<td>2.83</td>
<td>0.0060</td>
<td>0.059</td>
</tr>
<tr>
<td></td>
<td>BR/S-4</td>
<td>100 (0.26)</td>
<td>3.10</td>
<td>0.0080</td>
<td>0.078</td>
</tr>
<tr>
<td></td>
<td>BR/S-5</td>
<td>200 (0.42)</td>
<td>3.37</td>
<td>0.0100</td>
<td>0.091</td>
</tr>
<tr>
<td>Butyl rubber-BZT composites</td>
<td>BR/BZT-1</td>
<td>10 (0.01)</td>
<td>2.45</td>
<td>0.0010</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>BR/BZT-2</td>
<td>25 (0.03)</td>
<td>2.50</td>
<td>0.0012</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td>BR/BZT-3</td>
<td>50 (0.06)</td>
<td>2.71</td>
<td>0.0015</td>
<td>0.043</td>
</tr>
<tr>
<td></td>
<td>BR/BZT-4</td>
<td>100 (0.10)</td>
<td>3.11</td>
<td>0.0016</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>BR/BZT-5</td>
<td>200 (0.19)</td>
<td>3.49</td>
<td>0.0018</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>BR/BZT-6</td>
<td>300 (0.26)</td>
<td>4.45</td>
<td>0.0019</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>BR/BZT-7</td>
<td>400 (0.32)</td>
<td>5.46</td>
<td>0.0021</td>
<td>0.057</td>
</tr>
</tbody>
</table>

$^a$ parts per hundred rubber.

$^b$ The corresponding ceramic volume fraction is given in parenthesis.

Table 3.2 shows the dielectric and water absorption properties of butyl rubber-silica and butyl rubber-BZT composites. The relative permittivity and loss tangent of both the composites increases with filler content. The increase in $\varepsilon_r$ of the composites is mainly due to the high relative permittivity of silica and BZT as compared to rubber matrix. The connectivity among the filler particles increases at higher filler content which in turn
increases the relative permittivity of the composites [56]. The interfacial area and the possibility of accumulation of space charges at interface of polymer-ceramic composite increases with increase in the ceramic loading which in turn increases the loss tangent of the composites. The tanδ of BR/S composite is found to be higher than that of BR/BZT composites. This may be due to the presence of more moisture content in the silica powder. The moisture content significantly influences the electrical properties of the composites since the relative permittivity and loss tangent of water is high [57]. Hanna et al. reported a similar observation in styrene butadiene rubber-silica composites [34]. It is also evident from the Table 3.2 that the volume % of moisture content increases with filler content for both BR/S and BR/BZT composites. This may be due to the hydrophilic nature of ceramic. It has been reported that materials with moisture absorption upto about 0.1% can be used for electronic packaging applications [58]. The present composites exhibit moisture absorption within this limit.

Figure 3.13 (a) and (b) depicts the microwave dielectric properties of BR/S and BR/BZT composites at 5 GHz. The relative permittivity of both the composites increases with filler loading. The increase in total polarizability of composite material with filler content contributes to the increase in relative permittivity of the composites. The relative permittivity of BR/S composites at 5 GHz is less than that at 1 MHz as expected due to the absence of certain polarization mechanisms at microwave frequencies. But the \( \varepsilon_r \) of BR/BZT composites at 5 GHz is higher than that at 1 MHz. The relative permittivity of BR/S composite is 3.09 for the maximum silica loading of 0.42 v_f. The relative permittivity of BZT filled butyl rubber composites has \( \varepsilon_r \) of 5.72 for the maximum filler loading of 0.32 v_f. The BZT based composite has higher relative permittivity since silica has a lower relative
permittivity. From the figure it is also clear that the loss tangent of BR/S and BR/BZT composites shows similar trend as that of relative permittivity with increase in filler loading. The tanδ of BR/S composites is higher than that of BZT filled composites. The tanδ of BR/S-5 and BR/BZT-7 composites at 5 GHz are 0.0045 and 0.0025 respectively. The increase in loss of BR/S composites is due to the presence of more moisture content in silica composites than that of BR/BZT composites which is evident from Table 3.2. The dipole relaxation of water molecule in the microwave frequency contributes to loss tangent of the composites [59].

![Fig. 3.13 Variation of εr and tan δ of (a) BR/S and (b) BR/BZT composites with filler content at 5 GHz](image1)

![Fig. 3.14 Comparison of theoretical and experimental relative permittivity of (a) BR/S and (b) BR/BZT composites at 5 GHz](image2)
The precise prediction of effective relative permittivity of the composites is very important for electronic packaging applications. Fig. 3.14 shows the comparison of experimentally observed relative permittivity with the values predicted using the equations (2.6) to (2.9). It is clear from Fig. 3.14 (a) that the experimental relative permittivity of butyl rubber-silica composites are in agreement with theoretical models upto a filler loading of 0.15 v_f and shows deviation at higher silica content. Among the theoretical models, the EMT model proposed by Rao et al. [60] holds good for BR/S composites. EMT model considers the composite as an effective medium in which random unit cell (RUC) is embedded. The RUC is defined as a core of filler surrounded by a concentric matrix layer. The basic assumption of EMT model is that the RUC embedded in effective medium cannot be detected in an electromagnetic experiment which makes it possible to predict the relative permittivity of the composite. 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 BR/S composites is 0.2. It is evident from Fig. 3.14 (b) that the values of ε_r predicted by Maxwell-Garnett equation shows considerable deviation from the experimental values of BR/BZT 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 0.19 and shows deviation at higher BZT loading. This may be due to the lack of consideration of interfacial interaction between the polymer and the filler particles. The Jayasundere-Smith equation is in agreement with experimental data since this equation considers the interactions between the fields of neighbouring filler particles [61]. The experimental relative permittivity of BR/BZT
composites are also very well fit with EMT model. The ‘n’ value is determined empirically and the value of ‘n’ for BR/BZT composite is 0.2.

The effect of bending on microwave dielectric properties of butyl rubber-silica and butyl rubber-BZT composites is shown in Fig. 3.15 and 3.16. It is evident from the Fig. 3.15 (a) and (b) that the $\varepsilon_r$ of BR/S composites shows a slight decrease after a bending cycle of 75 for butyl rubber loaded with 0.42 $v_f$ of silica content. This may be due to the aggregating tendency of silica at higher loading. The relative permittivity of BR/BZT composites is nearly independent of repeated bending. From the Fig. 3.16 (a) and (b) it is clear that the tan$\delta$ of silica filled composites shows small variation with bending. The loss tangent of the butyl
rubber- BZT composites also shows a small variation with repeated bending. But the variation is only marginal [62].

Figure 3.17 (a) and (b) shows the variation of relative permittivity of butyl rubber-silica and butyl rubber-BZT composites with temperature at 1 MHz. It is noted that the variation of relative permittivity with temperature is small and the relative permittivity of both the composites decreases 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. 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 [63]. Both BR/S and BR/BZT composites are almost thermally stable in the measured temperature range.

![Variation of thermal conductivity of (a) BR/S and (b) BR/BZT composites with filler loading](image)

The variation of thermal conductivity of BR/S and BR/BZT composites with filler content are shown in Fig. 3.18. The thermal conductivity of butyl rubber is 0.13 Wm\(^{-1}\)K\(^{-1}\). As the thermal conductivity of fillers silica (1.4 Wm\(^{-1}\)K\(^{-1}\)) and BZT (3.9 Wm\(^{-1}\)K\(^{-1}\)) are higher than that of matrix, the thermal conductivity of both BR/S and BR/BZT composites increased with filler content. The increase in thermal conductivity of both the composites at higher filler content is due to the presence of more connecting paths between the filler particles [16]. The thermal conductivity of BR/S composites increases from 0.13 to 0.56 as the silica loading increases from 0-0.42 \(v_f\) and that of BR/BZT composites from 0.13 to 0.35 as the...
filler loading increases from 0-0.32 v_f. The thermal conductivity of the composite can be further enhanced by adding high thermal conductivity fillers such as aluminium nitride, silicon nitride etc. Fig. 3.18 also compares the experimental thermal conductivity with those calculated using equations 2.13 to 2.17. From Fig. 3.18 (a) it is evident that all the theoretical models match with measured thermal conductivity of butyl rubber-silica composites at lower silica loading and deviates from predicted values after a filler loading of 0.15 v_f. The wide variations in filler geometry, orientation and dispersion makes it difficult to compare composites filled with different materials. Moreover, the interfacial boundary thermal resistance between the filler particles and the matrix, referred to as Kapitza resistance, [64] is not taken into account while calculating the thermal conductivity of composites. It is not possible to measure it at the molecular level where it takes place. As a result, experimental and theoretical thermal conductivity data are often not in agreement. From the Fig. 3.18 (b) it is clear that the TC values of BR/BZT composites lies within the range of series and parallel models. It is worth to be noted that the geometric mean model and Cheng-Vachon model is in good agreement with experimental values. Maxwell-Eucken model shows slight deviation from experimental values at higher filler loading.

The variation of coefficient of thermal expansion of butyl rubber composites filled with silica and BZT are shown in Fig. 3.19. It is seen that the CTE of BR/S and BR/BZT composites decreases with filler loading as the CTE of the fillers, silica (0.5 ppm/°C) and BZT (4.2 ppm/°C) are lower than that of rubber matrix (191 ppm/°C). In polymer-ceramic composite there is a region of tightly bound polymer chains in the immediate vicinity of the filler particles followed by a region of loosely bound polymer chains [65]. The filler particles will largely restrict the thermal expansion of polymer chains tightly bound to them. But the
Chapter-3

thermal expansion of loosely bound polymer chains may not be that much constrained. The addition of more filler leads to the reduction in volume fraction of loosely bound polymer chains. Consequently the thermal expansion of the composite will get suppressed.

Figure 3.20 shows the stress-strain curves of BR-0, BR/S-5 and BR/BZT-7. The stress needed for elongation increases with filler content. The interfacial adhesion plays a major role in mechanical properties of the composites. Todorova et al. [66] reported that the interfacial adhesion increases with filler loading which in turn increases the effectiveness of the stress transfer from rubber chains. Salaeh et al. [67] reported that the mobility of molecular chains decreases due to the incorporation of ceramic particles and hence the increase in stiffness of the composite. From the figure it is clear that the silica filled composite shows higher reinforcement than that of BZT filled composite. Silica is reported to be good reinforcing filler for rubber composites [68, 69].
3.4 Effect of coupling agent on microwave dielectric properties of butyl rubber-BZT composites

In order to improve the compatibility between butyl rubber and ceramic of elastomer-ceramic composites, mercapto group based coupling agents are employed [70]. These are bifunctional silanes with different reactivity, where the double functionality allows them to react with the hydroxyl groups present on the surface of filler particles and the second sulfur based reactive groups interact with polymer macromolecules during the vulcanization step. Mercaptopropyltrimethoxy silane (MPTMS) coupling agent was used for the present investigation. Silane coupling agent acts as a bridge between butyl rubber and BZT ceramic and is shown in Fig. 3.21

![Fig. 3.21 Silane coupling mechanism](image)

The infrared spectrum of surface treated BZT is shown in Fig. 3.22. The peak in 620 cm\(^{-1}\) is the result of Ba-O bond vibrations. The peaks in 2920-2690 cm\(^{-1}\) range indicate –CH\(_2\) stretching vibration of silane coupling agent. The peak in 1445 cm\(^{-1}\) indicates the scissoring vibration of –CH\(_2\) groups. The peaks at around 1000 cm\(^{-1}\) (\(\nu_{as}, Si-O\)) and 570 cm\(^{-1}\) (\(\delta, Si-O-Si\)) attribute to the success of hydrolysis and condensation reactions (\(\nu\) represents stretching, \(\delta\) in-plane bending). This confirms the coating of MPTMS on BZT.
Table 3.3 Microwave dielectric properties of untreated and silane treated BZT–butyl rubber composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varepsilon_r$ at 5 GHz</th>
<th>$\tan\delta$ at 5 GHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR/50BZT</td>
<td>2.77</td>
<td>0.0018</td>
</tr>
<tr>
<td>BR/50sBZT</td>
<td>2.82</td>
<td>0.0030</td>
</tr>
<tr>
<td>BR/100BZT</td>
<td>3.24</td>
<td>0.0019</td>
</tr>
<tr>
<td>BR/100sBZT</td>
<td>3.51</td>
<td>0.0052</td>
</tr>
</tbody>
</table>

The microwave dielectric properties of selected composition of BR/BZT and silane treated BZT loaded butyl rubber composites (BR/sBZT) are given in Table 3.3. From the Table 3.3 it is clear that the silane coupled composites does not exhibit much improvement in relative permittivity of the composites. The silane treated composite shows higher loss tangent than that of untreated one. This may be due to the presence of additional phases from coupling agent. Xu et al. observed a similar behaviour in aluminium/epoxy composites [71].
As far as microwave electronic packaging and substrate applications are concerned, a low loss material is preferred. Hence coupling agents are not used in our further works.

### 3.5 Conclusions

- The effect of low permittivity fillers such as alumina, silica and barium zinc tantalate on the dielectric, thermal and mechanical properties of butyl rubber composites was investigated. The influence of filler particle size on the performance of butyl rubber-alumina composites was also studied.

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

- For 0.1 volume fraction of micron alumina loading, the composite have relative permittivity of 2.82 and loss tangent of 0.0023 at 5 GHz and for the same volume fraction of nano alumina content the composite have $\varepsilon_r$ of 3.15 and tanδ of 0.0140 at 5 GHz. However, the nano alumina filled butyl rubber composites shows higher loss tangent than that of micron composite.

- The dielectric properties of the composites were studied at 1 MHz and 5 GHz and are found to be improved with ceramic loading. The butyl rubber-silica composites attained $\varepsilon_r = 2.79$, tanδ = 0.0039 for a optimum silica loading of 0.26 $v_f$ and the butyl rubber-BZT composite have $\varepsilon_r = 4.88$, tanδ = 0.0022 for a optimum BZT loading of 0.26 $v_f$ at 5 GHz.

- The thermal properties of the composite were also improved with filler content. The thermal conductivity and coefficient of thermal expansion of BR/AL composite is 0.21 Wm$^{-1}$K$^{-1}$ and 142 ppm/°C and that of BR/nAL composite is 0.27 Wm$^{-1}$K$^{-1}$ and
100 ppm/°C respectively for 0.1 v_f of filler loading. The water absorption of both composites for 0.1 v_f of filler loading are 0.065 vol% and 0.700 vol% respectively.

- The butyl rubber-silica composites attained CTE = 102 ppm/°C, TC = 0.40 Wm⁻¹K⁻¹ and water absorption = 0.078 vol% for a optimum silica loading of 0.26 v_f. The butyl rubber-BZT composite have CTE = 112 ppm/°C, TC = 0.30 Wm⁻¹K⁻¹ and water absorption= 0.047 vol% for an optimum BZT loading of 0.26 v_f.

- Various theoretical models were used to fit the experimental values of relative permittivity and thermal conductivity of all the composites.

- The stress-strain curves of all composite shows the mechanical flexibility of the composites. The butyl rubber-nano alumina composite shows better mechanical properties than that of micron composite due to the more homogenous dispersion of nano particles in the rubber matrix.

- The measured properties suggest that butyl rubber-micron Al₂O₃, butyl rubber-SiO₂ and butyl rubber-Ba(Zn₁/₃Ta₂/₃)O₃ composites are suitable candidates for microwave substrate and electronic packaging applications.
3.6 References


58. T. S. Laverghetta, Microwave materials and fabrication techniques, Artech House, Dedham MA (1985).


