Chapter 6

Electrical behavior of ionomers at microwave frequencies

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6.1 Introduction

Microwaves, even though constitute only a small portion of the electromagnetic spectrum, but their uses have paramount importance in the material characterisation for industrial scientific and medical applications (ISM). Characterisation of the material is essential for the proper selection and implementation of a substance for ISM applications. The dielectric parameters over the microwave frequencies are needed to assess their suitability for use in dielectric wave guides, lenses, dielectric resonators and microwave integrated circuit (MIC) substrates; and on lossy material
for estimating their heating response in microwave heating applications. The dielectric data, besides being useful on lossy ceramics for their use as microwave absorbers; lossy pastes for the design of new food packages, for heating in microwave ovens and on biological materials for diathermy serve as a tool for investigating the intermolecular and intramolecular mechanisms of compounds. It has also been useful to estimate the amount of moisture in wood, sand and agricultural products. As the dielectric properties aid the calculation of internal electric fields resulting from the exposure to the nonionising electromagnetic (EM) fields, it has excellent medical applications. The radio and microwave frequencies are effectively used in the treatment of hyperthermia of tumors and other disorders. For ISM applications, which covers from few kHz to several GHz, the range of relative permittivity ($\varepsilon_r$) for the materials of interest is manifold. The real part $\varepsilon'$ of relative complex permittivity ($\varepsilon_r$) can vary from a value of about two to few thousand while the imaginary part $\varepsilon''$ of relative complex permittivity from a small fraction to a large value of about hundreds for some materials.

There is considerable interest in the microwave probing of the electrical behavior of many polymers and their compounds due to their potentially wide range of microwave applications [1–4]. Nagakabo et al [5] have showed that composite dielectric materials could be used to make a solid organism phantom in a useful microwave frequency band. All these studies direct us to the wide possibility of the use of polymers as components in microwave applications. Development of new dielectric polymers showing response at any particular frequency of the microwave region becomes a topic of much attention, of late. A special class of polymers called ionomers, in this respect, may become an important group of materials [6]. Incorporation of low level of ionic groups in to the elastomers transforms it in to a reprocessable material possessing thermal stability [7]. Existence of ionic groups as simple or larger multiplets in the elastomer matrix may act as the thermo labile cross-links. Under a suitable microwave frequency these ionic centers may be polarizable and hence dielectric. Hence it seemed worthwhile to investigate the dielectric properties of the ionomers at the microwave region. In spite of the relatively extensive effort on the radio and microwave investigations on the dielectric properties of many conductive polymers, very little effort has been devoted to the dielectric
characterization of ionomers [8-11]. The literature describing the dielectric behaviors of ionomers, besides being fewer, are mainly dealt with the measurement at the radio frequency [12,13]. Microwave studies on the electrical behavior of the ionomers, however, have been made extensively with swollen ionomer membranes [14]. Except the studies of Dabek in which the author compares the complex dielectric permittivity of the dry and the swollen ionomer membranes measured at the S-band frequencies of the microwave region, no other extensive studies on the dielectric behavior such as complex dielectric permittivity, dielectric loss factor, a.c. conductivity, and microwave heating coefficient of the dry ionomers at room temperature in the S-band frequencies of the microwave region have been reported yet. Unlike the impedance method with the capacitance modification employed in the microwave dielectric measurement by Dabek, a novel microwave measurement technique called cavity perturbation technique has been used in our experiment. The present study envisages a new and convenient microwave method called cavity perturbation technique, where the samples can be used in the pellet, powdered, solution, bulk, or in any desired form.

Cavity perturbation technique [15] is a highly sophisticated method for the evaluation of the dielectric characterisation of the materials. The experimental set-up consists of a transmission type S-band rectangular cavity resonator, HP 8714 ET network analyzer and an interfacing computer and has been described in detail in the section 2.7 of chapter 2. The cavity resonator is excited in the TE$_{10p}$ mode. The sample was molded in an electrically heated hydraulic press for 5 minutes at 120°C, under a pressure of 10 Mpa. The molded samples were dried in a vacuum oven at room temperature for 72 hrs. Samples prepared in the form of thin strips of dimension 6 x 2 x 35 mm are introduced into the cavity resonator through the non-radiating slot. Samples were again dried in an oven at 120°C for 24 hrs and the measurements were repeated for the consistency of the results. As microwave devices for industrial scientific and medical (ISM) applications [16] have been found to use S-band or preferably 2.45 GHz frequencies, only the dielectric investigations of the ionomers at the S-band frequencies of the microwave region has greater industrial importance.

This chapter deals with the microwave probing of the dielectric properties such as complex dielectric permittivity, dielectric loss factor, a.c. conductivity, and microwave heating coefficient of the ionomers based on radiation induced styrene
grafted natural rubber [17] at room temperature under the S-band (2-3 GHz) frequencies of the microwave region using the cavity perturbation technique.

### 6.2 Microwave measurement.

According to the theory of cavity perturbation, the complex frequency shift [18] is related as:

\[
- \frac{d\Omega}{\Omega} \approx \frac{(\varepsilon_r' - 1) \int \frac{E}{V_s} dV}{2 \int \left| \frac{E}{V_c} \right|^2 dV}
\]  

(1)

But

\[
\frac{d\Omega}{\Omega} \approx \frac{d\omega}{\omega} + \frac{i}{2} \left[ \frac{1}{Q_s} - \frac{1}{Q_0} \right]
\]  

(2)

d\Omega is the complex frequency shift. E₀ and E are the electric fields in the unperturbed and perturbed states respectively. Equating (1) and (2) and separating real and imaginary parts we get

\[
\varepsilon_r' - 1 = \frac{f_e - f_s}{2 f_s} \left( \frac{V_e}{V_s} \right)
\]  

(3)

\[
\varepsilon_r'' = \frac{V_e}{4 V_s} \left( \frac{Q_o - Q_s}{Q_o Q_s} \right)
\]  

(4)

Here, \( \varepsilon_r = \varepsilon_r' - i \varepsilon_r'' \), \( \varepsilon_r' \) is the relative complex permittivity of the sample, \( \varepsilon_r' \) is the real part of the relative complex permittivity, which is usually known as dielectric constant and \( \varepsilon_r'' \), the imaginary part of the relative complex permittivity, which is associated with the dielectric loss of the material. While \( f_o \) and \( Q_o \) represent the
resonant frequencies and quality factors of the vacuum, $f_s$ and $Q_s$ represent that of the sample. $V_s$ and $V_c$ are the volumes of the sample and the cavity resonator respectively. Using the experimental data for $\varepsilon_r', \varepsilon_r''$ and the equation relating complex conductivity ($\sigma$) and relative complex permittivity ($\varepsilon_r$), we can write,

$$\sigma = i\omega \varepsilon_r = i\omega (\varepsilon_r' - i\varepsilon_r'')$$

If $\sigma$ is expressed in terms of its real and imaginary components

$$\sigma = \sigma' + i\sigma''$$

where $\sigma'$, the real part of complex conductivity

$$\sigma' = \omega \varepsilon_r'' = 2\pi f \varepsilon_0 \varepsilon_r''$$

and imaginary part

$$\sigma'' = \omega \varepsilon_r' = 2\pi f \varepsilon_0 \varepsilon_r'$$
6.3 Dielectric properties of ionomers

6.3.1 Microwave Investigations.

6.3.1a. Dielectric constant

The dielectric properties of the base polymer and their ionomers probed at 2-3 GHz frequencies of the microwave region have been investigated. These results reveal that the dielectric constant ($\varepsilon'$) of the ionomers increase, reach a maximum, and then decrease with the frequency of the microwave radiation (Fig. 6.1). The ionic content in the ionomer however shows direct relationship with $\varepsilon'$ up to the threshold ionic concentration of 26.5 meq. Figure 6.2 demonstrates the dependence of frequency ($\omega/2\pi$) on the dielectric loss-frequency product ($\varepsilon''\omega$) of the ionomer. The dielectric loss factor or the imaginary part of the relative complex permittivity ($\varepsilon''$) of the ionomers with 0, 14.5, 21.2, 26.5 and 40 meq of ionic content have been investigated.

![Fig. 6.2 Dependence of frequency on the dielectric loss-frequency product of the RISGNR containing 0, 14.5, 21.2, 26.5 and 40 meq of ionic groups](image)

6.3.1.b. Complex conductivity-real part
The relative complex conductivity or the a.c. conductivity (real part $\sigma'$) of the ionomer has been observed to be affected by both frequency (Fig 6.3) and ionic content in the ionomer (Fig 6.4). Logarithmic plot of $\sigma'$ against angular frequency ($\omega$) of the microwave region (Fig 6.5) may be considered as supplementary evidence for the above observations.

![Graph](image)

**Fig. 6.3** Dependence of frequency on conductivity (real part) of 26.5 ZnS-SGNR ionomer

6.3.1.c. Complex conductivity-imaginary part

Microwave investigations of the imaginary part of the relative complex conductivity $\sigma''$ of the ionomer has been influenced by the frequency $\omega (= 2\pi f)$. This has been shown in the $\log \sigma'' - \log \omega$ plot of the ionomer (Fig 6.6). The $\tan\delta = \varepsilon''/\varepsilon'$ is commonly employed as a direct measure of the dielectric loss, which in turn provides a measure of the conductivity [19].

6.3.1.d. Loss tangent

The loss tangents for these ionomers increase with ionic concentration (Fig. 6.8 & 6.9) and show a loss tangent threshold at 26.5 meq of ionic concentration.
Fig. 6.4. Conductivity of the ionomer as a function of ion content in the ionomer at the S-band frequencies of the microwave region

Although $\sigma'$ is customarily considered as a.c. conductivity [20] and is not well defined for disordered materials such as conducting polymers [21], $\sigma'$ is often used to describe the frequency dependence of conductivity. The figure 6.4 shows that the ionic content has a dramatic influence on the a.c. conductivity of the ionomer at 2 - 3 GHz frequencies of the microwave region. The maximum percolation behavior, for the zinc salt of sulfonated SGNR at the optimum conditions of 2.6 GHz frequency and 26.5 meq ionic content, may be manifested from an a.c. component (real part of complex conductivity - $\sigma'$) of $3.3 \times 10^{-4}$ S/cm in the ionomer. The same parameter for the nonionic SGNR was $1.8 \times 10^{-12}$ S/cm. The ionic conductivity of the SGNR ionomer is comparable with the conductivity of other polymers [22-25]. The natural rubber ionomer may be useful as an alternative material in Industrial scientific and medical devices that require specifications such as microwave active, thermoplastic, and ionic cross-linked elastomer of good physical properties.
6.3.2 Microwave conduction in ionomers based on RISGNR

The conductivity of the ionomer under the microwave field may be attributed to the polarization (scheme 6.1) caused by the alternating accumulation of ionic associations (Schemes 3.2 & 3.3 in chapter 3). Due to the orientation polarization of the dipoles, the possibility of dielectric relaxation (so also dielectric loss) cannot be ruled out at higher frequencies. This might result in the decrease of $\varepsilon'_r$ with frequency. This dipole polarization may be related to the "frictional" losses caused by the rotational displacement of molecular dipoles under the influence of the alternating microwave field.

![Graph showing the influence of frequency on the log (complex conductivity-real) of RISGNR containing 0, 14.5, 21.2, 26.5 and 40 meq ionic concentration.](image)

**Fig. 6.5** Influence of frequency on the log (complex conductivity-real) of RISGNR containing 0, 14.5, 21.2, 26.5 and 40 meq ionic concentration

The improvement in the dielectric constant with ionic content (Fig. 6.7) may be due to the increase in the polar centers such as unassociated ionic moieties, multiplets, ionic clusters and zinc metal ions in the polymer matrix. The microwave responses of these charge centers may be contributing towards the dielectric constant. At higher frequency, the rotatory motion of the molecules may not be sufficiently rapid for the attainment of equilibrium with the field. The polarization then acquires a component...
Scheme 6.1 Proposed model showing the dipole orientation in an alternating microwave field. (1), (2), (3), (4), (5), and (6) schematically represent the progressive change in the charge of polarized matrix between conducting elements modeled as a capacitor network and the resultant position of a dipole during one cycle of an a.c. field.

Fig. 6.6 Influence of frequency on the complex conductivity (Imaginary) of the ionomers.

out of phase with the field, and the displacement current acquires a conductance component in phase with the field, resulting in thermal dissipation of energy. When
this occurs, dielectric losses will be generated. At higher ionic content, the molecular interactions would lose the flexibility of the polymer chains.

![Graph showing dielectric constant vs ionic content](image)

*Fig. 6.7 Influence of ionic concentration on the dielectric constant.*

The dipole attached to a flexible chain can reorient more easily than one attached to a stiff chain. Phase inversion and percolation threshold also would be occurring at higher ionic concentration [6]. At very high frequencies, the viscosity of the polymer hinders dipole movement and they cannot orient in the rapidly reversing field. Consequently, the dipoles do not influence the a.c. characteristics at very high frequencies. The many fold initial increase in the conductivity of the base polymer up on incorporating zinc sulfonate groups may be attributed to the formation of the ionic nano clustering, which act as centers of conductance [19]. Because the hydrocarbon backbone cannot transport the charge carriers, the formation of the ionomers multiplets represented in scheme 3.2 (chapter 3) may be expected to be the main factor for the initial increase in the complex conductivity with the increase of the ion contents.

At higher ionic content, the mobility of the charge carrier decreases. The reason may be related to the fact that the ion - dipole interaction within the clustering increases the microscopic viscosity of the phase separated polar ionic cluster region. The microscopic viscosity of the ion rich phase governs the conduction and
consequently, low microscopic viscosity is required for obtaining the high conductivity. In the case of the RISGNR based ionomers, the microscopic viscosity of the ion rich phase will be more significantly increased than the natural rubber matrix, due to the interaction between the metal ions and sulfonated groups within the cluster of the ionomer. In our ZnS - RISGNR ionomers, the zinc cations may be interacting with the sulfonic acid moieties during neutralization forming the higher multiplets.

![Graph](image)

**Fig. 6.8. Relationship between the loss tangents of the ionomers as a function of ionic content at 2.4 GHz frequencies.**

The increase in the interactions within the ionomer may increase the thickness of the restricted mobility region or the ion rich phase. This may be consequently increasing the microscopic viscosity [25] of the ion rich phase. The decrease in the polarization ability due to the increase of the microscopic viscosity is expected to be the reason for the decrease of the conductivity at higher concentration of ionic groups. Ionic associations that influence the physical properties [26-28] of the
ionomer may be believed to affect their dielectric properties at the S-band frequencies of the microwave region.

Fig. 6.9 Influence of ionic content on the tanδ of the 26.5 ZnS-SGNR ionomer at different frequencies

Fig. 6.10 Dependence of ionic concentration in the ionomer on the microwave-heating coefficient at different frequencies
The increase in the tanδ up on increasing ionic concentration may be attributed to the plasticising [29] effect of the low molecular weight fractions, which may be formed during the synthesis of the ionomers. The plasticization is believed to be facilitating the polarization of the dipoles at the microwave frequencies.

Table 6.1 Dielectric behaviors of the filled ionomeric materials at the S-band frequencies

<table>
<thead>
<tr>
<th>Frequency (GHz)</th>
<th>Materials</th>
<th>Dielectric constant</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.439</td>
<td>1</td>
<td>3.46</td>
<td>2.8 x 10^4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.33</td>
<td>3.2 x 10^3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.59</td>
<td>6.0 x 10^5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7.69</td>
<td>6.8 x 10^3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.88</td>
<td>2.1 x 10^4</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>5.87</td>
<td>5.2 x 10^3</td>
</tr>
<tr>
<td>2.683</td>
<td>1</td>
<td>3.46</td>
<td>3.3 x 10^4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.19</td>
<td>2.2 x 10^3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.44</td>
<td>7.0 x 10^5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7.29</td>
<td>8.8 x 10^3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.64</td>
<td>1.9 x 10^4</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>5.67</td>
<td>4.9 x 10^3</td>
</tr>
<tr>
<td>2.970</td>
<td>1</td>
<td>3.27</td>
<td>3.2 x 10^4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.14</td>
<td>5.2 x 10^3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.84</td>
<td>6.2 x 10^5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7.09</td>
<td>9.2 x 10^3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.74</td>
<td>1.4 x 10^4</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6.37</td>
<td>4.3 x 10^3</td>
</tr>
</tbody>
</table>

Material-1. represents neat ionomer, 2, 3, 4, 5 and 6 show ionomer filled with 10-phr of HAF black, silica, nylon, glass and zinc stearate respectively.

Figure 6.8 shows the variation of the loss tangent as a function of the ionic content in the ionomer at 2.4 GHz. At higher ionic concentrations, though there is plasticization,
the higher micro phase viscosity arising out of the strong inter-dipole attraction may offset the increase in the tan δ. The ionomers, at higher ionic concentration, may be transformed into an ionically "cured" system. The loss tangent studies of the ionomers at microwave frequencies may be considered as one of the examples of analogy between the mechanical and electrical properties of the ionomers [29].

6.3.3 Microwave heating coefficient (J)

Practically all applications of polymers in electrical and electronic engineering require materials with a low tan δ. However, one application that takes advantage of a high value of tangent loss is high frequency dielectric heating. In this application, the efficiency of heating is usually compared [29] by means of a comparison coefficient J, which is defined as

\[ J = \frac{1}{\varepsilon_r \tan \delta} \]

Fig. 6.11 Effect of 10 phr fillers on the dielectric constant of the ionomer at 2.247 GHz

Filled materials are neat ionomer (I). Compounds of carbon (C), silica (S), nylon (N), glass (G) and zinc stearate (Z)

Figure 6.10 shows the variation of J with ionic content at four different microwave frequencies. Smaller the J value better will be the polymer for dielectric heating purposes.
Fig. 6.12 Effect of 10 phr fillers on the a.c. conductivity of the ionomer at 2.247 GHz

Filled materials are neat ionomer (I). Compounds of carbon (C), silica (S), nylon (N), glass (G) and zinc stearate (Z)

Fig. 6.13 Effect of 10 phr fillers on the dielectric loss of the ionomer at 2.247 GHz

Filled materials are neat ionomer (I). Compounds of carbon (C), silica (S), nylon (N), glass (G) and zinc stearate (Z)
There has been considerable improvement in the microwave-heating coefficient of the polymers up on the ionomeric modifications. Of course, the heat generated in the polymeric material comes from the loss tangent, but that loss may not come entirely from the relaxation loss. Rather, conductivity of the polymeric material may also contribute to the Tan δ. This situation may be compared with ohmic heating of metals: where the charge carriers are electrons; however, the polar centers are the causative in dielectric polymeric materials.

6.4 Dielectric properties of filled Ionomers

The fillers selected for the study are carbon black (HAF), silica, nylon fibers, glass fibers and zinc stearate. Fillers have been added to the ionomer at the level of 10-phr. Figure 6.11 shows the dielectric behavior of the ionomer with fillers at 2.2 GHz frequencies. Silica and glass show low dielectric constant and conductivities at the S-band frequencies of the microwave region. The dielectric constant (ε′), dielectric loss factor (ε″) and a.c. conductivity (σ′) of the nylon filled ionomer shows the highest values at 2.2 GHz frequencies of the microwave region. Zinc stearate and carbon black fillers also give improved electrical characteristics in comparison with the neat ionomer. This has been found to be the trend from 2-3 GHz frequencies as is shown by the table 6.1 and figure 6.12 and figures 6.13. Ionomer with silica shows lowest conductivity in this frequency range. As the conductivity of nylon, zinc stearate and carbon black is found to be higher than other fillers, these filled ionomers may be used as components in microwave devices.

6.5 Conclusion

The ionic associations in the ionomer, which are held through coulombic forces, may act as the centers of polarization at the S-band frequencies of the microwave region. The measurement of the dielectric properties of the ionic SGNR at 2 – 4 GHz frequencies at room temperature showed that the complex permittivity and the
relative complex conductivity increased with increase in the ionic concentration. The ionomer had its highest microwave conductivity at 2.6 GHz. At this frequency, the maximum conductivity was obtained at a concentration threshold of 26.5 meq. In the present study it has been found that the incorporation of 26.5 meq zinc sulfonate groups in to the base polymer increases its $\sigma'$ from $1.8 \times 10^{-12}$ S/ cm to $3.3 \times 10^{-4}$ S/ cm.

Microwave probing of ionomers filled with fillers such as carbon black (HAF), silica, nylon, glass and zinc stearate reveal that $\epsilon'$ and $\sigma'$ of the ionomer has been affected. Silica and glass filled ionomers show lower dielectric properties compared to other fillers. Among the microwave active fillers such as carbon black, zinc stearate and nylon fibers, the nylon filled ionomer shows the highest electrical properties at the microwave region. The microwave response of these ionomers and their filled compounds may pave the way for the large-scale consumption of natural rubber in microwave devices.

6.6 References

Chapter 6

Microwave studies


