4.1 Introduction

When presented with a new material every one immediately want to know the thing: how the electrons in the material respond to electrical forces and it can be summed up by the Ohm’s law

\[ V = RI \]

where \( V \) is the potential difference across the conductor, \( I \) is the current through the conductor, and \( R \) is the electrical resistance of the conductor.

Ohm’s law is a general formula applicable to one, two and three dimensional conductors. In a typical conductor charges are moving and scattering at random with no net movement of charge across the sample. This situation changes when a voltage difference, \( V \), is applied across the conductor. The voltage difference creates an electric field, \( E \), which gives a net force to randomly scattered electrons in one direction. Some of the possible scattering mechanisms are phonons in the material, defects in the lattice, or charge in-homogeneities in the material. The velocity with which the charges move in the direction of the applied field is known as the drift velocity, \( v_d \) and is related to the current density \( J \) by:

\[ J = nev_d \]

where \( n \) is the charge carrier density and \( e \) is the charge on electron. The ratio between drift velocity and applied electric field gives the value of the mobility,

\[ \mu = \frac{V_d}{E} \]

and is an important quantity that is used to characterize scattering in conductors. The resistivity of a material in terms of its mobility expressed as,
\[ \rho = \frac{1}{ne\mu} \]

The reciprocal of electrical resistivity gives the value of electrical conductivity:

\[ \sigma = ne\mu \]

For electronic conductors the electron charge, \( e = 1.6 \times 10^{-19} \text{ C} \), is constant and independent of temperature. The mobility, \( \mu \) usually decreases with increasing temperature because of lattice vibrations caused due to collisions between electrons and phonons. In metallic conductors, \( n \), the number of charge carriers remains constant, but in case of semiconductor and insulator increases exponentially. Thus at high temperatures some insulators becomes semiconductors, while at low temperatures some semiconductors become insulators.

### 4.1.1 Electrical Conductivity

The electrical conductivity \( \sigma \) is the degree to which a specified material conducts electricity, calculated as the ratio of the current density in the material to the electric field which causes the flow of current. It is an intrinsic property of the material, because the materials may be good conductor or bad conductor or insulator depending on their band structure. In most of the solids, valence electrons are responsible for electrical conductivity. Most electrons in solids are bound to the atoms in local orbits, but a small fraction of the electrons are available to move easily through the entire crystal. These so-called conduction electrons carry the electrical current. Solids with many conduction electrons are metals, conduction and valence bands are overlapped. While in case of semimetals or semiconductors, the gap is exist between conduction and valence bands called band gap or energy gap. In insulators, nearly all the electrons are bound and the large energy gap exist between conduction
and valence bands. In crystals, electrical current is due to the motion of both ions and electrons. Ions move by hopping occasionally from site to site; all solids can conduct electricity in this manner. The electricity conducted by this process is quite small and is usually negligible compared with that carried by the electrons. The ions hop more often at high temperature.

The reciprocal of the electrical conductivity gives the value of specific resistance or resistivity \(\rho\) of the material of the substance. Most conductive materials change specific resistance with changes in temperature. The rate of change of resistance per degree change in the temperature of the substance is called temperature coefficient of resistance (TCR) \(\alpha\) of the substance. For pure metals, TCR is a positive number that means the resistance increases with increasing temperature. For the elements like carbon, silicon and germanium, the TCR is a negative that means the resistance decreases with increasing temperature. For some metal alloys, the temperature coefficient of resistance is very close to zero that means the resistance hardly changes at all with variations in temperature.

This chapter describes ampere-voltage characteristics and the dc and ac conductivities of pure PANI and all PANI-GRA composites to investigate charge transport mechanism. The dc conductivity dependence on temperature and ac conductivity dependence on ac frequency are studied for all prepared samples.

### 4.1.2 Electrical properties of GRA

GRA is a crystalline allotropic form of carbon substance has four valence electrons where three of them are covalently bonded to three other carbon atoms, forming a layered structure. However, the fourth valence electron is left unbonded,
and thus is able to move freely. These valence electrons allow the flow of electricity through the substance in certain directions when an electrical current is applied to graphite. There are four atoms per unit cell and hence there are sixteen energy bands among which twelve are $\sigma$-bands and four are $\pi$-bands. Lower energy $\sigma$ bands are bonding and higher energy six $\sigma$ bands are anti binding. These two groups of $\sigma$-bands are separated by approximate energy gap $5eV$. The $\pi$-bands lies between these two groups of $\sigma$-bands. The two $\pi$-bands are bonding and two are anti-bonding. All bonds are coupled and four $\pi$-bonds are strongly coupled. GRA has sixteen electrons per unit cell and only eight energy bands are filled. Thus the Fermi level lies in the middle of the four $\pi$-bands. The upper $\pi$-bands form the highest valence bands, making GRA a semi-metal [1]. The band overlap energy is about $0.03eV$. The schematic one dimensional energy bands as shown in Figure-4.1. The electrical resistivity of GRA is $(4$ to $6) \times 10^{-7}\Omega m$ and possess negative temperature coefficient of resistance (TCR) and the melting point of 3973K.

Figure-4.1: Conduction and Valence bands of GRA
4.1.3 Electrical properties of PANI

The process of transforming a polymer to its conductive form via chemical oxidation or reduction is called doping. The conductivity of polymers depends directly on the doping level [2,3]. The conducting polymers are not one dimensional conductors, they are quasi one dimensional. If they were truly only one dimensional, no matter how high the conductivity of an individual chain, the bulk conductivity would be zero since a single molecule does not stretch from one end of a bulk piece of a conducting polymer to the other. The electrons have to be transported from one polymer chain to the other. At lower doping levels, this transportation is called “hopping” or “phonon-assisted quantum mechanical tunneling” [4] At higher doping levels (metallic state), band structure will develop - both along the polymer chains and between chains. The bulk conductivity of conducting polymer consists of contributions from intra-molecular, inter-molecular and inter-domain; i.e.

\[ \sigma_{total} = \sigma_{intera} + \sigma_{inter} + \sigma_{domain} \]

The electrons have to move along a polymer chain (intra-molecular contribution), then “hopping” to another polymer chain (intermolecular contribution) and from one domain to another (inter-domain contribution) so that the polymer can be electrically conductive.

A radical cation that is partially delocalized over some polymer segment is called a polaron. If another electron now is removed from the already oxidized polymer containing the polaron, two things can happen: if the electron come from the different segment of the polymer chain, leads to the formation of another independent polaron, and if the electron come from the first polaron level (remove the unpaired electron)
leads to creation of a special dication, which is called a **bipolaron**. The different excitations in the conjugated polymers differ in the charge they carry: A positive/negative polaron is an excitation that carries a single positive/ negative electron charge. A bipolaron is a double charged excitation. The mechanism of conduction and behavior of charge carriers in the conducting polymers have been explained using the concept of polarons and bipolarons. Both polarons and bipolarons

![Diagram of charged defects in conducting polymer](image)

**Figure-4.2** Mechanism of formation charged defects in conducting polymer
are mobile and can move along the polymer chain by the rearrangement of double and single bonds in the conjugated system that occurs in an electric field. Conducting polymers either have a zero energy band gap or a very low band gap. A reduction in the optical band gap increases the conductivity of the polymers. So, attempts have been made to reduce the band gap in conducting polymers by various methods.

The conducting polymers require partial oxidation with electron acceptors (i.e. anions) or partial reduction with electron donors (i.e. cations) [5]. The partial oxidation and reduction are referred as p-doping and n-doping respectively [6]. Charged defects, such as polarons, bipolarons and solitons, are introduced into the polymer structure as a result of the doping process. These defects play the vital role of charge carriers. The Figure-4.2 shows the mechanism of formation of charged defects. In first step, the addition/removal of electrons to the bottom of the conduction band, or from the top of the valence band, makes the conduction/valence band partially filled, and hence facilitates the creation of a radical anion/cation (i.e. polaron). The injection of states into the band gap from the bottom of the conduction band or the top of the valance band results from the creation of the polarons. Further addition/removal of another electron results in the formation of a dianion/dication (i.e. bipolaron). The solitons are a special type of charged defect that are unique to conducting polymers with a degenerate ground state and are not present in conducting polymers like PANI polythiophene, poly(3,4-ethylenedioxythiophene) and polypyrrole. They are formed when bipolarons further lower their energy state by dissociating into two solitons at half of the energy gap.[6]
4.2 Results and discussion

4.2.1 Volt-ampere characteristics: For each sample, two pellets (one for dc measurements and one for ac measurements) of thickness 2.42mm and diameter 12.06mm were prepared by a pressure of 5 ton and the conducting silver paste was deposited on each face of the pellet used to get better ohmic contacts. The dc current-voltage characteristics of all the samples recorded at room temperature. The circuit used to analyze current-ampere characteristics of prepared samples is shown in figure-4.3. \( V_{in} \) and \( V_o \) are the high resistance digital voltmeters of range (0-30) V analyzing supply voltage and potential drop across the sample respectively and the highly sensitive digital ammeters of range (0-2500µA and 0-100mA) are measuring the current through the samples. For each sample the supply voltage \( V_{in} \) varies from 0 to 30V and to study the corresponding variations in ammeter (A) and \( V_o \).

![Diagram of circuit for analysis of current-ampere characteristics](image-url)
The curve in the figure-4.4 presents the current-voltage characteristics of pure PANI. The increased potential difference across the sample results in increased current. This may be due to vibration of lattice ions. The range of applied voltage $V_{in}$ is (0-30) V and the corresponding range of current through the sample is (0-140) µA. The reciprocal of the slope gives the value of differential resistance or incremental resistance or slope resistance and its calculated value is $127k\Omega$.

Figure-4.4: Current-Voltage characteristics of pure PANI PANI. The increased potential difference across the sample results in increased current. This may be due to vibration of lattice ions. The range of applied voltage $V_{in}$ is (0-30) V and the corresponding range of current through the sample is (0-140) µA. The reciprocal of the slope gives the value of differential resistance or incremental resistance or slope resistance and its calculated value is $127k\Omega$.

The Figures-4.5 (a),(b),(c),(d)and(e) represents the current-voltage characteristics curves of PANI-GRA composites with GRA composition 5wt%,10wt%,15wt%,20wt% and 25wt% respectively. The 5wt%GRA sample exhibit linear current-voltage characteristic curve, with maximum potential drop $V_{omax}=28V$ and maximum current $I_{max}=1800\mu A$. The 10wt% is also exhibit linear curve with $V_{omax}=21.6V$ and $I_{max}=8mA$.Similarly the curve is linear curve with $V_{omax}=4.3V$ and $I_{max}=23.18mA$ for 15wt% sample. For 20wt% sample the curve is found to be non-
linear with $V_{omax}=3.93V$ and $I_{max}=25.5mA$. Finally the 25wt% sample also exhibit non-linear curve $V_{omax}=3.502V$ and $I_{max}=26.76mA$.

The Figures 4.6 (a), (b), (c), (d) and (e) are the respective current-voltage characteristics curves of 5wt%, 10wt%, 15wt%, 20wt% and 25wt% PANI-GRA composites treated with L A. For 5wt% sample $V_{omax}=24.33V$ and $I_{max}=5.47mA$ and the curve is linear, for the remaining four samples curves are non-linear with

\[ V_{omax}=15.38V \text{ and } I_{max}=14.72mA \text{ for 10wt%, } V_{omax}=10.25V \text{ and } I_{max}=19.64mA \text{ for 15wt%, } V_{omax}=12.57V \text{ and } I_{max}=17.98mA \text{ for 20wt% and } V_{omax}=11.65V \text{ and } I_{max}=18.73mA \text{ for 25wt%}. \]

The Figures 4.7 (a), (b), (c), (d) and (e) are the current-voltage characteristics curves of PANI-GRA composites treated by T X-100 with GRA composition 5wt%, 10wt%, 15wt%, 20wt% and 25wt% respectively. All the five samples exhibit non-linear relation between current and voltage with $V_{omax}=6.45V$ and $I_{max}=13.82mA$ for 5wt%, $V_{omax}=4.4V$ and $I_{max}=25.5mA$ for 10wt%, $V_{omax}=3.16V$ and $I_{max}=26.87mA$ for 15wt%, $V_{omax}=2.47V$ and $I_{max}=27.62mA$ for 20wt% and $V_{omax}=2.58V$ and $I_{max}=27.74mA$ for 25wt%.

In all the samples increment in current can be observed with increment in wt% of GRA. The composites treated with L A shows ohmic behavior and all the samples treated with T X-100 exhibit semiconducting behavior. The values of incremental resistance of all the samples are recorded in the following Table-
Figure 4.5 (a-e): Current-Voltage characteristic curves of PANI-GRA composites with different composition of GRA.
Figure 4.7 [a-e]: Current-Voltage characteristics of PANI-GRA composites with different composition of GRA treated by T X-100.
Figure 4.6 (a-e): Current-Voltage characteristics of PANI-GRA composites with different composition of GRA treated by L.A.
### Table 4: Resistances of different samples at room temperature

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>RESISTANCE (kΩ)</th>
<th>SAMPLE</th>
<th>RESISTANCE (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>127</td>
<td>15wt% GRA with L A</td>
<td>0.428</td>
</tr>
<tr>
<td>5wt% GRA</td>
<td>13.98</td>
<td>20wt% GRA with L A</td>
<td>0.3728</td>
</tr>
<tr>
<td>10wt% GRA</td>
<td>9.128</td>
<td>25wt% GRA with L A</td>
<td>0.286</td>
</tr>
<tr>
<td>15wt% GRA</td>
<td>0.147</td>
<td>5wt% GRA with T X-100</td>
<td>0.3117</td>
</tr>
<tr>
<td>20wt% GRA</td>
<td>0.0810</td>
<td>10wt% GRA with T X-100</td>
<td>0.1272</td>
</tr>
<tr>
<td>25wt% GRA</td>
<td>0.0566</td>
<td>15wt% GRA with T X-100</td>
<td>0.0565</td>
</tr>
<tr>
<td>5wt% GRA with L A</td>
<td>3.364</td>
<td>20wt% GRA with T X-100</td>
<td>0.047</td>
</tr>
<tr>
<td>10wt% GRA with L A</td>
<td>0.677</td>
<td>25wt% GRA with T X-100</td>
<td>0.0302</td>
</tr>
</tbody>
</table>
4.2.2 D.C. Conductivity

For each sample, two pellets of thickness 2.42mm and diameter 12.06mm were prepared by a pressure 5 ton and the conducting silver paste was used for ohmic contacts. The dc resistance of all the samples recorded in the temperature range 310K to 460K by using highly sensitive Keithely ohm-meter. From dc resistance values were converted into conductivity data using the pellet dimensions. The TCR value is determined by using the formula

$$ TCR = \frac{1}{\Delta \sigma \Delta T} \sigma(T_1) \quad \ldots \ldots \quad (1) $$

Where

$$ \Delta \sigma = \sigma(T_1) - \sigma(T_2) $$

and

$$ \Delta T = T_2 - T_1 $$

The variation in D.C. electrical conductivity of pure PANI as a function of temperature measured using 2-probe technique. The temperature range chosen was 323K to 453K. The measurements were recorded during cooling cycle. The resistance of PANI increases with decreasing temperature exhibiting semiconducting behavior. The electrical conductivity $\sigma_{dc}$ was calculated by the formula,

$$ \sigma_{dc} = \frac{A}{Rl} $$

Where $R$ is the resistance of the pallet of the sample, $A$ is the cross-sectional area of the pallet and $l$ is the pallet thickness.
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The image of the apparatus used to determine dc conductivity is as shown in figure-4.8. The apparatus consisting heating chamber, sample holder, digital thermometer, ac variac and Keithely 6514 electrometer.

![Image of DC conductivity measuring apparatus.](image)

Figure-4.8: D C conductivity measuring apparatus.

4.2.2.1 D.C. Conductivity of PANI

The variation in dc conductivity of PANI as function of its temperature represented by the curve shown in figure-4.9. The electrical conductivity almost remains constant for the temperature range (320-380)K. The exponential increment in electrical conductivity of PANI is observed from temperature 320K to 380K in which the polarons, bipolarons and solitons present sufficient energy to hop between various
favorable localized states. The polaron, bipolaron and soliton are the self-localized particles like defects associated with characteristic distortions of the polymer backbone due to lattice coupling [7]. Here the maximum conductivity is $3.6 \times 10^{-2} \text{Sm}^{-1}$ and hence the conductivity is due to hopping [8]. Another factor affecting electrical conductivity is molecular alignment of the chains within the entire system. Thermal curing causes to a better alignment of the polymer chains leads to conjugation length increment and increase in electrical conductivity i.e. molecular rearrangement takes place during the process of heating.

Figure-4.9: Temperature dependent dc conductivity of PANI
4.2.2.2 D.C. Conductivity of PANI-GRA composite

Figure-4.10 shows the variation in dc conductivity as a function of temperature of PANI-GRA nano-composites. For all the composites dc conductivity remains constant for the temperature range (320-380) K. and after the temperature 380k, the exponential increment can be observed. The temperature dependence dc conductivity of all the composites is higher than PANI and is directly proportional to the wt% GRA and the values of $\sigma_{dc}$ varies from 0.0558Sm$^{-1}$ to 0.15Sm$^{-1}$. The magnitude of $\sigma_{dc}$ depends on number of charge carriers as well as their mobility with
temperature. The gradual increment in $\sigma_{dc}$ is due to increment in wt% of GRA particles in PANI. The $\sigma_{dc}$ (T) is dominated by hopping process.

### 4.2.2.3 D.C. Conductivity of PANI-GRA composites treated with L A.

![DC Conductivity Graph](image)

Figure-4.11: Temperature dependent dc conductivity of PANI-GRA composites treated with L A

The curves in figure -4.11 present the variation in dc conductivity as a function of temperature of PANI-GRA nano-composites treated by the surfactant L A. Here also the increment in $\sigma_{dc}$ observed with rise in temperature as well as with increase in GRA wt% in PANI. The 5wt% and 10wt% samples show linear variation up to the temperature range 410K, but for other composites the non-linear behavior begins from initial temperature. The more fluctuations can be seen in $\sigma_{dc}$ (T) in all the
samples after the temperature 410K, it may be due to complex impact of the surfactant LA. The maximum value of $\sigma_{dc}$ is 0.39Sm$^{-1}$ for 25wt%GRA.

### 4.2.2.4 D.C. Conductivity of PANI-GRA composites treated with T X-100

![DC Conductivity Graph](image)

Figure 4.12: Temperature dependent dc conductivity of PANI-GRA composites treated with T X-100

Figure 4.12 shows the variation in dc conductivity as a function of temperature of PANI-GRA nano-composites treated by the surfactant TX-100. The temperature dependent electrical conductivity $\sigma_{dc}$ (T) of 5 and 10w% composites is almost constant. The other three composites of 15, 20 and 25wt% composites exhibit semiconducting behavior i.e. exponential conductivity increment is produced. At temperature 453K, $\sigma_{dc}$ varies from 0.00655Sm$^{-1}$ to 0.877Sm$^{-1}$. Here also, the electrical conductivity of the composites is dominated by hopping. The increase in electrical
conductivity with increase in temperature is due to the complex interaction between PANI, GRA and T X-100. The $\sigma_{dc}$ (T) curves are smooth for these samples relative to other two sets of composites.

In all the samples dc conductivity is dominated by hopping process and depends on percolation behavior of the GRA wt%. The samples possess negative temperature coefficient of resistance (TCR) and the values were estimated by the relation (1) and are as recorded in table-2.

Table-2: TCR of different samples at room temperature

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TCR (K$^{-1}$)</th>
<th>SAMPLE</th>
<th>TCR (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>-0.005266</td>
<td>15wt% GRA with L A</td>
<td>-0.0075</td>
</tr>
<tr>
<td>5wt% GRA</td>
<td>-0.002735</td>
<td>20wt% GRA with L A</td>
<td>-0.00629</td>
</tr>
<tr>
<td>10wt% GRA</td>
<td>-0.00815</td>
<td>25wt% GRA with L A</td>
<td>-0.0132</td>
</tr>
<tr>
<td>15wt% GRA</td>
<td>-0.0105</td>
<td>5wt% GRA with T X-100</td>
<td>-0.0099</td>
</tr>
<tr>
<td>20wt% GRA</td>
<td>-0.0247</td>
<td>10wt% GRA with T X-100</td>
<td>-0.00239</td>
</tr>
<tr>
<td>25wt% GRA</td>
<td>-0.0159</td>
<td>15wt% GRA with T X-100</td>
<td>-0.00095</td>
</tr>
<tr>
<td>5wt% GRA with L A</td>
<td>-0.004372</td>
<td>20wt% GRA with T X-100</td>
<td>-0.00623</td>
</tr>
<tr>
<td>10wt% GRA with L A</td>
<td>-0.01128</td>
<td>25wt% GRA with T X-100</td>
<td>-0.004309</td>
</tr>
</tbody>
</table>
4.3 A C Conductivity

The ac conductivity measurements have been widely used to investigate the nature of ionic motion in ironically conducting materials, since it is assumed that they are responsible for this type of conduction [9]. The ac conductivity as a function of frequency can generally be described as frequency independent conductivity is the sum of dc conductivity $\sigma_{dc}$, and a strongly frequency dependent component $\sigma(\omega)$. The frequency dependent electrical conductivity has three components; one is low frequency dispersion, where the conductivity variation is due charge accumulation magnitude at electrode and electrolyte. The second one is an intermediate frequency plateau, where the conductivity is almost independent of ac frequency and is equal to dc conductivity. Third one is the extended frequency region where the conductivity varies due to electronic hopping.

The frequency dependence of conductivity or universal dynamic response (UDR) of ionic conductivity is related by a simple expression given by Jonscher’s power law

$$\sigma_{ac} = \sigma_o + A\omega^S$$

Where $\sigma_{ac}$ – ac conductivity, $\sigma_o$ – zero frequency conductivity ($\sigma_{dc}$), A is the pre exponential constant, $\omega=2\pi f$ is the angular frequency and S is the power law exponent and $0\leq S\leq 1$ [10, 11].
Theory: If $J$ is the current density and $E$ is the electric field strength, then the ac conductivity is given by

$$\sigma_{ac} = \frac{J}{E} \quad \text{..................(1)}$$

If $D$ is the displacement vector and $\mathcal{E}$ is the complex permittivity of the material, then the electric field

$$E = \frac{D}{\mathcal{E}} \quad \text{.............(2)}$$

For a parallel plate capacitor, if $V$ potential difference across the capacitor plates and $d$ be the distance between the plates and $Q$ be the charge, then current density

$$J = \frac{dQ}{dt} = \frac{d}{dt} \left( \frac{V}{d} \right) = \frac{\mathcal{E} \, dV}{d \, dt}$$

$$J = \frac{\mathcal{E}}{d} \, V j \omega \quad \text{...........(3)}$$

Using equations (2) and (3), equation (1) can be written as

$$\sigma_{ac} = \mathcal{E} j \omega \quad \text{........... (4)}$$
But the relation between complex permittivity $\varepsilon$, real part of dielectric constant $\varepsilon'$ and an imaginary part of dielectric constant $\varepsilon''$ is

$$\varepsilon = (\varepsilon' - j\varepsilon'') \quad \ldots \quad (5)$$

Thus equation (4) can be written as

$$\sigma_{ac} = (\varepsilon' - j\varepsilon'')j\omega$$

$$\sigma_{ac} = j\omega\varepsilon' + \omega\varepsilon'' \quad \ldots \ldots (6)$$

The real part of the equation (6) is

$$\sigma_{ac} = \omega\varepsilon'' \quad \ldots \ldots (7)$$

But $\tan\delta$ is the dielectric loss or dielectric factor which represents the energy dissipation in the dielectric medium and is given by

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad \ldots \ldots (8)$$

Thus equation (7) becomes,

$$\sigma_{ac} = \omega\varepsilon'\tan\delta \quad \ldots \ldots \ldots \ldots \ldots (10)$$
If C is the capacitance of the pellet and A is the cross-sectional area of the pellet, then

\[ \varepsilon' = \frac{Cd}{A} \]  

.......................... (11)

Therefore equation (10) becomes

\[ \sigma_{ac} = \omega \frac{Cd}{A} \tan\delta \]  

......(12)

The equation (12) can be used to calculate ac conductivity [12,13].

The Figure-4.13 is the image of LCR meter Newton Model: PSM -1735 is used to determine the frequency dependent electrical conductivity of materials. The sample of pure PANI and PANI-GRA composite powder samples were pelletized to form of uniform size pellets. The pellet dimensions are 12.06 mm in diameter and about 2.42 mm in thickness. These samples were placed in between the probes in a sample holder and the impedance is measured varying the frequency from 50Hz to 5 MHz at room temperature.
4.3.1 A C Conductivity of PANI

The ac conductivity of pure PANI is shown figure-4.14 where the frequency varies from 50 Hz to 5MHz at room temperature. The ac conductivity remains constant for the frequency range 50 Hz to 20 kHz. This plateau region of the curve corresponds to frequency independent conductivity equal to dc conductivity of the sample. Ionic polarization has an effect in low frequency region where the polarization is slightly changing and $\sigma_{ac}$ becomes less dependent on frequency and dc component of conductivity dominates in this region of frequency. After 20 kHz, dispersion of conductivity is observed and this increase in $\sigma_{ac}$ with increasing frequency is due to electronic polarization and hopping.
Since the space charge is fluctuating across the interface and thus causing intrinsic conduction that means the a.c conductivity dominates at higher frequencies region. The frequency at which electrical conductivity transforms from frequency independent dc conductivity to frequency dependent ac conductivity is called hopping frequency. In this case hopping frequency is 20 kHz and $\sigma_{ac}$ increases from $0.156 \times 10^{-2}$ Sm$^{-1}$ to $4.37 \times 10^{-2}$ Sm$^{-1}$.

![Figure- 4.14: Frequency dependent ac conductivity of pure PANI](image)

### 4.3.2 A C Conductivity of PANI-GRA composites

The variation in frequency dependent electrical conductivity of all five prepared PANI-GRA composites is as shown in figure-4.15(a). The curves of composites with 5wt%, 10wt% and 15Wt% GRA composition attain equal values of $\sigma_{ac}$ for all the range of frequencies.
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The respective individual graphs of these composites are as shown in figures 4.15 (b), (c) and (d). The sudden rise in conductivity is observed for the 20wt% composition and altered abruptly with respect to frequency. The decrease in conductivity is observed for 25wt% composition, this may be due to accumulation of charge carriers in the internal surface of PANI matrix.

Figure- 4.15: Frequency dependent ac conductivity of (a) PANI – GRA composites, (b) 5wt% GRA, (c) 10wt% GRA and (d) 15wt% GRA
4.3.3 A C Conductivity of PANI-GRA composites treated by L A

The figure-4.16 representing the frequency dependent conductivity curves of five different composites treated by L H. Here also the frequency varies from 50Hz to 5MHz at room temperature. The ac conductivity remains constant for the frequency range 50Hz to 100 kHz, for this range polarization is slightly changing and $\sigma_{ac}$ becomes less dependent on frequency. After hopping frequency, dispersion of conductivity is observed and this increase in $\sigma_{ac}$ with increasing frequency is due to electronic polarization and hopping. Again the increase in GRA wt% increases the ac conductivity, the maximum $\sigma_{ac}$ value varies from $6.2 \times 10^{-2}$ Sm$^{-1}$ to $46.48 \times 10^{-2}$ Sm$^{-1}$.

Figure-4.16: Frequency dependent conductivity of PANI-GRA composites treated by L A
4.3.4 A C Conductivity of PANI-GRA composites treated by T X-100

The figure-4.17 representing the frequency dependent conductivity curves of composites treated by surfactant T X-100. Here also the frequency varies from 50Hz to 5MHz at room temperature. Due to small variations in the polarization ac conductivity remains constant for the frequency range 50 Hz to 100 kHz. After hopping frequency, the nonlinear increment in conductivity is observed and this increase in $\sigma_{ac}$ with increasing frequency is due to electronic polarization and hopping. Again the increase in GRA wt% increases the ac conductivity; at highest frequency the dispersion of $\sigma_{ac}$ varies from $2.5 \times 10^{-2}$ Sm$^{-1}$ to $7 \times 10^{-2}$ Sm$^{-1}$. 

![Figure 4.17: Frequency dependent conductivity of PANI-GRA composites treated by T X-100](image-url)
All the samples demonstrate frequency independent behavior at all frequencies lower than hopping frequency and nonlinear response at frequencies higher than hopping frequency. The increase in conductivity is based on electronic hopping, creating energetic free electrons, ions and free radicals.
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References:

7. Safenaz M. Reda1, Sheikha M. Al-Ghannam, Advances in Materials Physics and Chemistry, 2012, 2, 75-81