CHAPTER IV

EFFECT OF PERCOLATION ON ELECTRICAL, DIELECTRIC AND MECHANICAL PROPERTIES OF COMPOSITES

4.1 Introduction

As mentioned in chapter III, at the onset of the percolation there is a drastic change in the conductivity of the composite. This dramatic change in conductivity may be having an impact on other electrical, dielectric, mechanical, physical and thermal properties of these materials. In order to investigate the effect of percolation on electrical properties the current voltage characteristics of the composites with different filler contents have been studied. The variations of dielectric constant, dissipation factor and the loss factor with the frequency of the measuring field and graphite content have been studied at ambient temperature for both polyvinyl chloride/graphite (PVC/Gr) and acrylonitrile butadiene styrene/graphite (ABS+Gr) composite systems to see any observable change in the dielectric properties of these composites below and above percolation threshold. From the dielectric data the ac conductivity was calculated and its variation with the filler loading and frequency was studied. Finally for detecting any deterioration in the mechanical properties of the polymer due to the addition of conducting filler D Shore hardness of both the composite systems have been studied as a function of graphite content. Here also the effect of percolation has been under the scanner.
4.2 Current-Voltage Characteristics

It is well established that nonlinear current-voltage behavior is one of the electrical characteristics for most of the conducting polymer composite materials [1-10]. It has been observed that this non-linear behaviour is dependent on the conducting filler content in the composite. Various mechanisms have been proposed to explain this non-linear electrical behaviour. Among them the most common mechanism is based on the electron conduction between the conductive filler particles by electron tunneling and hopping.

In the case of DC conduction the current-voltage characteristics of most filled polymers satisfies the following equation:

\[ I = CV^m \] (4.1)

where \( V \) stands for the applied voltage, \( I \), the corresponding current, \( C \) is the reciprocal of resistance and \( m \) is the slope of the \( \log V - \log I \) plot. When \( m = 1 \), we have the ohmic behavior.

4.3 Dielectric Studies

A perfect conductor is one that does not have any capacitance and a perfect dielectric is that which does not have any conductance. Most of the polymers are typical dielectrics, which can be polarized by an external electric field. The polarization in polymers is contributed by two basic components, deformation (electronic and atomic) and orientation components [11].
Polymeric dielectrics are materials with a very low conductivity, which is therefore, difficult to measure and the poor reproducibility of conductivity measurements also causes difficulty. Both the micro and macro structure of these materials are sensitive to their thermal, mechanical and electrical history. Their amorphous, or at least partly amorphous, structure is complex. Polymers contain many impurities, additives and imperfections. These are some reasons for today's limited and unreliable knowledge of the kind of charge carriers involved, of their transport mechanism in the polymer and of the charge transfer mechanism through the dielectric-filler boundary. In an attempt to describe the complicated observed behaviour, various theories and hypotheses, often contradictory and transferred from other groups of materials, have been applied.

4.3.1 Current in a dielectric on the application of electric field

When an electric field is applied to a dielectric, the field interacts with the bound and free charges causing their motion. The motion of charge manifests itself as a current flow in the external circuit. Generally, this current depends on the time elapsed after the application of voltage to the electrodes; usually, it falls off at first (often it is termed polarization, absorption or anomalous charging current) and then it may become steady. This effect has been known for more than one hundred years and many explanations of the observed behaviour in different dielectric materials have been given. At low fields, in general, the following processes may take place [12]:

(1) charging of the geometrical vacuum capacitance;

(2) fast kinds of polarization, e.g. resonance and some types of dipole orientation

(3) slow types of dipole relaxation polarization ;
(4) flow of conduction current caused by the motion of charges injected from the electrodes or generated by thermal ionization of impurities or of the dielectric itself, or produced by photo-ionization or high-energy radiation ionization;

(5) relaxation polarization of the Maxwell-Wagner type caused by micro- or macro-heterogeneities of a continuous or discrete nature;

(6) electrode polarization due to complete or partial electrode blocking;

(7) trapping of charge carriers in the bulk of the dielectric.

The above list may not be exhaustive, but does include the most common phenomena.

Low frequency dielectric spectroscopy can be used to study interfacial polarization in heterogenic polymeric systems. Interfacial polarization occurs within systems in which the different components have different conductivities. The conductivity of the filler layers can cause interfacial polarization when they are present in a non-conductive polymer matrix. Interfacial polarization can increase the dielectric constant substantially.

When a material is placed in an electric field, two interaction mechanisms can be observed [13]:

1. the storage of field energy (expressed by the dielectric constant or $\varepsilon'$).

2. dissipation of field energy (expressed by the loss factor or $\varepsilon''$).

Both dielectric constant and loss factor are functions of the frequency of the alternating electric field besides other physical parameters such as temperature. The storage of field energy obviously is a capacitive effect, caused by the polarisibility of the material. On applying an external electric field polarization results and distinction can be made between three polarization mechanisms:
1. Electric/atomic polarization: the displacement of binding electrons or atoms from their equilibrium position on a molecular level (induced dipoles). This process is very fast and can be regarded as frequency independent.

2. Dipole orientation: the orientation of permanent dipoles along electric field lines. This process has typical relaxation times of $10^{-6} - 10^{-8}$ s.

3. Interfacial or Maxwell-Wagner polarization: a macroscopic build-up of charges at internal interfaces. This occurs when two materials with dissimilar conductivities are subjected to an electric field. This process is relatively slow (relaxation time > 1 s) and can be investigated by low frequency dielectric spectroscopy. The dielectric behavior of carbon black/graphite filled polymer composites is subjected to interfacial polarization. [12].

The dissipation of field energy is an irreversible effect. Main mechanisms are:

1. The conductivity of the material: field energy will dissipate as heat of conduction, depending upon the current ($I$) passing through the system, its resistance ($R$) and the time ($t$) of the passage of current. This process takes place only at low frequencies.


The polarisibility of a material is given by its relative dielectric constant $\varepsilon_r$. This is the ratio between the permittivity of the examined material and the permittivity of vacuum $\varepsilon_0$ (8.85 pF/m). To describe both storage and dissipation properties the relative dielectric constant is expressed in its complex form $\varepsilon^* (\omega)$:

$$\varepsilon^* (\omega) = \varepsilon' (\omega) - i \varepsilon'' (\omega) \quad (4.2)$$
where \( i = \sqrt{-1} \) and \( \omega = 2\pi f \) is angular frequency of the measuring electric field. The real part of the relative permittivity, \( \varepsilon^' (\omega) \), commonly known as the “dielectric constant” is associated with the polarization or capacitance of the material and the imaginary part, \( \varepsilon^"(\omega) \), of the complex dielectric constant generally called the “loss factor” or “dielectric loss” is associated with its conductance. The ratio of the imaginary to the real parts \( (\varepsilon^"/\varepsilon^') \) is called the dissipation factor, represented by \( \tan\delta \). where \( \delta \) is the angle between the voltage and the charging current. This angle \( \delta \) is called the “loss angle” [16]. Basic parameters characterizing a dielectric are, electrical conductivity \( \sigma \) (S/m), permittivity \( \varepsilon^' \), dielectric loss tangent and dielectric strength \( E_p \), (V/m) [17].

**Electrical conductivity**

Electrical conductivity depends upon the presence of free charges (electrons or ions) and their mobility. A dielectric usually contains very few charge carriers and therefore has a poor conductivity (of the order of \( 10^{-13} \) S/cm or less). With rising temperature the conductivity of a dielectric increases owing to increasing mobility of free charges.

**Dielectric Constant**

Dielectric Constant is the ratio of the capacity of a condenser made with a particular dielectric to the capacity of the same condenser with air as the dielectric at a definite electric field frequency. For a plastic used to support and insulate components of an electrical network from each other and ground, generally it is desirable to have a low level of dielectric constant. For a material to function as the dielectric of a capacitor, on the other hand, it is desirable to have a high value of dielectric constant, so the capacitor may be physically as small as possible.
**Dissipation Factor**

Dissipation Factor is the ratio of $\varepsilon''$ to $\varepsilon'$. It is the tangent of the loss angle ($\delta$). Dissipation factor is a measure of the conversion of reactive power to real power, showing as heat.

**Loss Factor**

Loss Factor is the product of the dielectric constant and the power factor and is a measure of total losses in the dielectric material. It is the part of the energy of an electric field that is dissipated irrecoverably as heat in the dielectric.

**Dielectric Strength**

Within the field intensity range of $10^5$-$10^6$ V/cm the conductivity of a dielectric increases with increasing field intensity. After a certain potential difference is reached between the electrodes further increase of the field intensity will sharply increase the current passing through the dielectric, i.e. will cause dielectric breakdown. The material loses its dielectric properties, becomes a conductor and fails. The electric field intensity at which the breakdown occurs is the measure of the dielectric strength of the dielectric.

**4.3.2 Heterogeneous systems**

Numerous authors have described the dielectric behavior of heterogeneous systems. The approach of Sillars [18], Wagner [19] and Maxwell-Garnett [20] was limited to rather small filler volume fractions. Böttcher [21], Looyenga [22] and Bruggeman [23] extended the equations to higher filler volume fractions. Bruggeman derived a relation, which in its simplified form for a non-conductive filler material embedded in a nonconductive matrix material, both having a frequency independent dielectric constant, gives the dielectric constant of the composite:
where \( \varepsilon_c \) is the dielectric constant of the composite; 
\( \varepsilon_{m/f} \) is the dielectric constant of the matrix/filler; 
\( \nu_2 \) is the volume fraction of filler material.

### 4.3.3 Heterogeneous systems with conducting filler

During the last few decades theoretical and empirical equations for calculating the dielectric constant in heterogeneous systems have been proposed [24]. However, these equations are valid for concentrations below the percolation threshold and are usually applicable in two layer systems or for inclusions of particles with definite geometric form. The complex structure and geometry of graphite aggregates and agglomeration effect prevent the correlation of dielectric properties with these equations.

Steeman [25] described a special case of such a two-phase system, namely a two-phase system with a conducting interlayer. In case of spherical filler particles Steeman has derived the following equation for low limiting frequencies (fully relaxed situation):

\[
\varepsilon_c = \varepsilon_m \left( \frac{1 + 2\nu_f}{1 - \nu_f} \right)
\]  

(4.4)
where $\varepsilon_c$ dielectric constant of the composite
$\varepsilon_m$ dielectric constant of the matrix
$\nu_f$ filler volume fraction.

In this case, the dielectric constant of the composite is only a function of the
dielectric constant of the matrix material and the filler volume fraction. This is
because the conducting interlayer shields the entire filler volume. In dielectric point of
view the system is then reduced to a two-phase system consisting of a non-conducting
matrix and filler with infinite dielectric constant. At high filler volume fraction ($\nu_f \to
1$), very high values of the dielectric constant of the composite can be expected.

The dielectric properties of a polymer composite depend upon the following
three major factors.
1). The properties of the constituent phases, specifically permittivity and conductivity.
2). Their relative volume fractions and
3). The morphology in which the different phases are connected in three dimensions.

The conductivity of the filler layers can cause interfacial polarization when they are present in non-conducting polymer matrix. Interfacial polarization can increase the dielectric constant substantially. Dielectric spectroscopy is a powerful technique to study the distribution of filler material into polymer matrix.
4.4 A.C. Conductivity

Most of the conductivity studies in polymer composites have been done on dc conductivity/resistivity. However, a few researchers have reported ac conductivity measurements in composites at different field frequencies [26]. A.C. Conductivity has been evaluated from the dielectric data in accordance with the relation:

\[ \sigma_{ac} = \omega \varepsilon_0 \varepsilon_r \tan \delta \]  \hspace{1cm} (4.5)

where
- \( \omega = 2\pi f \) is the angular frequency of the measuring field
- \( \varepsilon_0 \) is the permittivity of vacuum
- \( \varepsilon_r \) is the relative permittivity
- \( \tan \delta \) is the dissipation factor

4.5 Hardness Studies

Hardness test, being a relatively simple and non destructive technique, has been employed widely and accepted as one of the useful methods for determining the mechanical properties of all kinds of materials. Hardness has been well established for characterizing metals and ceramics for many years, but less for polymers [27-28]. However due to its usefulness, this technique has been increasingly employed for polymer characterization in the recent years. Hardness test has been shown to be able to determine the changes in morphology and microstructure of polymers and polymer blends [29]. Hardness value can also be applied to approximate the yield stress of materials. This was originated by Tabor [30] who found that hardness, \( H \), of metals, which can be considered as rigid perfectly plastic bodies, could be related to the yield stress, \( \sigma_y \), by the following simple relation:
\[ H = C \sigma_y \]  

(4.6)

Where \( C \) is a constant and its value is approximately equal to 3. This implies that the pressure employed in hardness test is higher than the stress needed to initiate yield in quasi-static test since the stressed material in hardness test is constrained by the surrounding unstressed matrix. This relation is found to be useful since yield stress of materials can be estimated from a nondestructive and simpler hardness test. However, this simple correlation is not universal for all the cases. In the case of polymers it has been reported that this relation is valid to a limited extent and that too in some specific cases [31,32]. This discrepancy may be due to the greater complex deformation process in polymeric materials as compared to metals and also the testing conditions, which may be of dissimilarity.

### 4.6 Results and discussion

#### 4.6.1 I-V Characteristics

Figures 4.1 to 4.5 show the current-voltage characteristics of PVC/Gr pre-localized composite with different Gr contents. LogV- log I behaviour of the corresponding sample (s) is exhibited as inserts in these figures. Figures 4.6 to 4.10 show similar plots for the ABS/Gr composite. It is clear from Figures 4.1 to 4.10 that the I-V behaviour of the pre-localized composites is dependent on the Gr content.

Equation (4.1) can be rewritten as

\[ \log I = m \log V + \log C \]  

(4.7)
From the logV-logl plots the values of exponent ‘m’ have been determined and are given in Tables 4.1 and 4.2 for PVC/Gr and ABS/Gr composite systems respectively.

It is evident from Table 4.1 and 4.2 that all the composites with high content of filler exhibit value of m close to 1 although a moderate increasing trend can be seen in its value as the volume fraction of the conductive filler approaches the percolation threshold value. In the vicinity of the percolation threshold a sharp increase in the value of m is observed. Therefore it is reasonable to conclude that the percolation threshold should be defined as that value of volume fraction where the transition from ohmic to nonohmic current behavior takes place. The dependence of exponent m on the volume fraction for both the systems is collectively shown in Fig. 4.11.

**Fig. 4.1 Variation of current with voltage for 2.1 Gr volume% in PVC**
Table 4.1 Value of exponent m for PVC/Gr composite

<table>
<thead>
<tr>
<th>Gr volume%</th>
<th>Value of exponent m</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>1.275</td>
</tr>
<tr>
<td>3.3</td>
<td>1.0223</td>
</tr>
<tr>
<td>4.3</td>
<td>1.008</td>
</tr>
<tr>
<td>6.6</td>
<td>1.0073</td>
</tr>
<tr>
<td>10.1</td>
<td>1.00041</td>
</tr>
</tbody>
</table>

Similar results have been reported by Mamunya et al. [1] in polyethylene (PE)/polyoxymethylene (POM) as matrix and dispersed iron (Fe) composites where with an increasing value of the volume fraction of the conductive filler, a decrease in the value of m has been observed. As filler content decreases and approaches the percolation threshold, m starts increasing and attains the value 1.8.

Fig. 4.2 Variation of current with voltage for 3.3 Gr volume% in PVC
Table 4.2 Value of exponent ‘m’ for ABS/Gr composite

<table>
<thead>
<tr>
<th>Gr volume%</th>
<th>Value of exponent m</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4</td>
<td>1.481</td>
</tr>
<tr>
<td>2.9</td>
<td>1.0678</td>
</tr>
<tr>
<td>3.6</td>
<td>1.0248</td>
</tr>
<tr>
<td>4.9</td>
<td>1.0024</td>
</tr>
<tr>
<td>7.6</td>
<td>.9969</td>
</tr>
</tbody>
</table>

Fig. 4.3 Variation of current with voltage for 4.3 Gr volume% in PVC
Fig. 4.4 Variation of current with voltage for 6.6 Gr volume% in PVC

Fig. 4.5 Variation of current with voltage for 10.1 Gr volume% in PVC
Fig. 4.6 Variation of current with voltage for 2.4 Gr volume% in ABS

Fig. 4.7 Variation of current with voltage for 2.9 Gr volume% in ABS
Fig. 4.8 Variation of current with voltage for 3.6 Gr volume% in ABS

Fig. 4.9 Variation of current with voltage for 4.9 Gr volume% in ABS
Fig. 4.10 Variation of current with voltage for 7.6 Gr volume% in ABS

Figure 4.11 Exponent m versus filler volume fraction.

Various mechanisms have been proposed to explain this nonlinear electrical behavior in conducting polymer composites. The reason of nonlinearity of
the I-V characteristics in the polypropylene (PP)/Nickel (Ni) polymer metal composite according to Chen and Johnson [10] is the creation of strong local electric fields between the conductive clusters. The following three mechanisms of charge transport can exist in composites loaded with conducting fillers.

1.) Ohmic conductivity through direct contact of filler particles.
2.) Non-ohmic conductivity by means barrier tunneling between particles, which have no direct contact.
3.) Other, nonohmic types of conductivity processes, for example, space charge limited conductivity.

Decrease in interparticle distances as well as the number of tunneling gaps causes the transition. The transition of the conduction behaviour from non-ohmic to ohmic is thus expected in the vicinity of the percolation threshold. The filler concentration is an important parameter in determining the network microstructure in a given composite system. When volume fraction of the filler \( v_f \) is less than the volume fraction of the filler at percolation threshold \( v_{fc} \), gap among particles are too large to permit electronic tunneling to occur and the conduction of the composite is mainly controlled by that of the polymer matrix. As \( v_f \) approaches \( v_{fc} \) from below enough particles begin to come closure decreasing tunneling gaps significantly and the network highly develops. Within the regime of the percolation transition above \( v_f \), the particles clusters are joined together in a bond percolation model that governs the conduction. Polymer layers inevitably exist inside the clusters and when the gaps among the clusters are small enough, electron tunneling occurs readily. At sufficiently high filler content, for \( v_f > v_{fc} \) agglomeration of the clusters takes place and an infinite percolation network generates resulting into ohmic conduction. With the
decrease of tunneling gaps and the gradual change from cluster separation to contact, a scaling power law arises for the conductivity as a function of filler concentration, which is generally governed by the statistical percolation theory described in chapter III.

4.6.2 Dielectric Constant as a function of composition and frequency

Figures 4.12-4.25 show the dielectric properties obtained for PVC/Gr and ABS/Gr composite systems. The variations of dielectric constant with filler concentration in PVC/Gr and ABS/Gr composite systems are presented in Figures 4.12 and 4.13 respectively. The measurements taken at four different frequencies i.e. 10kHz, 100kHz, 1MHz and 10MHz are shown in the figures. The dielectric constant increases moderately up to a point slightly higher than the percolation threshold obtained form the resistivity concentration curves (Chapter III, Figures 3.11 and 3.12). Above this point the dielectric constant increases at a much faster rate and exhibit an abrupt change [33,34]. Just beyond the percolation threshold, the dielectric constant values are upto ten times larger than the next lower concentrations. The dielectric constant increases due to space charge built up at the interfaces between the conducting phase and the insulating phase due to difference in the conductivity of two phases [35]. Space charge polarization occurs when more than one material component is present or when segregation occurs in a material containing incompatible chemical sequences and when translating charge carriers become trapped at the interfaces of these heterogeneous systems. The electric field distortion caused by the accumulation of these charges increases the overall capacitance of a material, which appears as an increase in the dielectric constant. In the present study also the relative mobility of the charge carriers in PVC and ABS and graphite results
in the carriers being absorbed in the dielectric through entrapment at the interfaces of separation. Bergman and Imry [36] and Wilkinson and Langer [37] by computer simulation using models based upon random distributions of resistors and capacitors generated dielectric constant curves that increase as the percolation threshold is approached from either side. However, in the present work the dielectric constant was rising and did not show any maxima within the range of the filler concentration studied. In fact after the percolation threshold (i.e. when the samples become highly conductive) a rapid increase is observed in the value of the dielectric constant and finally the reading in the measuring equipment went out of scale suggesting a still higher value of the dielectric constant. A plausible explanation for this type of behaviour may be that as the graphite content increases, the interparticle distance decreases and local fields created by neighbouring particles enhance the rise in the value of the dielectric constant. At lower field frequencies it is more pronounced.

![Graph showing variation of dielectric constant with Gr content in PVC/Gr composite](image)

**Fig. 4.12 Variation of dielectric constant with Gr content in PVC/Gr composite**
The dielectric constant data also do not fit any of the empirical or theoretical correlations described in the literature [38]. This is a direct consequence of the structural properties of the graphite and the complexity of the filler distribution in the polymer matrix. Graphite-polymer systems thus deviate strongly from the predicted percolation concentration for dispersed conductive filler particles. The main reason for this discrepancy is attributed to the aggregate structure rather than spherical structure, which requires significantly lower concentration to reach the critical concentration.

The dielectric data as calculated by using Steeman's Model (equation 4.4) at 10 kHz is also plotted in figures 4.12 and 4.13 for PVC/Gr and ABS/Gr composite respectively for a comparison. It is clear from these figures that the model is applicable to the dielectric constant values below the threshold concentration of the conducting filler for both the systems. For higher filler loadings strong deviations are
observed. Thus better modeling of the dielectric constant behaviour of the composites is required.

Figures 4.14 and 4.15 exhibit the variations of dielectric constant with the frequency of the applied measuring field, ranging from 10kHz to 10MHz for the two composite systems under study. In case of ABS/Gr composite, the dielectric constant of the neat polymer and of other samples below the percolation threshold concentration (2.9 volume%) show a moderate decrease with increasing frequency with $\varepsilon'$ values lying between 2 and 6. Above the percolation threshold a pronounced fall in the value of $\varepsilon'$ is observed. Contrary to this, in PVC/Gr composite the samples both below and above the percolation threshold show a decrease in the value of $\varepsilon'$ with increase in frequency. The dielectric constant values of the composites were

![Figure 4.14 Variation of dielectric constant with frequency in PVC/Gr composite](image)

**Fig. 4.14 Variation of dielectric constant with frequency in PVC/Gr composite**
high at lower frequencies, as a consequence of the interfacial Maxwell Wagner Polarization effect between the polymer and graphite [34].

4.6.3 Loss Factor as a function of composition and frequency

The variation of loss factor, \( \varepsilon'' \), with concentration of the filler is shown in Figures 4.16 and 4.17. The response appears to increase with elevated graphite content in a manner similarly observed with the dielectric constant values (Figs. 4.12 and 4.13) though the change in the losses in the composites is more pronounced than in their corresponding dielectric constant values.

![Graph showing variation of dielectric constant with frequency in ABS/Gr composite](image)

Fig. 4.15 Variation of dielectric constant with frequency in ABS/Gr composite
Fig. 4.16 Variation of Loss Factor with Gr content in PVC/Gr composite

Fig. 4.17 Variation of Loss Factor with Gr content in ABS/Gr composite
Fig. 4.18 Variation of Loss Factor with frequency in PVC/Gr composite

Fig. 4.19 Variation of Loss Factor with frequency in ABS/Gr composite
The losses too thus increase with the increase in Graphite concentration within the frequency range studied in accordance with the Maxwell Wagner polarization theory. The material therefore does not operate efficiently as a high dielectric constant material. Therefore, these materials cannot be used as dielectric materials in capacitors. However due to the increased conductivities these can be used for electromagnetic shielding applications. The percolation threshold is clearly discernible in $\varepsilon'$ and $\varepsilon''$ versus graphite concentration curves in both PVC/Gr and ABS/Gr composite systems.

Figures 4.18 and 4.19 show the loss factor, $\varepsilon''$, as a function of frequency for PVC/Gr and ABS/Gr composites respectively. The losses decrease with increasing frequency within the range studied in case of PVC/Gr samples for graphite concentrations both below and above percolation threshold. On the contrary in ABS/Gr composite the Loss Factor behaviour is interesting as it predicts a decreasing value for the conducting samples and an increasing value for the insulating samples while the percolation threshold is flat with increasing frequency.

4.6.4 Dissipation Factor as a function of composition and frequency

The variation of dissipation factor with Gr content is shown in figures 4.20 and 4.21 for the systems under study. The dissipation factor moderately increases with the Gr content roughly up to the percolation threshold by the interfacial polarization mechanism similar to that of the dielectric constant. As the graphite loading increases and surpasses threshold concentration an abrupt rise in the value of the dissipation factor is observed. A further increase in the graphite concentration causes a decrease in the concentration of the induced charges due to the formation of a network of conductive channels, leading to a decrease in the dissipation factor value. Despite a
fall in the dissipation factor, its value is still high in comparison to that of the unfilled polymer (.00487 at 10kHz for ABS/Gr and .3102 for PVC/Gr composite).

![Graph](image)

Fig. 4. 20 Variation of Dissipation Factor with Gr content in PVC/Gr composite

The maximum tan\(\delta\) values are roughly associated with the percolation threshold in case of both PVC/Gr and ABS/Gr composite systems. Yacubowicz and Narkis [34,39] have also reported that dissipation factor-concentration curves are bell shaped with maximum values at approximately the percolation concentration in carbon black filled polyethylene composites. The high values of the dissipation factor obtained for these composite systems may be attributed to the skin effect associated with a relatively high penetration level of electrical field into graphite particles.
Fig. 4.21 Variation of Dissipation Factor with Gr content in ABS/Gr composite

Fig. 4.22 Variation of Dissipation Factor with frequency in PVC/Gr composite
In figures 4.22 and 4.23 the dependence of dissipation factor upon the frequency of the measuring field is shown. The dissipation factor behaves somewhat like the loss factor and a gradual decrease for samples at and below percolation threshold and a more pronounced decrease for samples above percolation threshold with increase in frequency is observed in case of PVC/Gr composite system. In ABS/Gr composite the tanδ behaviour is again similar to that of the loss factor where a decreasing value for the conducting samples and an increasing value for the insulating samples while frequency independent behaviour at percolation threshold is noticed.

Fig. 4.23 Variation of Dissipation Factor with frequency in ABS/Gr composite

Generally the magnitude of dissipation factor, as well as other dielectric properties, is sensitive to the polar sites in the polymer matrix. These sites increase the dissipation factor and may confuse the dependence of tanδ upon frequency. For a
given concentration above the critical concentration, the dissipation factor decreases with an increasing frequency because the induced charges gradually fail to follow the reversing field as the electric field changes too fast causing a reduction in the electronic oscillations as the frequency is increased.

4.6.5 AC conductivity as a function of composition and frequency

Figure 4.24 and 4.25 shows the variation of AC conductivity with Gr content at selected frequencies for PVC/Gr and ABS/Gr composite systems respectively. In both the systems the percolation threshold seems to be coinciding with the percolation threshold in case of dc conductivity i.e. 2.1 Gr volume% for PVC/Gr system and 2.9 Gr volume% for ABS/Gr systems.

Fig. 4.24 Variation of AC conductivity of PVC/Gr composites as a function of Gr volume% at different frequencies
Fig. 4.25 Variation of AC conductivity of ABS/Gr composites as a function of Gr volume% at different frequencies

Fig. 4.26 Variation of AC conductivity of PVC/Gr composites as a function of frequency at different Gr concentrations

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Due to the increased conductivity above percolation threshold the measuring instrument failed to measure the capacitance of the composites and thus the data regarding the relative permittivity and hence the AC conductivity could not be generated for these composite systems for concentrations of graphite higher than 3.3 volume% for PVC/Gr and 3.6 volume% for ABS/Gr within the frequency range studied. This hinders the observance of a more pronounced and easily perceptible percolation threshold in ac conductivity versus graphite content plots.

The variation of AC conductivity as a function of frequency of the measuring field ranging from 10 kHz to 10 MHz at different filler loadings both below and above the critical concentration is shown in figure 4.26 for PVC/Gr composite and in figure 4.27 for ABS. Perusal of the figures reveal that ac conductivity is increasing almost linearly with the frequency of the applied field.
4.6.6 Hardness as a function of composition

For testing hardness of the samples Scientico Durometer (model No. SRHT-501D) is used. In the present study Shore-D hardness is measured on a scale that is graduated from 0 to 100 divisions; 0 denoting the lowest and 100 the highest degree of hardness. The flat surfaces of 6 mm thick samples prepared especially for testing hardness were smoothed with a fine abrasive paper and the hardness was measured according to the procedure described in Section 2.6.1 of Chapter II.

Figures 4.28 and 4.29 show the D Shore Hardness as a function of graphite content for PVC/Gr and ABS/Gr composites respectively. In both the cases a pronounced decrease in the hardness with initial increase in graphite content roughly upto the percolation concentration and a relatively small decrease thereafter is observed. This is suggestive of a decreased adhesive force between the polymer particles due to the presence of graphite particles in the interfacial regions.

![Graph showing variation of D Shore Hardness with Gr volume% in PVC/Gr composite](image)

Fig. 4.28 Variation of D Shore Hardness with Gr volume% in PVC/Gr composite
4.6.7 Morphology

The surface morphology of the composites was investigated by scanning electron microscopy (SEM). Figure 4.30 shows the SEM Photographs showing shape and dimensions of (a) Pure graphite powder (b) Pure PVC powder (c) PVC particles encapsulated with graphite particles in the composite. The graphite particles seem to be flaky. The PVC particles are of irregular shape showing resemblance to boxer’s gloves. The size of the graphite powder particles i.e. 10-20 μm and PVC i.e. 105-150 μm powder particles as revealed by SEM photographs matches with the size reported by the supplier. Figure 4.31 shows the SEM of the surface of compression-molded samples of the composites containing (a) 3.3 wt% (b) 5 wt% (c) 6.67 wt% and (d) 10 wt% of graphite. The darker lines indicate the presence of graphite in the interfacial regions between the PVC particles, forming a network of graphite conductive channels/paths. The visible increase in thickness of the channels in Figs.4.31 (a) to 4.31(d) can be linked with the increase in graphite content.
Fig. 4.31 SEM photographs of PVC/graphite composites containing graphite: a) 3.3 wt%, b) 5 wt%, c) 6.7 wt%, and d) 10 wt%.
Fig. 4.30 SEM Photographs showing shape and dimensions of (a) Pure graphite powder (b) Pure PVC powder (c) PVC particles encapsulated with graphite particles in the composite.
4.8 Conclusions

The percolation threshold is found to have a phenomenal impact on current-voltage characteristics, the dielectric behaviour and the hardness of the composites. The non-linear relationship between the applied dc voltage and the current changes to a linear one as the filler concentration is increased beyond the percolation threshold. Below the percolation threshold the conductivity is because of tunneling of charge carriers through the non-conducting gaps, as the filler particles at low filler loadings are not touching each other. The non-conducting thin polymer layers generally termed as tunneling gaps, separating graphite particles in the network, decreases as filler content increases and the contribution of ohmic conductivity increases.

The dielectric constant increases moderately roughly up to the percolation threshold and then exhibits an abrupt increase. The relative mobility of the charge carriers in polymer (ABS as well as PVC) and graphite results in the carriers being trapped in the interfaces of separation and space charge gets accumulated at the interfaces. The electric field distortion caused by the accumulation of these charges increases the overall capacitance of a material, which appears as an increase in the dielectric constant. The dielectric constant values of the composites were high at lower frequencies, as a consequence of the interfacial Maxwell Wagner Polarization effect between the polymer and graphite. The losses too increase with the increase in graphite concentration within the frequency ranges studied as the composite becomes conductive and the material therefore cannot be efficiently used as a high dielectric constant material. However due to the increased conductivities the composites can be used for electromagnetic shielding applications.
The losses decrease with frequency in case of PVC/Gr. However in ABS/Gr composite the Loss Factor exhibits a decreasing value for the conducting samples and an increasing value for the insulating samples while the percolation threshold is flat with increasing frequency. The dissipation factor-filler content curves are bell shaped with the crests of these curves i.e. maximum tanδ values lying roughly in the vicinity of the percolation threshold. The dissipation factor as a function of frequency behaved more or less like loss factor.

In both the systems the percolation threshold in ac conductivity seems to be coinciding with the percolation threshold in case of dc conductivity i.e. 2.1 Gr volume% for PVC/Gr system and 2.9 Gr volume% for ABS/Gr systems. For all the concentrations of the filler studied, the ac conductivity was found to increase almost linearly with the frequency of the applied field.

In both the cases a pronounced decrease in the hardness with initial increase in graphite content roughly up to the percolation concentration and a relatively small decrease thereafter is observed.
4.9 References