Dielectric and ac conductivity studies of Titania/poly (vinyl-pyrrolidone) nanocomposites

Titania/poly (vinyl-pyrrolidone) nanocomposites with varying concentrations of TiO$_2$ were prepared by the non hydrolytic sol-gel route. The dielectric response and the ac electrical conductivity of the samples were investigated for the frequency range 100Hz -2MHz at room temperature. The dielectric studies show low values for dielectric constant and loss at high frequencies. Both dielectric constant and dielectric loss decreased with increasing wt% of TiO$_2$. AC conductivity obeyed the Jonscher’s power law, which decreased with increasing wt% of TiO$_2$. The conductivity values are found to be of the order of $10^{-7}$-$10^{-8}$ S/cm for the nanocomposites. In addition, the experimental dielectric data have been analyzed by considering electric modulus formalism. The Cole-Cole parameters were calculated and the semi arcs observed in the plots indicate a single relaxation process. The complex impedance plots indicate the presence of ionic contribution to the electrical conductivity of these materials.
4.1. Introduction

Impedance Spectroscopy is a general term that includes the small signal measurement of the linear electrical response of a material of interest and the subsequent analysis of the response to yield useful information about the physicochemical properties of the system. With the incorporation of nanosized inorganic particles into suitable polymer matrices, nanohybrid materials are of high interest since they can exhibit unique physical and chemical properties, which greatly differ from those of their individual constituents [1]. Low frequency conductivity and dielectric relaxation measurements especially have proven to be valuable in giving additional information on the conduction mechanism as the dc conductivity measurement alone does not provide. The relaxation of an electric field in a charge carrier system is attributable to the charge hopping of mobile carriers, which can lead to both short range ac conductivity and long range dc conductivity.

AC conductivity is an immensely important parameter, used to characterize the dielectric properties of materials. Measurement of AC conductivity of semiconductors has been extensively used to understand the transport mechanism in the materials [2-4] and to investigate the nature of defect centers, since they play a major role in the conduction process. The amorphous structure of PVP also provides a low scattering loss, which makes it as an ideal polymer for composite
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materials for different applications. PVP is easily soluble in water, so it is preferred to avoid phase separation in the reactions [5-7]. In this work we report the results of frequency dependent AC and dielectric response of TiO₂/PVP hybrids at various concentrations of TiO₂. We have analyzed the experimental data by means of two different formalism complex permittivity ε* and complex electric modulus M*. Transformation from one formalism to another may help to study particular aspects of the electrical and dielectric behavior.

4.2. Experimental

Samples containing varying concentrations of TiO₂ doped samples were prepared by sol-gel route as explained in Chapter 2. The compositions of the prepared samples are summarized in Table 4.1.

Table 4.1: Compositions of the prepared samples

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>TiO₂ (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25%</td>
</tr>
<tr>
<td>B</td>
<td>50%</td>
</tr>
<tr>
<td>C</td>
<td>75%</td>
</tr>
</tbody>
</table>
Impedance measurements were performed using the complex impedance method. The AC conductivity and dielectric measurements were done using the Agilent E4980A over the frequency range of 100Hz-2MHz. To measure the AC response, samples were prepared as 1 cm diameter pellets by pressing the powder under a hydraulic pressure of 10,000 psi and then applying conducting silver paste to form the electrodes in contact with the two circular faces. The thickness of the pellets was measured by using a micrometer screw gauge. The cylindrical samples had a diameter of 10mm and a thickness of typically 1mm. The data acquisition was done over frequency ranges from 100 Hz to 2 MHz. The pellets were sandwiched between the two stainless disc electrodes of a sample holder and connected to the impedance spectrometer to measure their conductivities.

4.3. Results and discussion

4.3.1. Dielectric study of nanocomposites

The dielectric permittivity of a material is usually given relative to that of free space, and is known as relative permittivity ($\varepsilon_r$), or dielectric constant (k). The dielectric response of the nanoparticle composites at various frequencies is described in terms of the complex permittivity ($\varepsilon^*$) which is represented by its real and imaginary parts [8, 9]

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$
where $\varepsilon'$ is the dielectric permittivity and $\varepsilon''$ is the dielectric loss.

The complex permittivity formalism has been used to describe the electrical and dielectric properties. The dielectric permittivity which is the real part of the complex is calculated at the various frequencies by using the measured capacitance values from the relation [10, 11]

$$\varepsilon' = \frac{C_p d}{\varepsilon_o A}$$

where $C_p$ is the parallel equivalent static capacitance, $d$ is the thickness of the sample, $A$ is the surface area of the sample in cm$^2$ and $\varepsilon_o$ is the electric permittivity of free space ($\varepsilon_o = 8.85 \times 10^{-14}$ F/cm).

The imaginary part of the complex permittivity, the dielectric loss ($\varepsilon''$), at the various frequencies is calculated using the measured conductance values from the relation,

$$\varepsilon'' = \frac{\sigma_{ac}}{\varepsilon_o \omega}$$

where $\sigma_{ac}$ is the conductance in Siemens per centimetre and $\omega = 2\pi f$, $f$ being the frequency in hertz.
4.3.1.1. Frequency dependence of dielectric permittivity

Figure 4.1 presents the variation of real part of dielectric constant ($\varepsilon'$) as a function of frequency ($\omega$) at room temperature for different samples whose compositions are given in Table 4.1. We have also tabulated dielectric constants ($\varepsilon'$) at certain selected frequencies along with their average taken over these frequencies for different samples (Table 4.2).

![Figure 4.1: Variation of real part of dielectric constant with log f](image-url)
Table 4.2: Dielectric constant of the samples at selected frequencies

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dielectric constant (ε')</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f = 10 kHz</td>
</tr>
<tr>
<td>A</td>
<td>3.22</td>
</tr>
<tr>
<td>B</td>
<td>2.61</td>
</tr>
<tr>
<td>C</td>
<td>1.77</td>
</tr>
</tbody>
</table>

It is apparent from the figure that the dielectric constant (ε’) decreases with the frequency of applied AC signal. Similar behavior is also observed in a number of polymers like PVA, PMMA etc., verifying the fact that for polar materials, the value of ε’ is high for low frequency range and begins to drop as frequency increases [12-14]. This can be appropriately explained on the basis of the electrode effect and interfacial effect of the sample, i.e. charge carriers being blocked at the electrodes. This may be attributed to the tendency of dipoles in the samples to orient themselves in the direction of applied field in the low frequency range. When the frequency is increased the dipoles cannot rotate sufficiently rapidly, so that their oscillations lag behind those of the field. As the frequency is further raised, the dipole will be completely unable to follow the field and the orientation polarization ceases, so ε’ decreases and approaches a constant value at high frequencies due to the interfacial polarization only [15]. Also, as
depicted in the figure, the sample having larger concentration of TiO₂ has lower dielectric constant. It is likely that as the concentration of TiO₂ increases; the distance between the TiO₂ nanoparticles is reduced, thereby increasing the interaction between them [16]. Such an increase in interaction among the nanoparticles along with a reduction in polymer content could possibly reduce the dipole-dipole interaction, leading to a reduction in the dielectric constant.

4.3.1.2. Frequency dependence of dielectric loss

The variation of imaginary part of dielectric constant (dielectric loss) \( \varepsilon'' \) with frequency for TiO₂/PVP nanocomposites at different

\[ 2.5 \quad 3.0 \quad 3.5 \quad 4.0 \quad 4.5 \quad 5.0 \quad 5.5 \quad 6.0 \quad 6.5 \]

\[ 0 \quad 1 \quad 2 \quad 3 \quad 4 \]

Figure 4.2: Variation of imaginary part of dielectric constant with log \( f \)
concentration of TiO$_2$ nanoparticles is shown in Figure 4.2. It is clear from this graph that dielectric loss decreases with an increase in frequency. The decrease of $\varepsilon''$ with frequency can be attributed to the fact that, at low frequencies, the value of $\varepsilon''$ is due to the migration of ions in the material. At moderate frequencies $\varepsilon''$ is due to the contribution of ions jump, conduction loss of ions migration and ions polarization loss. At high frequencies ion vibrations may be the only source of dielectric loss and so $\varepsilon''$ has the minimum value [15]. The large value of $\varepsilon''$ at low frequency range is also due to the motion of free charge carrier within the material. As a result of it, power law dispersion in $\varepsilon''$ is observed and it does not reveal any peak in the measured frequency range [17].

4.3.1.3. Frequency dependence of loss tangent

The loss tangent (tan $\delta$) can be expressed as follows [18, 19]:

$$\tan \delta = \frac{\varepsilon'}{\varepsilon}$$

Variation of the loss tangent with respect to logarithmic frequency is shown in Figure 4.3 for different TiO$_2$ concentrations at room temperature. The loss tangent (tan $\delta$) is the ratio of the loss factor to the relative permittivity, and is a measure of the ratio of the electric energy lost to the energy stored in a periodic field. From the figure it is clear
that $\tan \delta$ decreases exponentially with increasing the frequency following the relation [20]

$$\tan \delta = \frac{4\prod \sigma_{ac}}{\omega \varepsilon}$$

![Figure 4.3: Variation of loss tangent with log f](image)

The decrease of $\tan \delta$ with $f$ could be accounted for using Koops's model. In the low frequency region which corresponds to high resistivity (due to grain boundaries), more energy is required for electron exchange. Thus the energy loss is high. In the high frequency range which corresponds to low resistivity (due to the grains) a small energy is needed for electron transfer and hence the energy loss is
small. The large dielectric loss at lower frequency is due to free charge build up at the interface between the electrolyte and the electrodes [21]. At higher frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The polarization due to the charge accumulation decreases, leading to the decrease in the value of the dielectric loss. It is clear that \( \tan \delta \) is in close relation with the conductivity. The increase of the conductivity \( \sigma \) is accompanied by an increase of the eddy current which in turn increases the energy loss \( \tan \delta \).

4.3.2. Frequency dependent conductivity studies

Figure 4.4 shows the variation of AC conductivity with frequency. The plots of the conductivity as a function of frequency can be divided into a low frequency dispersion region and an almost frequency independent plateau region at high frequency [22]. A plateau region means it is equivalent to the true conductivity value for that particular sample as ions have time to migrate over large distance in polymer chains. The dispersion region is referring to the electrode being polarized as charge accumulates due to the slow periodic reversal of the electric field at low frequency.

The low-frequency dispersion may be due to the interfacial impedance or space charge polarization. The conductivity in this low-frequency region is slightly constant owing to the transport of charge
occurring at an infinite path. As the frequency decreases, more and more charge is accumulated at the electrode and electrode interface, which will lead to a decrease in the number of mobile ions and eventually a drop in conductivity at low frequency. At the high-frequency region, the conductivity increases with frequency due to the mobility of charge carriers and the hopping of ions from the infinite cluster. As a result, the ion exchange process occurs effectively in the high-frequency region. The conductivity values show weak frequency dependence at low frequencies but show strong dependence at high frequencies. The conductivity values are found to be in the range $10^{-7}$-$10^{-8}$ S/cm. The conductivity decreases steeply with increasing wt% of TiO$_2$ of the composites. This could be due to an increase in the disorderliness of the composite with increasing amount of TiO$_2$.

DC conductivity ($\sigma_{dc}$) was extracted from the AC conductivity data. It can be seen from the figure that at low frequencies the conductivity is constant, which corresponds to the DC conductivity.
The AC conductivity $\sigma_{ac}(\omega)$ increases as a function of applied frequency according to the relation [23,24]

$$\sigma_{ac}(\omega) = \sigma_{tot}(\omega) - \sigma_{dc} = A\omega^s$$

where $\omega$ is the angular frequency, $\sigma_{tot}(\omega)$ is the measured total electrical conductivity, $\sigma_{dc}$ is the DC electrical conductivity, $s$ is the frequency exponent ($s < 1$) and $A$ is constant, $s$ and $A$ are material and temperature dependent. Jonscher has applied this equation to many materials and analyzed the ac conductivity behavior. Since this equation is accepted universally for considering the sample conductivity, hopping charges, frequency dependence of conductivity

![Figure 4.4: Variation of ac conductivity with log f](image_url)
etc., it is also called universal behavior. The values $\sigma_{dc}$, $s$ and $A$ popularly known as power-law parameters are tabulated in Table 4.3. The values of $s$ are found to increase with concentration of samples while the values of $A$ are decreasing.

**Table 4.3: Power-law parameters of the samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{dc}$</th>
<th>$s$</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.21 E-09</td>
<td>0.68</td>
<td>1.99 E-12</td>
</tr>
<tr>
<td>B</td>
<td>1.77 E-09</td>
<td>0.71</td>
<td>0.78 E-12</td>
</tr>
<tr>
<td>C</td>
<td>2.31 E-10</td>
<td>0.86</td>
<td>0.32 E-12</td>
</tr>
</tbody>
</table>

4.3.3. Dielectric modulus studies

A further analysis of the dielectric behaviour would be successfully achieved by using the formulation of dielectric moduli, which suppresses the effects of the electrode polarization. The electric modulus formalism is introduced by McCrum *et al.* [25] and it is used to study electrical relaxation phenomena in many samples [26–28].

The electric modulus is defined by the equation (4.1)

$$M' = \frac{1}{\varepsilon}, \varepsilon' = \varepsilon - i\varepsilon, M' = M' - iM''$$

$$M' = \frac{\varepsilon'}{\varepsilon + \varepsilon}, M'' = \frac{\varepsilon'}{\varepsilon + \varepsilon}$$

(4.1)
where \( M' \) and \( M'' \) are the real and the imaginary part of electric modulus respectively, and \( \varepsilon' \) and \( \varepsilon'' \) are the real and the imaginary part of dielectric permittivity. Figure 4.5(a) and (b) shows the calculated values of real and imaginary parts of electrical modulus for the nanocomposites for different concentration of TiO\(_2\). The low value of \( M' \) indicates the removal of electrode polarization \([29–31]\). The peak appears to shift towards higher frequency as the dopant concentration increases. In the figures, \( M' \) and \( M'' \) show an increase at the high frequency end, but well-defined dispersion peaks are not observed. The curve peaks at higher frequencies may be attributed to the bulk effect \([32]\). However, both the \( M' \) and \( M'' \) will decrease towards low frequencies, showing the fact that the electrode polarization phenomena make a negligible contribution. The plot also gives a long tail at low frequencies. The long tail is probably the result of the large capacitance associated with the electrode \([33]\). The possible presence of peaks in the modulus formalism at higher frequencies for all the polymer systems indicates that the samples are ionic conductors \([34]\).
Figure 4.5: (a) Variation of real part of modulus, $M'$ with log $f$
(b) Variation of imaginary part of modulus, $M''$ with log $f$
4.3.4. Complex impedance analysis

The frequency dependence of real part of impedance is shown in Figure 4.6.

![Figure 4.6: Variation of real part of impedance with log f](image)

From the figure it is clear that for all the three samples values of real part of the impedance are found to be decreasing as frequency increases and the rate of change is almost a constant within the range 10 kHz-2MHz. At high frequencies, it is commonly observed that as the AC coupling increases the impedance falls off due to the electrical nature of the specimen. Also, it can be seen that as TiO$_2$ concentration
increases the real part of the impedance increases and then rapidly decreases with an increase in frequency.

Figure 4.7 shows the variation of imaginary part of impedance with frequency. It can be seen that for all the three samples value of imaginary part of the impedance are found to be decreasing with increasing frequency and the rate of change is almost a constant within the range 10 kHz-2MHz. As the TiO$_2$ concentration increases, the imaginary part of the impedance also increases at the low frequency regime while they merge to a very low value at high frequencies.

![Figure 4.7: Variation of imaginary part of impedance with log f](image-url)
Figure 4.8 depicts the representation of real and imaginary part of the impedance value which interprets the Cole-Cole plot and derives the value of $R_b$, $C_b$ and $\tau$ known as Cole-Cole parameters [eqns (4.2)-(4.5)]. Single semicircles are observed for all the samples which can be modelled by an equivalent parallel RC circuit. The peaks of the semicircles are used to determine the relaxation time ($\tau$). The low frequency intercept made by the semicircle on the real impedance axis can be used to determine the dc (frequency independent) resistance of the sample. The values of $R_b$, $C_b$ and $\tau$ are tabulated in Table 4.4.

![Complex impedance plot](image_url)
In the complex impedance diagrams are shown in Figure 4.8, the arcs formed are not exact semicircles. The depressed semicircles with the centers below the real impedance axis are fit. The relaxation time $\tau$ is not single valued but varies with the variations in the concentration of TiO$_2$. The angle by which such a semicircular arc is depressed below the real axis is related to the width of the relaxation time distribution. This only confirms the argument that the relaxations observed are non-Debye in character. The inverse of the frequency corresponding to the maximum of the imaginary component of impedance indicates relaxation time $\tau$ and the intercept indicates resistance of the materials. The grain and grain boundary effects could not be separated in the present case, as grain boundary conduction and relaxation effects are negligible in comparison with bulk effects. We can represent all samples with a single parallel resistance and capacitance circuit. The Cole–Cole curves in both the cases start at the origin and hence it can be inferred that the series resistance in the equivalent circuit, in this case, is inconsequential.

It is derived from an equivalent circuit representing the dielectric response of the sample, consisting of an RC element. This ‘RC’ element is characterized by a relaxation time, $\tau$, which is a product of $R$ and $C$.

$$\omega_{\text{max}} R C = 1$$

$$\omega_{\text{max}} = \frac{1}{2\pi \tau}.$$  

(4.2)  

(4.3)
\[ C_b = \frac{1}{2\pi f_p R_b} \]  
\[ \tau = R_b C_b = \frac{1}{2\pi f_p} \]  

where, \( R_b \) is the bulk resistance, \( C_b \) the bulk capacitance, \( f_p \) the peak frequency and \( \tau \) the relaxation time. The values of \( R_b, C_b \) and \( \tau \) are known as Cole-Cole parameters. We see that relaxation time increases with increasing wt % of TiO\(_2\) in the prepared samples. Since relaxation is related to charge transport by hopping mechanism, an increase in relaxation time indicates the increase in hopping length due to stretching effect of the TiO\(_2\) added to polymer, with a consequent reduction in conductivity as seen in Figure 4.4. It can be seen that \( R_b \) and \( \tau \) increases with increase in concentration of the samples while the value of \( C_b \) decreases with increase in the concentration of the samples.

### Table 4.4: Cole-Cole parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>( R_b (\Omega) )</th>
<th>( C_b (\text{pF}) )</th>
<th>( \tau (\text{sec}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( 9.09 \times 10^7 )</td>
<td>2.18</td>
<td>( 1.99 \times 10^{-4} )</td>
</tr>
<tr>
<td>B</td>
<td>( 1.58 \times 10^8 )</td>
<td>1.67</td>
<td>( 2.65 \times 10^{-4} )</td>
</tr>
<tr>
<td>C</td>
<td>( 2.06 \times 10^8 )</td>
<td>1.54</td>
<td>( 3.18 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

### 4.4. Conclusions

The dielectric and low frequency ac conduction studies of TiO\(_2\)/PVP nanocomposites have been carried out with the aid of complex/dielectric spectroscopic investigations. This includes measurements involving the
variation of real and imaginary part of dielectric constant as well as conductivity with frequency. The values of dielectric constant and loss show frequency dispersions at low frequencies and show low values at high frequencies. The characteristics of low dielectric constant and dielectric loss with high frequency for the samples suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is of vital importance for various nonlinear optical materials and their applications. The conductivity curves of polymer nanocomposites show an increasing tendency with increase in frequency and found to obey Jonscher’s power law. The conductivity values are found to be of the order of $10^{-7}$-$10^{-8}$ S/cm. The power law parameters were calculated and the values of $s$ are found to increase with concentration of TiO$_2$ doped samples while the values of $A$ are decreasing. Single semiarcs are observed in the complex impedance plots of the samples and these semiarcs reveal a single relaxation process. The spike observed at low frequencies indicates the presence of an ionic contribution to the electrical conductivity of these materials. On comparison of the results obtained, we can conclude that these materials could be found to be more suitable for their potential applications in the progress of battery materials and ionic devices.
References


