7.1 Introduction

Polymer composites filled with electrically conducting particles exhibit a broad spectrum of properties useful for a variety of applications in science and technology. Their unique electric and dielectric properties together with the mechanical and chemical stability are made use of in the production of various components for electronic applications [1]. The most important application being protection against radiation, as in microwave absorbers for electromagnetic interference shielding of various devices [2]. Polymer composites containing conductive fillers like carbon black, carbon fiber and metal fibers have been extensively studied, particularly for electromagnetic interference shielding, radar absorption, electronic packaging etc. But the high filler volume used in these cases deteriorates their overall mechanical properties. Thus carbon nanotubes and graphene replaced these conventional fillers in polymer composites [3].

Dielectric and microwave properties of graphene filled and nanotube filled NR composites were studied by Al-Hartomy, O.A.et al. [4-6].
Microwave measurement techniques used for the study of dielectric properties fall under two categories (1) resonance technique and (2) transmission technique. Dielectric property measurement by resonant technique has higher accuracy than measurement by transmission technique especially for dielectric loss [7]. Resonance techniques can further be divided into dielectric resonance technique and perturbation technique.

Cavity perturbation technique has been extensively used for measuring dielectric parameters of materials at microwave frequency [8]. The main advantages of cavity perturbation technique are

1) There is no tolerance limit on the shape and dimension of measured specimen.

2) Specimen is usually a small piece of rod, sheet or bar of 1mm$^2$ cross section. For thin rod shaped samples the perturbation technique is the most suitable method for the measurement of dielectric properties at microwave frequencies.

The basic concept of perturbation technique is that the presence of a small piece of the dielectric sample in the resonant cavity will result in a shift of resonant frequency and a decrease of the quality factor of the cavity. Rectangular or cylindrical wave guide resonators are used in this technique. The volume of the sample is much smaller than the volume of the resonant cavity. The sample is introduced into the cavity resonator at the position of maximum electric field, where the contribution of magnetic field for the perturbation is minimum [9]. From the measurement of perturbation due to sample, the dielectric parameters can be determined.


7.2 Experimental Materials

XNBR latex: Chemigum CLX 530 was supplied by Eliokem India Pvt. Ltd. Bombay.

SBR latex: Encord 204 was supplied by Jubilant Organosys Limited, Gujarat.

NBR: Kumho NBR, KNB 35L manufactured supplied by Kumho Petrochemicals

SBR: Kumho SBR (SBR-1502) supplied by Kumho Petrochemicals

MWCNT: MWCNT Baytub̆e® 150P was obtained from Baeyer Materials Science AG (Leverkusen Germany)

Graphene: Graphene nanoplatelets, supplied by Quantum Materials Limited, Bangalore.

Preparation of nanocomposites:

Formulation used in the preparation of XNBR latex compound (Table 3.3), SBR latex compound (Table 3.4), NBR(dry) compound (Table 3.5) and SBR (dry) compound (Table 3.6) are given in Chapter 3. A detailed description for the methods of preparation of latex (XNBR /SBR) based MWCNT/graphene nanocomposites are given in Section 3.11.3. Preparation of dry rubber (NBR/SBR) based MWCNT/graphene nanocomposites are given in Section 3.11.5.

MWCNT and graphene were added in concentration ranging from 0-0.3 phr
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Methods

The dielectric properties in the microwave frequency (S band 2-4 GHz) of the prepared nanocomposites (XNBR/MWCNT, XNBR/graphene, SBR/MWCNT, SBR/graphene, NBR(dry)/MWCNT, NBR(dry)/graphene, SBR(dry)/MWCNT, SBR(dry)/graphene were evaluated by Cavity Perturbation Technique [10,11] using Agilent Performance Network Analyzer E8362B (Section 2.5.2).

The resonant frequency $f_0$ and the corresponding quality factor $Q_0$ of each resonant peak for the empty cavity were first determined. Then a particular resonant frequency in the S band region was selected. The dielectric sample was introduced into the cavity and the position adjusted for maximum perturbation. At this position there was maximum shift of resonant frequency towards the low frequency region with minimum amplitude of the peak. The new resonant frequency $f_s$ and the quality factor $Q_s$ were observed. The procedure was repeated for other frequencies and measurements were done [12]. From the volume of the sample and the cavity resonator the dielectric parameters were evaluated [13, 14].

The parameters were calculated using the following formula:

Dielectric constant $\varepsilon' = 1 + \frac{V_c}{V_s} \cdot \frac{f_0 - f_s}{2f_s}$  \hspace{0.5cm} (1)

Dielectric loss $\varepsilon'' = \frac{V_c}{4V_s} \cdot \left( \frac{Q_0 - Q_s}{Q_0 \cdot Q_s} \right)$  \hspace{0.5cm} (2)

Skin depth $\delta f = \frac{1}{\alpha f}$  \hspace{0.5cm} (3)

AC conductivity $\sigma_e = 2\pi f \varepsilon_0 \varepsilon''$  \hspace{0.5cm} (4)
Here $f_0$ and $Q_0$ are the resonant frequency and quality factor of the empty cavity resonator, $f_s$ and $Q_s$ are the corresponding parameters of the cavity loaded with the sample. $V_c$ and $V_s$ are the volumes of the cavity and sample respectively. $\alpha f$ is the absorption coefficient.

7.3 Results and Discussion

Dielectric constant

The dielectric constant is a measure of the ability of the material to be polarized or it is a measure of how much energy from an external electric field is stored in the material [15]. Generally the dielectric constant of a material arises due to the polarization of molecules. The different types of polarization possible in a material are (1) electronic polarization (2) atomic polarization and (3) orientation polarization. Higher the polarizability of the material greater will be the dielectric constant [12].

Fig. 7.1. (A) and (B), shows the frequency dependence of real part of permittivity of MWCNT and graphene filled XNBR in the S band frequency region (2-4GHz). From the figure it is seen that the dielectric constant of the nanocomposites are enhanced by the incorporation of MWCNT and graphene. Since it is a measure of polarization, the interaction of XNBR containing polar CN and COOH groups with MWCNT and graphene containing pi electrons were more pronounced. $\varepsilon'$ value also increased with frequency, although a small dip was seen at the intermediate frequency. Thus XNBR-MWCNT and XNBR-graphene nanocomposites had values 4.09 and 3.6 respectively at 3.9 GHz.

Fig. 7.1(C) and (D), shows the variation of dielectric constant with frequency of SBR-MWCNT and SBR-graphene nanocomposites. At higher
concentrations of MWCNT and graphene, E’ value decreased with increase in frequency. The decrease in permittivity with increase in frequency revealed that the system exhibited strong interfacial interaction only at low frequency. The composites prepared might be considered as a heterogeneous system where conducting nanotube and graphene were covered with the insulating SBR. In such cases interfacial polarization arises from the difference in the conductivities of the two phases. This was analogous to Maxwell-Wagner double layer structure [16, 17]. High dielectric constant at low frequency might be due to induction polarization and migration of charge carriers. But at higher frequency, the migration of charge carriers lags behind the applied field decreasing the dielectric constant.

Fig.7.1(E),(F) and (G), (H) gave the variation of E’ with frequency for NBR (dry)/MWCNT, NBR(dry)/graphene and SBR(dry)/MWCNT, SBR(dry)/graphene nanocomposites respectively. E’ value increased with loading of nanotube and graphene as well as with increase in frequency. Polar NBR gave higher values of E’ than non polar SBR. Table 7.1 gives the values of dielectric constants of gum rubber at the highest frequency (4GHz). The low values for SBR was characteristic of its non polar nature.

Table.7.1. Values of dielectric constants of unfilled rubber at a frequency of 4GHz

<table>
<thead>
<tr>
<th>Raw rubber samples</th>
<th>Dielectric constant at 4 GHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>XNBR(latex)</td>
<td>3.34</td>
</tr>
<tr>
<td>SBR (latex)</td>
<td>2.65</td>
</tr>
<tr>
<td>NBR (dry)</td>
<td>3.04</td>
</tr>
<tr>
<td>SBR (dry)</td>
<td>1.8</td>
</tr>
</tbody>
</table>
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Fig. 7.1. Variation of dielectric constant with frequency of (A) XNBR/MWCNT (B) XNBR/graphene (C) SBR/MWCNT (D) SBR/graphene (E) NBR (dry)/MWCNT (F) NBR (dry)/graphene (G) SBR (dry)/MWCNT and (H) SBR (dry)/graphene nanocomposites.
Dielectric loss

The mechanism of occurrence of dielectric loss is related mostly to the nature of dielectric polarization. The dielectric loss $E''$ in XNBR latex and NBR dry rubber nanocomposites increased with concentration and frequency as shown in Fig 7.2. (A) (B) and (E) (F). Interfacial polarization and conductivity contributed to $E''$ value. Addition of MWCNT and graphene containing pi electrons, to the polar XNBR and NBR increased the dipole polarity of the nanocomposite in the interfacial region [18]. Also, the free and mobile electrons in MWCNT and graphene increased with the increase in filler loading. This contributed to conductive chain formation leading to an increase in $E''$ value [19]. When frequency increased the inertia of the molecule and the binding forces became dominant. This also led to an increase in dielectric loss [20].

$E''$ values of SBR dry rubber composites increased with frequency. The increase was due to the conductive nature of pi electrons in MWCNT and graphene.

$E''$ values of SBR latex/MWCNT nanocomposites showed a very small decrease with increase in frequency. While, for SBR latex/graphene nanocomposites the decline in value was more prominent. This might be because of the nonpolar nature of SBR and the presence of non ionic surfactant vulcastabV,L used in the preparation of graphene dispersion. The presence of this nonionic surfactant might have prevented graphene from making direct contact between themselves. So the contribution from conductivity of graphene was very low in SBR nanocomposite.
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Fig. 7.2. Variation of dielectric loss with frequency of (A) XNBR/MWCNT (B) XNBR/graphene (C) SBR/MWCNT (D) SBR/graphene (E) NBR (dry)/MWCNT (F) NBR (dry)/graphene (G) SBR (dry)/MWCNT and (H) SBR (dry)/graphene nanocomposites
Skin depth

Penetration depth otherwise called skin depth ($\delta f$) is basically the effective distance of penetration of an electromagnetic wave into the material. $\delta f = 1/\alpha f$ where $\alpha$ is the absorption coefficient. Skin depth can be applied to a conductor carrying high frequency signal. With increase in frequency, skin depth decreases. The self inductance of the conductor limits the conduction of the signal to the outer shell and the shell thickness is the skin depth [21].

The conductivity of nanotube and graphene reduced the depth of penetration of the signal. Fig.7.3 (A)-(H) shows the decrease in skin depth with frequency and filler loading.
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Fig. 7.3. Variation of skin depth with frequency of (A) XNBR/MWCNT (B) XNBR/graphene (C) SBR/MWCNT (D) SBR/graphene (E) NBR (dry)/MWCNT, (F) NBR (dry)/graphene (G) SBR (dry)/MWCNT and (H) SBR(dry)/graphene nanocomposites.
AC conductivity

The honey comb lattice of graphene consists of a monolayer of sp² bonded carbon atoms where each carbon atom is attached to three carbon atoms in the XY plane and a weak pi electron cloud in the Z axis. Carbon nanotubes are cylindrical shells made by rolling graphene sheets. This gives carbon nanotube and graphene its unique electrical properties [22].

Electrical properties of nanocomposites depend primarily on the way the filler particles are distributed throughout the polymer matrix. In the presence of AC field, the growth of the conducting filler takes place from both electrodes. Since the poles change alternatively the formation of filler network does not start immediately on applying the electric field. The properly aligned filler starts moving towards each other and forms network overtime. With increase in filler loading the onset of network formation takes place earlier. Increasing the filler loading also increases the number of networks and decreases the number of dead points [23].

Variation of AC conductivity with frequency at different concentration of nanotubes and graphene are plotted in Fig. 7.4. (A)-(H). In all the nanocomposites, except SBR latex based nanocomposites conductivity increased with increase in filler concentration and with frequency. Since only a very small concentration of nanotube and graphene (0, 0.05, 0.15 and 0.3 phr) were used, increase in conductivity was also moderate. For all nanocomposites (except SBR latex nanocomposites) maximum value of conductivity were obtained at the highest frequency 4 GHz.
At low levels of filler loading, the conductivity of the nanocomposites was slightly higher than that of the base polymer, because filler particles were isolated from each other by the insulating rubber matrix [24]. When the concentration of nanofiller in the composite increased, the contact between the filler particles also increased. This led to the formation of a continuous path for the electrons to travel through the entire volume of the sample [25].

From the figure it is observed that the conductivity of unfilled and filled XNBR latex was the highest. The presence of polar CN group and carboxyl group contributed to the conductivity of XNBR. When compared to XNBR latex based nanocomposites, conductivity was poor for NBR dry rubber nanocomposites which had only polar CN group and no carboxyl group. Introduction of polar hydroxyl and carbonyl groups on the MWCNT surface during purification had increased its conductivity as compared to graphene nanocomposites.

In SBR latex/MWCNT nanocomposites conductivity value remained almost constant at different frequencies. For SBR latex/graphene nanocomposites conductivity decreased with frequency. This showed the absence of a continuous network structure in the nanocomposite. The surfactant used for dispersing graphene might have isolated the graphene particles preventing electrical contact between them.
Fig. 7.4. Variation of conductivity with frequency of (A) XNBR/MWCNT (B) XNBR/ graphene (C) SBR/MWCNT (D) SBR/graphene (E) NBR (dry)/ MWCNT, (F) NBR (dry)/graphene (G) SBR (dry)/ MWCNT and (H) SBR(dry)/ graphene nanocomposites
7.4 Conclusions

Dielectric permittivity, dielectric loss and AC conductivity of all the nanocomposites (except SBR latex nanocomposite) increased with increase in frequency. Enhancement in properties was marginal, since nanotube and graphene were used only in very small concentration ranging from 0-0.3 phr.

Penetration of electromagnetic waves into the material was reduced by the presence of conducting fillers. Thus there was a decrease in skin depth or penetration depth of all the nanocomposites with increase in frequency. Maximum conductivity and minimum skin depth were observed at a frequency of 4 GHz. Dielectric permittivity, dielectric loss and AC conductivity were maximum for XNBR nanocomposites. The nonpolar SBR latex vulcanizate showed some discrepancy in their behaviour.
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Reference


[10] Venkatesh, M. S. Raghavan, G. S. V. Canadian Biosystems Engineering, 2005, 47, 7.15

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Studies on the use of Nanokaolin, MWNT and Graphene in NBR and SBR