The dielectric properties of PANI, and NR and CR based CPCs were measured in the frequency range 0.1 to 8 MHz and in the temperature range 303 to 393 K. Both NR and CR based CPCs showed Maxwell-Wagner type of polarization. The conduction mechanism in the composites was primarily hopping. CR based composites exhibited better dielectric properties due to its polar nature. At 303 K and 0.1 MHz, a dielectric permittivity as high as 177 was obtained for the composite CP, which was almost double the value obtained for NR-PANI composite. The F series CPC of CR, CF, had a permittivity of 70 at the same frequency and temperature. At 303 K, a maximum conductivity of $6.2 \times 10^{-3}$ S/m at 5 MHz was obtained for CR based CPC, CP. The composite CF of the F series gave a conductivity of $1.01 \times 10^{-3}$ S/m. The dielectric dispersion could be fitted well with well known empirical equations.

Chapter 5

Dielectric properties of conducting elastomer composites

5.1 Introduction

Development of electronic devices working at high operating frequencies, such as fast computers, cellular phones, etc. requires new high-dielectric constant materials that combine good dielectric properties with sufficient mechanical strength and ease of processing. In particular, high dielectric constant materials are required for making embedded capacitors for integrated electronic devices [1, 2]. The unique combination of dielectric and mechanical properties is hard to achieve in a one-component material. Pure polymers are easy to process into mechanically robust components but generally suffer from low dielectric constants [3]. On the other hand, typical high dielectric constant materials, such as ferroelectric ceramics, are brittle and require high-temperature processing, which is often not compatible with current circuits integration technologies [4]. The ideal solution for developing such a one-component material would be designing a high dielectric constant material that is mechanically
robust and processable at ambient temperatures. This has raised a great interest in hybrid materials, such as polymer/ceramic composites and conducting polymer/polymer composites, which combine desired properties of the components.

Polymer/ceramics composites have been of great interest as embedded capacitor material because they combine the processability of polymers with the high dielectric constant of ceramics [5-7]. Some novel nanostructure composites made of epoxy and lead magnesium niobate-lead titanate (PMN-PT)/BaTiO$_3$ were reported to have very high dielectric constant ($\varepsilon' = 110$) [5]. A similar epoxy-based composite with an ultra high dielectric constant ($\varepsilon' = 1000$) has been developed by the same group, which was claimed by these researchers to be the highest $\varepsilon'$ value of the polymer based composite ever reported, while no experimental details were disclosed except the volume fraction of ceramics [7]. The high dielectric constant ceramics employed in the polymer composites generally belongs to the categories of niobates, titanates, zirconia (ZrO$_2$), tantalum oxide (Ta$_2$O$_5$) and aluminum oxide (Al$_2$O$_3$), etc. The adhesion between these ceramics and polymer matrix is poor, especially when ceramics loading is high [8]. Conducting polymer systems constituted by a conducting polymer dispersed inside an insulating polymer matrix have been extensively investigated in the last decades in the electronics industry. The good mechanical properties and intriguing electronic properties and high dielectric constants of these materials indicate that they can be used in many device applications.

Some studies observed that PANI and some PANI/polymer blends are capable of obtaining a high dielectric constant. As a consequence, its conducting composites are very close to applications on a large scale in electromagnetic shielding and microwave absorption [9-12] and many studies are going on the dielectric behavior of PANI and PANI composites. For instance, a dielectric constant $\geq 10^4$ can be observed in a partially crystalline PANI sample system [13]. An inhomogeneous disorder model was proposed for this system, in which ordered (crystalline) region, described by three-dimensional metallic states, is connected through amorphous region of polymer chains where one-dimensional disorder-induced localization is dominant. High dielectric constant values ranging between 200-1000 have been
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reported for a PANI/polyvinyl alcohol (PVA) composite by Dutta and co-workers [14]. The frequency range investigated was 1 kHz - 5 kHz from room temperature to 80 K. This report gave no structural analysis results for the composite, but just stated that the dispersed submicronic PANI particles are suspended in the insulating PVA matrix. They reported that the temperature dependence of DC conductivity followed variable range hopping (VRH) and that the hopping transport occurred between the superlocalized states of polymer. The frequency dependence of conductivity satisfied the $\omega^s$ law and the AC conduction was reported to be due to correlated barrier hopping (CBH). High dielectric constant PANI/polyurethane (PU) blends were synthesized by using the technique of in situ polymerization of aniline in an aqueous dispersion of PU (ISP blends) by Chwang et al. [15]. A dielectric constant of $\sim 1120$ was obtained for the PANI/PU blend containing 17 wt % of PANI, which surpassed the highest value of $\varepsilon'$ ever reported for the high dielectric constant polymer composites. A parallel study was carried out with a similar PANI/PU blend prepared by simple mixing of PANI dispersed solution with an aqueous solution of PU. The totally different microstructures exhibited by these two types of blends could adequately explain their discrete dielectric behavior. Based on the results of morphological study as well as the existence of a percolation threshold for the conductivity of the ISP blends, the enhancement of dielectric constant in the ISP blends was established to be chiefly due to electrode polarization.

Tabellout et al. studied the dielectric properties of conducting polymer composite films based on doped and dedoped PANI located in a thin layer in the vicinity of the surface of some insulating polymer matrices like polyamide and poly(ethylene terephthalate), using dielectric relaxation spectroscopy over a wide temperature and frequency range [16]. Several relaxation processes related to the film surface conductivity and influenced by the nature of the polymer matrix were found in these composites. At low temperature, in addition to sub-glass relaxation processes occurring in the polymer matrix and in the non-doped composite as well, three relaxation processes were observed in the doped one related to its conductive properties. In the low frequency region, interfacial polarization relaxations were observed arising due to the layered and clustered structure. At higher frequency,
conductivity relaxation was connected to the conductivity in the PANI clusters. They found that the nature of the polymer matrix, especially matrix crystallinity, influenced the relaxations by frequency shift, change in relaxation strength and activation energy.

The dielectric properties of the styrene-butadiene-styrene (SBS) triblock copolymer matrix loaded with different amounts of PANI in the protonated conducting form and in non-protonated, non-conducting form, emeraldine base, prepared by mechanical mixing, were studied by Leyya and co-workers [17]. They reported that the dielectric constant and loss factor increased with increase in PANI-DBSA concentration. The dielectric loss factor data of SBS and their blends with PANI-DBSA revealed a sharp increase at temperatures above the glass transition because of interfacial polarization and ionic conductivity contributions. These phenomena were important at low frequency measurements. The electrical properties of polyaniline/polyimide blends [18], polyaniline/polychloroprene composite [19], polyaniline/polyvinyl chloride blends [20] were also reported by different authors.

The dielectric behavior of conducting composites depends mainly on the method of preparation, conductivity, molecular structure, particle size and crystal structure. It also depends on external factors such as frequency of the applied voltage, temperature, pressure and humidity [21]. Since the properties of the conducting polymers and CPCs are very much dependent on the microstructure, nature of dopant used, type of matrix and the processing variables, study of dielectric properties of these materials assume significance. Dielectric properties of polymers and polymer composites, like those of other dielectric materials are usually expressed in terms of its resistivity, conductivity and complex permittivity. These quantities are functions of temperature and the type i.e. AC/DC and magnitude of the voltage applied. Frequency and temperature dependence of dielectric properties of the CPCs throw light on the dielectric polarization and on the conduction mechanisms. The frequency and temperature dependence of dielectric properties of PANI, as well as CR and NR based PANI/PANI coated short Nylon fiber composites are presented in this chapter. Different theoretical equations and mixture equations are applied to fit the observed dielectric data of the CPCs.
5.2 Dielectric measurements

5.2.1 Method of measurements

The dielectric constant or permittivity is defined as the ratio of the field strength in vacuum to that in the material for the same distribution of charges. Dielectric constant is dependent on parameters like temperature, orientation, molecular structure of the material and frequency of the applied field. An electrical conductor charged with a quantity of electricity \( q \) at a potential \( V \) is said to have a capacity \( C=q/V \). The capacity of a sample parallel plate capacitor is given by:

\[
C = \epsilon A / d
\]

where \( A \) is the area of the parallel plates, \( d \) is the separation between the plates and \( \epsilon \) is the ratio of dielectric constant of the medium between the plates to that of free space. When a parallel plate capacitor with a dielectric in between is charged, then the capacitance, \( C \) is given by:

\[
C = \epsilon_0 \epsilon_r A / d
\]

where \( A \) is the area of the sample, \( d \) is the separation between the plates, \( \epsilon_0 \) is the permittivity of free space and \( \epsilon_r \) is the dielectric constant of the material between the plates. Dielectric constant of the samples can thus be calculated if the capacitance, area and thickness of the samples are known. Thus, dielectric constant,

\[
\epsilon_r = C d / \epsilon_0 A
\]

The AC electrical conductivity can be calculated utilizing the dielectric parameters using the formula:

\[
\sigma_{AC} = 2\pi f \tan \delta \epsilon_0 \epsilon_r
\]
where $f$ is the frequency of the applied field and $\tan \delta$ is the loss factor. The principle and theory underlying the evaluation of $\sigma_{AC}$ from dielectric measurements is based on a treatment dealt by Goswamy [22].

5.2.2 Cell for the measurements

The schematic design of the cell employed for the electrical measurements is given in fig. 5.1. All the necessary facilities like temperature sensing facility, high vacuum facility, facility for measuring the pressure inside the cell and facility to carry out optical and electrical studies have been incorporated. The cell is made up of mild steel with a cylindrical stem having provisions for fixing various attachments such as electrical connections and vacuum gauges. The cell is connected to a rotary pump to maintain a pressure of $10^{-2}$ Torr inside the chamber. The inner diameter of the cell is about 18 cm and the length of the cell is 30 cm. The sample holder assembly consists of a mild steel stem of diameter 5 cm with mild steel flange and O-rings. The sample holder is fixed at the bottom of a one-end closed metallic tube to be embedded to the top flange. It consists of two copper disc electrodes. For high temperature measurements, a solderon heater is kept at the back side of the sample holder. An Fe-K thermocouple is placed on the sample to sense the temperature and is controlled by a digital temperature controller.
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1. BNC                                              7. Glass window
2. Neoprene O-ring                                  8. Metal electrodes
3. Mild Steel chamber                               9. Sample
4. SS pipe                                          10. Heating filament
5. Sample holder                                    11. Mild Steel flange
6. Liquid nitrogen cavity                           12. To vacuum pump

Fig. 5.1 Schematic of the cell for dielectric and conductivity measurements

The dielectric properties of the CPCs were studied using the dielectric cell and an impedance analyzer, Hewlett Packard 4192A. The cell was standardized using Teflon pellets and lead. The fringe capacitance was eliminated by employing a procedure suggested by Ramasasthry et al. [23]. The samples, in the form of pellets of diameter 12 mm and ~ 2 mm thickness were mounted in between two copper disc electrodes. The capacitance of the samples was measured in the frequency range 0.1 to 8 MHz and in the temperature range 303 to 393 K. The data acquisition was automated by interfacing the impedance analyzer with a computer. For this, a virtual instrumentation package, based on a graphical programme was employed. This package is called LabVIEW (Laboratory Virtual Instrument Engineering
Workbench), a base software package for implementing virtual instrumentation and G programming. LabVIEW is a programming language for data acquisition, analysis, simulation or computer control of instruments and techniques or processes. Appropriate modifications were incorporated in the software so as to enable the data acquisition automatic and visual observation of the graphs on the computer screen. The characteristic feature of this automatic data acquisition is that it is possible to acquire 20,000 data points or more in a matter of 5 to 10 minutes. By using the modified package, the data can be plotted and analyzed. After obtaining capacitance and dielectric loss from the instrument, the LabVIEW software first calculates the dielectric constant and then evaluates the AC conductivity of the samples.

5.3 Results and discussion

5.3.1 Dielectric permittivity

5.3.1.1 Frequency dependence of pristine PANI

Fig. 5.2 presents the variation of dielectric permittivity; $\varepsilon'$, i.e. the real part of complex permittivity, of pristine PANI with frequency. The permittivity decreases with increase in frequency at all temperatures. This is more pronounced at low frequencies. Finally, it reaches a constant value at all temperatures. The decrement in permittivity with increase of frequency reveals that the systems exhibit strong interfacial polarization at low frequencies. As reported by other authors, the strong low frequency dispersion of permittivity is a characteristic of charged carrier systems [24]. This is the normal behavior found in the case of PANI [25]. This kind of behavior can be explained on the basis of Maxwell-Wagner theory for interfacial polarization.
Fig. 5.2 Variation of dielectric permittivity of PANI with frequency

5.3.1.2 Temperature dependence of pristine PANI

Fig. 5.3 shows the variation of dielectric permittivity of pristine PANI with temperature at different frequencies. Generally, at any particular frequency, the dielectric permittivity decreases with temperature up to 333 K and then increases with increasing temperature. This behavior is more pronounced at lower frequencies.

Fig. 5.3 Variation of dielectric permittivity of PANI with temperature

Dielectric behavior of conducting polymers depends on their structure. PANI aggregates are made up of small grains, which are formed from still smaller primary particles. These primary particles have a metallic core surrounded by an amorphous
non-metallic shell. This forms a heterogeneous structure as put forward by Maxwell-Wagner. In the Maxwell-Wagner model, well conducting grains are separated by poorly conducting grain boundaries. The increasing permittivity value with increasing temperature is in accordance with Maxwell-Wagner theory, which means that at higher temperatures, Maxwell-Wagner type of polarization is predominant. It can be seen from fig. 5.3 that at 303 K, PANI has a permittivity of 76 and at 393 K, the value is 712 at 0.1 MHz. The high values of dielectric permittivity at lower frequencies can be accounted for by employing Koop’s theory, which is based on Maxwell-Wagner model for heterogeneous double layer dielectric structures [26-28].

5.3.1.3 Frequency dependence of dielectric loss factor of pristine PANI

The variation of dielectric loss factor; \( \varepsilon'' \), i.e. the imaginary part of complex permittivity with frequency is presented in fig. 5.4. It decreases with frequency at all temperatures as in the case of dielectric permittivity and reaches a constant value. The decrease is more pronounced at lower frequencies. It is interesting to observe that the dependence of loss factor of PANI with frequency appears as straight lines at lower frequencies, at low temperatures. Beyond 353 K, deviation from straight line is observed.

![Fig. 5.4 Variation of dielectric loss factor with frequency](image-url)
The loss factor, \( \varepsilon_{\text{obs}} \), must be regarded as the sum of contributions of three distinct effects as [29]:

\[
\varepsilon_{\text{obs}} = \varepsilon_{\text{DC}} + \varepsilon_{\text{MW}} + \varepsilon_{\text{D}}
\]  

(5.5)

where \( \varepsilon_{\text{DC}} \) is due to DC conductance, \( \varepsilon_{\text{MW}} \) is due to interfacial polarization and \( \varepsilon_{\text{D}} \) is the usual dipole orientation or Debye loss factor.

Different mathematical equations have been developed to distinguish between loss arising from a DC conductivity process and from other sources of different processes. These equations were developed by considering the sample as parallel resistor-capacitor circuit [29-31]. The loss factor due to DC conductance; \( \varepsilon_{\text{DC}} \), is given by the equation [30]:

\[
\varepsilon_{\text{DC}} = \frac{1.8 \times 10^{12} [G_{\text{spec}}]}{f}
\]  

(5.6)

where \( G_{\text{spec}} \) is the specific conductivity (S/cm) of the sample. The loss factor due to the Maxwell-Wagner or interfacial polarization; \( \varepsilon_{\text{MW}} \), is given by [32]:

\[
\varepsilon_{\text{MW}} = \varepsilon_{\infty} [1 + \frac{K}{1 + \omega^2 \tau^2}]
\]  

(5.7)

where \( \varepsilon_{\infty} \) and \( K \) are calculated considering two different dielectric permittivity of the sample at the interfaces and \( \tau \) is the relaxation time of the interfacial polarization. By expressing the above two equations in logarithm form and making the plot of \( \log \varepsilon_{\text{DC}} \) and \( \log \varepsilon_{\text{MW}} \) vs. logarithm of frequency, two different curves will be obtained. The \( \log \varepsilon_{\text{DC}} \) vs. \( \log f \) represents a straight line and the \( \log \varepsilon_{\text{MW}} \) vs. \( \log f \) represents a sigmoidal curve.

Fig. 5.4 shows that at lower frequencies and temperatures, the loss factor; \( \varepsilon_{\text{obs}} \), decrease linearly with increasing frequency. These results suggest that DC conductivity process is more significant than interfacial polarization at these frequencies and temperatures. Similar results have been reported elsewhere [25].
Chapter 5

Generally it is believed in dielectric analysis that the high frequency permittivity (dielectric constant) is mainly associated with dipolar relaxation, whereas at lower frequency and higher temperature, the contributions of interfacial polarization (Maxwell-Wagner type of polarization) and DC conductivity become more significant in both $\varepsilon'$ and $\varepsilon''$. Interfacial polarization arises mainly from the existence of polar and conductive regions dispersed in relatively less polar and insulating matrix. This phenomenon is particularly important in conjugated polymers and may interfere on the relaxation process analysis. Therefore, many authors prefer to describe the dielectric properties of these systems by using the electric modulus formalism [24, 33-36]. The complex electric modulus is derived from the complex permittivity, according to the relationship defined by Macedo et al. [37]. The real and imaginary parts of the electric modulus ($M'$ and $M''$) can be calculated from $\varepsilon'$ and $\varepsilon''$, as follows [38]:

\[
M' = \frac{\varepsilon'}{(\varepsilon')^2 + (\varepsilon'')^2} \tag{5.8}
\]

\[
M'' = \frac{\varepsilon''}{(\varepsilon')^2 + (\varepsilon'')^2} \tag{5.9}
\]

The electric modulus representations of dielectric process give us some idea of relaxation of dipoles that exists in different energy environments, independent of the strong effect of DC conductivity, which often mask the actual dielectric relaxation processes active in these types of systems. Figs. 5.5 and 5.6 show the isothermal and isochronal dependence of the imaginary part of electric modulus, $M''$ with frequency and temperature, respectively, of pristine PANI. PANI exhibits only one broad peak, both in isothermal and isochronal plots with a narrow distribution of the relaxation, indicating a uniform system and a single relaxation process. The peak shifts to higher frequencies in the isothermal plots with increasing temperature upto 333 K. With increasing frequency (fig. 5.6), the peak height increases initially upto 3 MHz which then decreases.
Dielectric properties of conducting elastomer composites

5.3.1.4 Effect of frequency of NR gum vulcanize

Variation of dielectric permittivity of NR gum vulcanize is shown in fig. 5.7. As the frequency increases, dielectric permittivity decreases at all temperatures. The decrease is gradual at lower frequencies and more significant at higher frequencies. The dielectric constant of the unvulcanized NR is reported to be in the range 2.6 to 3.04 [39]. A dielectric constant of 2.3 is obtained at 0.1 MHz in the present study.

Fig. 5.7 Variation of dielectric permittivity of NR gum vulcanize with frequency
The dielectric behavior of a polymeric material under the influence of an external electric field depends on the polarization effect that occurs within the material. The total polarization is the sum of the deformational polarization and orientational polarization. At low applied frequencies, both factors contribute to the total polarization. As the frequency is increased, the orientation polarization becomes out of phase with the applied field i.e. the dipolar motion can no longer follow the rapid vibration in the electric field. So the dielectric permittivity of polymeric materials decreases with increase in applied frequency. The polarization and hence the dielectric permittivity must be regarded as a complex quantity,

\[ \varepsilon^* = \varepsilon' - i\varepsilon' \]  

(5.10)

The complex dielectric permittivity, \( \varepsilon^* \), is given by the Debye equation as follows:

\[ \varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau} \]  

(5.11)

where \( \omega \) is the angular frequency, \( \varepsilon_0 \) is the static dielectric permittivity and \( \varepsilon_\infty \) is the dielectric permittivity at infinite frequency. The real and imaginary components \( \varepsilon' \) and \( \varepsilon'' \) are given by [40-42]:

\[ \varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (\omega\tau)^2} \]  

(5.12)

\[ \varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + (\omega\tau)^2} \]  

(5.13)

According to equation (5.12), the dielectric permittivity decreases with increase in frequency, and the decrease is more pronounced at higher frequencies.

5.3.1.5 Effect of temperature of NR gum vulcanizate

The effect of temperature on the dielectric permittivity of NR gum vulcanizate at selected frequencies is presented in fig. 5.8. The dielectric permittivity is found to
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decrease with increase in temperature at all frequencies. When the temperature increases, due to thermal expansion of matter, the ratio of the number of molecules to the effective length of the dielectric diminishes and as a result, dielectric permittivity decreases [43, 44]. In other words, as the temperature increases, the polymer density reduces which, in turn causes a decrease in dielectric permittivity.

Fig. 5.8 Variation of dielectric permittivity of NR gum vulcanize with temperature

5.3.1.6 Frequency dependence of the NR based CPCs

The dielectric properties of NR/PANI and NR/PANI/PANI-N composites containing different loadings of PANI and PANI-N, respectively, were studied. Effect of frequency on the dielectric permittivity of NR composites NP2, NP3 and NF3 at some selected temperatures is represented in figures 5.9, 5.10 and 5.11, respectively. The variation pattern shows almost similar behavior as that of PANI. The dielectric permittivity decreases with increasing frequency for all the composites. This indicates that more and more PANI dipoles can no longer keep up with the increasing frequency. This behavior is in accordance with Maxwell-Wagner interfacial polarization. As the frequency of the applied field increases, interfacial polarization decreases and hence dielectric permittivity decreases.
The absolute value of the dielectric permittivity of the CPCs is found to be much greater than the gum vulcanizate. Higher values are obtained for composites with higher PANI loading. Dielectric constants as high as 47, 73 and 45 are obtained for NP\textsubscript{2}, NP\textsubscript{3} and NF\textsubscript{3} composites, respectively at 0.1 MHz. Compared to most of the polymers which have $\varepsilon'$ values between 2 and 10 ($\varepsilon' = 10$ for poly(vinylidene fluoride), PVDF; $\varepsilon' = 5.6$ for polyurethane, PU) and many common ceramics such as SiO\textsubscript{2} ($\varepsilon' = 4.0$) and Si\textsubscript{3}N\textsubscript{4} ($\varepsilon' = 7.0$), the results obtained by NR based CPCs are quite remarkable.
5.3.1.7 Temperature dependence of the NR based CPCs

Variation of dielectric permittivity with temperature of NR based composites NP$_2$, NP$_3$ and NF$_3$ are presented in figures 5.12, 5.13 and 5.14, respectively. In all the three composites, the dielectric permittivity is found to increase initially with temperature up to 353 K, and then decreases. This effect is more pronounced at lower frequencies and nominal at higher frequencies.

Fig. 5.12 Variation of dielectric permittivity with temperature of 90 phr PANI-loaded NR/PANI CPC (NP$_2$)

Fig. 5.13 Variation of dielectric permittivity with temperature of 140 phr PANI-loaded NR/PANI CPC (NP$_3$)

Fig. 5.14 Variation of dielectric permittivity with temperature of 120 phr PANI-N-loaded NR/PANI/PANI-N CPC (NF$_3$)
The high dielectric permittivity at low frequencies found at high temperatures may be explained by the presence of permanent dipole moments indicating a small effective charge separation. Such a small separation must be due to asymmetry in the fields experienced by the presence of charged ions. In most cases, the atoms or molecules in the samples cannot orient themselves at low temperature region. When the temperature rises, the orientation of these dipoles is facilitated and this increases the dielectric polarization. At even high temperatures, the chaotic thermal oscillations of molecules are intensified and the degree of orderliness of their orientation is diminished and thus the permittivity passes through a maximum value. In the present case, this maximum temperature is 353 K. At very high temperatures, the dielectric permittivity decreases. This is due to the thermal expansion of the matrix as discussed earlier. At high frequencies, the temperature has little effect on dielectric permittivity [43, 44].

5.3.1.8 Effect of loading of NR based CPCs

Variation of dielectric permittivity with the loading of PANI and PANI-N at 303 K was followed and is presented in figs. 5.15 and 5.16, respectively. It is found to increase with increase in PANI and PANI-N content at all frequencies. The increase is more pronounced at lower frequencies. At 0.1 MHz, a maximum value of 73 is obtained at 140 phr PANI loading (CPC NP3) and a value of 45 at 120 phr PANI-N loading (CPC NF3). Thus, it is clear that the dielectric properties of the NR matrix gets modified by addition of PANI and PANI-N and the required dielectric constant can be achieved by varying their concentration.
5.3.1.9 Effect of frequency and temperature of CR gum vulcanize

The frequency and temperature dependence of CR gum vulcanizates is shown in figures 5.17 and 5.18, respectively. The dielectric permittivity of CR gum vulcanizate is found to be 5.3 at 0.1 MHz and it decreases with increase in frequency. The decrease is nominal at lower frequencies and significant at higher frequencies. The higher dielectric permittivity of the CR gum vulcanize compared to NR vulcanize may be due to its polar nature. It indicates that CR possesses better dielectric characteristics than NR. The decrease in permittivity with frequency is due to the decrease in polarization. At higher frequencies, the orientation polarization lags behind the applied frequency and hence the total polarization and the dielectric permittivity decrease with increase in frequency. Another factor that affects the dielectric permittivity of the polymer is its crystallinity. The dielectric permittivity of a semi crystalline polymer is the average of their respective values in the amorphous and crystalline phases.

The permittivity increases up to 333 K and then decreases with further increase in temperature. The initial increase in dielectric permittivity is more pronounced at higher frequencies. The initial increase at low temperature is due to the increase in
polarity of the C-Cl bond. At very high temperature, the increased polymer chain mobility decreases the density of the matrix and hence the dielectric permittivity decreases.

5.3.1.10 Frequency dependence of CR based CPCs

The dielectric properties of CR/PANI and CR/PANI/PANI-N composites containing different loadings of PANI and PANI-N at different temperatures were measured in the frequency range 0.1-8 MHz. Effect of frequency on the dielectric permittivity of CR/PANI composites at different temperatures with 100 phr (CP₂) and 150 phr (CP₃) PANI loadings and 120 phr PANI-N loading (CF₃) is represented in figures 5.19, 5.20 and 5.21, respectively. Frequency dependence of dielectric permittivity of CR based CPCs shows similar behavior as that of NR based CPCs. In the conducting polymer composites, the conducting particles are covered with the insulating matrix and space charge polarization occurs at the interfaces. This can also be explained by Maxwell-Wagner model. The interfacial polarization can take place at lower frequency. As the frequency is increased, the time required for the interfacial charges to be polarized or for the dipoles to be arranged is delayed, thus the dielectric permittivity decreases with frequency. Dielectric permittivity as high as 177 is obtained for the composite CP₂ at 0.1 MHz and 303 K, which is greater than double the value observed for NR composite. The composite CF₃ gives a permittivity of 30
at 0.1 MHz and 303 K. The $\varepsilon'$ values are comparable to those reported by Chwang et al. ($\varepsilon' = 167$) for PANI/PU blends at 0.1 MHz [15].

![Fig. 5.19 Effect of frequency on the dielectric permittivity of CR/PANI composite CP$_2$](image1)

![Fig. 5.20 Effect of frequency on the dielectric permittivity of CR/PANI composite CP$_3$](image2)

![Fig. 5.21 Effect of frequency on the dielectric permittivity of CR/PANI/PANI-N CPC CF$_3$](image3)

### 5.3.1.11 Temperature dependence of CR based CPCs

The effect of temperature on the dielectric permittivity of CR based CPCs with different loadings of PANI and PANI-N at some selected frequencies is presented in figs. 5.22, 5.23 and 5.24. The dielectric permittivity of 100 phr PANI-loaded CPC CP$_2$ increases marginally up to 313 K and then decreases at higher temperatures. For
150 phr PANI-loaded composite CP, the dielectric permittivity marginally increases up to 353 K, and then decreases. For 120 phr PANI-N-loaded CPC CF, the increase is up to 373 K. The initial increase in dielectric permittivity may be due to the increase in interfacial polarization, which is facilitated by the increase in temperature. But, as the temperature increases, the density of the polymer matrix decreases, which outweighs the increase in interfacial polarization. Thus, the dielectric permittivity decreases. Since the volume percentage of the matrix in the CPCs is lesser, this effect is less predominant for the higher loaded composites. Hence, the temperature at which the dielectric permittivity decreases is shifted to higher values.

**Fig. 5.22** Temperature dependence of dielectric permittivity of CR/PANI composite CP<sub>2</sub>  
**Fig. 5.23** Temperature dependence of dielectric permittivity of CR/PANI composite CP<sub>3</sub>  
**Fig. 5.24** Temperature dependence of dielectric permittivity of CR/PANI/PANI-N CPC CF<sub>3</sub>
5.3.1.12 Loading dependence of CR based CPCs

Variation of dielectric permittivity with loading of PANI of CR/PANI CPCs and PANI-N loading of CR/PANI/PANI-N CPCs at 303 K are shown in figs. 5.25 and 5.26. The dielectric permittivity increases with increase in weight percentage of PANI at all frequencies for CR/PANI composites. The increase is more rapid at lower frequencies. A dielectric permittivity of 177 is obtained for the composite CP$_3$ at 0.1 MHz at 303 K. For CR/PANI/PANI-N composites, the dielectric permittivity tends to increase with the introduction of PANI-N loading but it decreases with further loading. A maximum dielectric permittivity value of 70 is obtained for 40 phr PANI-N-loaded composite CF$_1$.

![Fig. 5.25 Dielectric permittivity vs. PANI loading of CR/PANI CPCs at 303 K](image1)
![Fig. 5.26 Dielectric permittivity vs. PANI-N loading of CR/PANI/PANI-N CPCs at 303 K](image2)

5.3.1.13 Tailoring of dielectric permittivity of the CPCs

Efforts were made to correlate the dielectric constant of the composite samples with those of pristine PANI, and gum NR and gum CR. Several mixture equations exist which can be employed to predetermine the dielectric permittivity of the composites correctly [45]. For this, the dielectric has to be considered as a mixture of several components. The observed permittivity of the CPCs can be predicted in terms of the permittivity of the host matrix and that of the conducting polymer by using well-known empirical equations with certain modifications. Among the different mixture
equations, the simplest one is the Lichtenecker equation [43, 46-48], which can be written as:

\[ \log \varepsilon_{\text{eff}} = (1 - V_f) \log \varepsilon_m + V_f \log \varepsilon_f \]  \hspace{1cm} (5.14)

where \( \varepsilon_{\text{eff}} \) is the dielectric permittivity of the composite, \( V_f \) is the volume fraction of the filler, \( \varepsilon_m \) and \( \varepsilon_f \) are the dielectric permittivity of the matrix and the filler respectively. The best-known formula for \( \varepsilon_{\text{eff}} \) for a binary mixture is associated with Maxwell and Wagner. Maxwell developed the idea of effective conductivity of a binary system consisting of spheres of a particular conductivity distributed uniformly in a continuum of different conductivity. Wagner adopted Maxwell’s expression to the dielectric case and the equation is as follows [49]:

\[ \varepsilon_{\text{eff}} = \varepsilon_m \left[ \frac{1 - 2V_f \left( \frac{\varepsilon_m - \varepsilon_f}{2\varepsilon_m + \varepsilon_f} \right)}{1 + V_f \left( \frac{\varepsilon_m - \varepsilon_f}{2\varepsilon_m + \varepsilon_f} \right)} \right] \]  \hspace{1cm} (5.15)

Another mixture equation of the form [50]:

\[ \varepsilon_{\text{eff}} = \frac{\varepsilon_m \varepsilon_f}{\varepsilon_m y_2 + \varepsilon_f y_1} \]  \hspace{1cm} (5.16)

is also found to be useful in predicting the loading dependence of dielectric permittivity of the CPCs. Here, \( y_1 \) and \( y_2 \) represent the weight fractions of the matrix and the filler respectively. For CPCs, the equations (5.14), (5.15) and (5.16) did not fit well with the experimental data. Deviations may have occurred due to the formation of agglomerates of PANI particles in the matrix. Hence modified versions of the equations were derived assuming that spherical shaped conducting particles are well distributed in the non-conducting medium. These modified equations are employed to fit the experimental data. For convenience, logarithmic values were calculated and plotted. The modified form of equation (5.14) used to calculate the dielectric permittivity of the CPCs is:
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\[
\log \varepsilon_{\text{eff}} = (1 - W_f)(\log \varepsilon_m) + W_f(\log \varepsilon_f)^k \quad (5.14a)
\]

Equations (5.15) and (5.16) were also modified with an exponential factor as:

\[
\log \varepsilon_{\text{eff}} = \log \varepsilon_m \left( \frac{1 - 2W_f}{(2\varepsilon_m + \varepsilon_f)} \right) + \log k \quad (5.15a)
\]

\[
\log \varepsilon_{\text{eff}} = \log \varepsilon_m \left( \frac{1}{\varepsilon_m y_2 + \varepsilon_f y_1} \right) + \log k \quad (5.16a)
\]

\(W_f\) is the weight fraction of the filler. Using equations (5.14a), (5.15a) and (5.16a), \(\log \varepsilon_{\text{eff}}\) was calculated and plotted against \(\log f\). Figures 5.27 to 5.32 shows the plots along with the plots of the experimentally observed values. It can be seen that, as the loading increases, the calculated permittivity deviates from the observed one at lower frequencies. For NR composites, the value of \(k\) in equation (5.14a) lies in the range 0.6-1.3, in equation (5.15a), in the range 0.38-0.73 and in equation (5.16a) between 0.2-0.7. For CR composites, the values lie between 0.23-0.88. The marginal variation of the empirical constant and the deviation from the observed value at higher loadings may be due to the difference in filler distribution and filler matrix interactions.
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Fig. 5.27 $\log \varepsilon'$ vs. $\log f$ for the observed and calculated permittivity of NR/PANI CPC with 40 phr PANI ($NP_1$) at 303 K

Fig. 5.28 $\log \varepsilon'$ vs. $\log f$ for the observed and calculated permittivity of NR/PANI CPC with 90 phr PANI ($NP_2$) at 303 K

Fig. 5.29 $\log \varepsilon'$ vs. $\log f$ for the observed and calculated permittivity of NR/PANI CPC with 140 phr PANI ($NP_3$) at 303 K

Fig. 5.30 $\log \varepsilon'$ vs. $\log f$ for the observed and calculated permittivity of CR/PANI CPC with 50 phr PANI ($CP_1$) at 303 K
5.3.2 AC conductivity

Taking into consideration the wide range of electrical conductivity of dielectric materials, there are many mechanisms of carrier transport to explain the conductivity over the entire range. Many mechanisms have been proposed, reflecting the evolution of the underlying electronic structure in the various regimes. The room temperature DC conductivity value is insufficient to differentiate among these various models. Measurements of the frequency and temperature dependence of the AC conductivity, $\sigma_{AC}$, provides important means to distinguish between the various conduction mechanisms. The AC conductivity values of the samples were computed from the dielectric data using equation (5.4).

The current passing through a sample of thickness $h$ and cross-sectional area $A$ can be determined from Ohm’s law and has two components, the in-phase component $I \cos \Phi$ and the out-of-phase component $I \sin \Phi$. The real and imaginary AC electrical conductivities are given by $\sigma_{AC} = (h/A) I \cos \Phi$ and $\sigma_{AC} = (h/A) I \sin \Phi$, respectively. The real part of AC conductivity $\sigma_{AC}$ consists of two terms, which can be written as:

$$\sigma_{ac} = \sigma_{1}(T) + \sigma_{2}(\omega)$$  \hspace{1cm} (5.17)
The first term; $\sigma_1(T)$ is related to drift electric charge carriers. It is frequency independent and temperature dependent, and is really the DC electrical conductivity. The second term; $\sigma_2(\omega)$, is related to the dielectric relaxation caused by bound charge carriers. $k$ is the Boltzmann’s constant and $E$ is the activation energy in eV. $\sigma_0$, $B$ and $n$ are constants, where $n$ is temperature dependent and $\omega$ is the angular frequency of the applied field [51].

5.3.2.1 Frequency dependence of pristine PANI

Variation of AC conductivity of pristine PANI with frequency at different temperatures is plotted in fig. 5.33. It shows a nominal increase initially up to 2 MHz, and then decreases at higher frequencies.

![Graph showing the variation of AC conductivity of PANI with frequency](image)

*Fig. 5.33 Variation of AC conductivity of PANI with frequency*

This can be explained using Maxwell-Wagner two layers or the heterogeneous model. The heterogeneities of the material as described by the Maxwell-Wagner model consist of two layered capacitors i.e. well conducting grains separated by layers of lower conductivity. The low-frequency AC conductivity is related to the

\[
\sigma_1(T) = \sigma_0 \exp \left( - \frac{E}{kT} \right) \tag{5.18}
\]

\[
\sigma_2(\omega) = B \omega^n \tag{5.19}
\]
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resistive grain boundaries, where as the high frequency AC conductivity is due to the conductive grains. Electrical conductivity in conducting polymers is due to the hopping of charge carriers. As the frequency of the applied field increases, the hopping of the charge carriers also increases thereby increasing the conductivity. Equations (5.4) and (5.18) also explain the increase in $\sigma_{AC}$ with increase in frequency. At high frequencies, greater than 2 MHz, AC conductivity decreases with increase in frequency as the hopping of charge carriers lags behind the applied frequency.

A plot of $\log \sigma_{AC}$ against $\log f$ from 2 MHz to 8 MHz at different temperatures is presented in fig. 5.34. This can be understood on the basis of equation (5.19), \[ \sigma(\omega) = B\omega^n \] where $n$ is an index less than or equal to unity which is used to understand the type of conduction/relaxation mechanism dominant in amorphous materials. The variation of the exponent $n$ with temperature gives information on the specific mechanism involved in the conduction process. This behavior has been ascribed to the inhomogeneity within the solid caused by the absence of long range crystalline order [52]. Carrier transport via hopping can be identified with this type of dielectric response. Jonscher [53] has proposed that such a dependence on frequency and temperature represents a universal law, applicable to a very wide range of materials irrespective of their chemical and physical structure and the type of dominant charge carriers. The value of $n$ obtained from the plots lies between -0.36 and -0.46 (table 5.1). This value is in accordance with the theory of hopping conduction in amorphous materials. The observed frequency dependence suggests that the mechanism responsible for AC conduction in pristine PANI is hopping [54].
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Fig. 5.34 $\log$ AC conductivity vs. $\log$ frequency of pristine PANI

Table 5.1 $n$ values of pristine polyaniline

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$n$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>-0.40</td>
</tr>
<tr>
<td>313</td>
<td>-0.36</td>
</tr>
<tr>
<td>333</td>
<td>-0.46</td>
</tr>
<tr>
<td>353</td>
<td>-0.43</td>
</tr>
<tr>
<td>373</td>
<td>-0.44</td>
</tr>
<tr>
<td>393</td>
<td>-0.38</td>
</tr>
</tbody>
</table>

5.3.2.2 Temperature dependence of pristine PANI

The effect of temperature on the AC electrical conductivity of pristine PANI is presented in fig. 5.35. As the temperature increases, the conductivity increases, reaches a maximum and then decreases. The increase in conductivity with temperature can be related to the increase in the drift mobility of thermally activated electrons, which increases the hopping conduction [55]. Mott’s variable range hopping mechanism (VRH) has been applied with varying degree of success to conducting organic systems [56-58]. Reghu et al. have shown the applicability of Mott’s VRH model in polyaniline film [59]. The thermal variation of conductivity with time and temperature in polyaniline has also been explained in terms of a
conduction mechanism consisting of electron tunneling between conducting grains embedded in an insulating matrix [60-62]. The thermal degradation was attributed to a decrease of the grain size with a simultaneous broadening of the barriers.

Fig. 5.35 log AC conductivity as a function of $1000/T$ for pristine PANI

5.3.2.3 Effect of frequency of NR based CPCs

Fig. 5.36 presents the frequency dependence of NR gum vulcanizate ($N_{P_0}$) and figs. 5.37 to 5.39 that of the corresponding CPCs at temperatures ranging from 303-393 K. Most of the polymeric materials are insulators and practically no conductivity is observed in unvulcanized elastomers.

The CPCs with different loadings of PANI and PANI-N show similar frequency dependence at different temperatures. With the incorporation of PANI and PANI-N, the AC conductivity increases with increase in frequency and drops after reaching a maximum at higher frequencies. The increase in AC conductivity with increase in frequency is due to the increase in hopping conduction. With increase in PANI loading, the AC conductivity shows an increase.
5.3.2.4 Effect of temperature of NR based CPCs

Effect of temperature on the AC conductivity at different frequencies for different loadings of PANI and PANI-N are shown in figs. 5.40, 5.41 and 5.42. The AC conductivity increases with temperature up to 353 K and then decreases. The temperature dependence of AC conductivity is similar to that of dielectric permittivity of these samples (figs. 5.12-5.14). The initial increase in conductivity is
due to the increase in hopping conduction, though at very high temperatures, the increased segmental mobility of the polymer may insulate the PANI particles and decrease the conductivity.

5.3.2.5 Loading dependence of NR based CPCs

The loading dependence of AC conductivity of NR based CPCs at 303 K at different frequencies is presented in figs. 5.43 and 5.44. As expected, it increases with increase in PANI and PANI-N loadings. The maximum conductivity ($2.13 \times 10^{-3}$ S/m at 5 MHz) is observed for CPC with 140 phr PANI loading (NP3). The 120 phr
PANI-N-loaded composite (NF₃) gives conductivity very close (1.68 × 10⁻³ S/m) to the NP₃ composite.

**5.3.2.6 Frequency dependence of CR based CPCs**

Figs. 5.45 to 5.48 present the effect of frequency on the AC conductivity of gum CR, CR/PANI and CR/PANI/PANI-N composites at 303 K. The conductivity of gum vulcanizate is due to the different ingredients added during vulcanization. CR is a semi-crystalline polymer and can be considered as a continuous matrix of an amorphous polymer in which the crystalline regions are randomly distributed. The crystallite centers tend to lower the conductivity. The elastomer can be visualized as a double layer made up of crystalline and non-crystalline centers, analogous to Maxwell-Wagner two layer model. If the conduction is ionic, ion mobility through the crystalline region will be low and in the case of electronic conduction, the crystalline-amorphous interface may act as a trapping region. At lower frequencies, the crystalline/non-crystalline interface may be more active and as the frequency increases, the ions cross over to the interface leading to an increase in conductivity. High frequency limit is reached when the applied frequency is greater than the hopping rate. Further increase in applied frequency leads to decrease in conductivity.
The CPCs with different loading of PANI and PANI-N show the same behavior as that of the gum vulcanize on frequency variation. The conductivity increases with increase in frequency, reaches a maximum and then decreases at higher frequencies. However, the rate of increase is higher for the CPCs compared to the gum vulcanize. The AC conductivity is found to be higher for CR based CPCs compared to NR based composites. This might be due to the presence of polar C-Cl bonds in chloroprene rubber. However, the behavior patterns with respect to frequency and temperature are the same for both.
5.3.2.7 Effect of temperature of CR based CPCs

The effect of temperature on AC conductivity of CR based CPCs is plotted in figs. 5.49, 5.50 and 5.51. For the composite CP$_2$ (fig. 5.49), the conductivity increases nominally with temperature. But as the frequency increases, the conductivity decreases with temperature and reaches a constant value. As the loading is increased to 150 phr (CPC CP$_3$), the conductivity shows an increase up to a temperature of 353 K and then decreases. For the composite CP$_3$, the conductivity increases with temperature up to 373 K, and then decreases. The initial increase in conductivity is due to the increase in hopping conduction, though at very high temperatures, the polymer chain mobility increases, which decreases the conductivity. The point beyond which the conductivity decreases is shifted to higher temperature for the CR/PANI-N composite, compared to the CR/PANI composite.

Fig. 5.49 Effect of temperature on the AC conductivity of CR/PANI CPC with 100 phr PANI loading (CP$_2$)

Fig. 5.50 Effect of temperature on the AC conductivity of CR/PANI CPC with 150 phr PANI loading (CP$_3$)
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Fig. 5.51 Effect of temperature on the AC conductivity of CR/PANI/PANI-N CPC with 120 phr PANI-N loading (CF$_3$)

5.3.2.8 Loading dependence of CR based CPCs

The effect of loading of PANI and PANI-N on AC conductivity of CR based CPCs are shown in figs. 5.52 and 5.53.

Fig. 5.52 AC conductivity vs. PANI loading for CR/PANI CPCs at 303 K
Fig. 5.53 AC conductivity vs. PANI-N loading for CR/PANI/PANI-N CPCs at 303 K

The conductivity increases with PANI content, as expected. The increment is sharper at higher frequencies. For CR/PANI/PANI-N composites, the AC conductivity tends to increase with PANI-N loading but it decreases at higher loadings as seen in the case of dielectric permittivity (fig. 5.26). The conductivity is slightly higher than that observed for NR/PANI CPCs (section 5.4.5). A maximum conductivity of
6.20 × 10^{-3} \text{ S/m} at 5 \text{ MHz} is recorded for CPC CP_3. The PANI-N-loaded composite gives a maximum conductivity of 1.01 × 10^{-3} \text{ S/m} for 120 phr loading (CPC CF_3).

### 5.4 Conclusions

The dielectric properties of PANI and the CPCs were measured in the frequency range 0.1 to 8 MHz and in the temperature range 303 to 393 K. The dielectric permittivity of pristine PANI decreases with increase in frequency revealing that PANI exhibit interfacial polarization at low frequencies. At 0.1 MHz, PANI shows a permittivity of 76 at 303 K and at 393 K, the permittivity is as high as 712. At low frequencies and temperatures, the loss factor of pristine PANI decreases linearly with increasing frequency suggesting that DC conductivity process is more significant than interfacial polarization at these frequencies and temperatures. The dielectric permittivity of the CPCs decreases with frequency owing to a decrease in interfacial polarization and increases with PANI and PANI-N loading. With increasing temperature it increases, reaches a maximum and then decreases. At 303 K and 0.1 MHz, a dielectric permittivity as high as 177 is obtained for 150 phr PANI-loaded CR CPC, which is almost double the value obtained for NR composite. The dielectric dispersion could be fitted well with the well known empirical equations. The effective permittivity of the CPCs can be predicted by employing one of these equations.

The conductivity in the CPCs is mainly due to hopping of charge carriers. AC conductivity increases with increase in frequency and temperature and drops after reaching a maximum for the CPCs due to an increase in hopping conduction. In the case of NR based CPCs, a maximum conductivity of 2.13 × 10^{-3} \text{ S/m} at 5 \text{ MHz} is observed for CPC with 140 phr PANI loading. The 120 phr PANI-N-loaded CPC gives conductivity (1.68 × 10^{-3} \text{ S/m}) very close to the 140 phr PANI-loaded CPC at the same frequency. The AC conductivity is found to be higher for CR based CPCs compared to NR based composites. A maximum conductivity of 6.20 × 10^{-3} \text{ S/m} at 5 \text{ MHz} is obtained for CPC with 150 phr PANI loading. The 120 phr PANI-N-loaded composite gives a conductivity of 1.01 × 10^{-3} \text{ S/m} at the same frequency. Better dielectric properties are exhibited by CR based composites due to its polar nature.
Thus, the dielectric properties of the rubber matrix can be modified by appropriate loadings of PANI and PANI-N according to the intended operating temperature and frequency.

References

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