Studies on Dielectric spectroscopy of titanium dioxide doped polyaniline (TiO$_2$/PANI) composite

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Abstract: The dielectric behaviour of PANI & TiO$_2$/PANI composite has been investigated in the frequency range 1kHz to 1MHz at room temperature. Dielectric measurements revealed about the strong interactions between PANI and TiO$_2$ particles causing a beneficial effect on stability of the composites. The parameters dielectric constant, dielectric loss and dissipation factor have been calculated. The frequency dependence of these parameters has been qualitatively explained on the basis of hopping of electrons.

Key Words: TiO$_2$/PANI, Dielectric, dielectric loss, dissipation factor

1. Introduction:
Research on polymer composite materials integrates the science and technology of polymeric materials. Polymers containing metal oxides constitutes polymer composites are well studied for its properties [1-3]. Conducting polymers have a variety of applications in the Industrial, Scientific and Medical (ISM) fields. Applications like anticorrosion, static coating electromagnetic shielding etc comes under first generation. Second Generation of electric polymers have applications such as transistors, LEDs, solar cells batteries etc. Controlled conductivity, high temperature resistance, low cost and ease of bulk preparation make these materials attractive in the engineering and scientific world [1-5]. The features of conducting polymers such as reversibility, availability in film form and good environmental stability enhance their potential use for practical applications. One of the most widely studied conducting polymers; Polyaniline can be obtained chemical or electrochemical route. Polymeric materials have become an area of increasing interest in research because of the fact that these materials have great potential for solid state devices [4-6]. Polyaniline has received much attention because of its unique reversible proton doping, high electrical conductivity, ease of preparation and cost effective. The demand of high quality materials for electromagnetic compatibility is alarmingly increasing [7, 8]. Metal oxides doped polymer composites have attracted a great deal of interest from researchers, because they frequently exhibit unexpected hybrid properties synergistically derived from both components. TiO$_2$ is one of the examples of oxide material, which is known for functional oxide materials with prominent applications [6-11]. Conducting PANI containing such metal oxide materials called PANI composite with variable compositions my lead to desirable properties. These materials are especially important owing to their bridging role between the worlds of conducting polymers [12-15]. However, in this paper we report the parameters dielectric constant, dielectric loss and dissipation factor have been calculated. The frequency dependence of these parameters has been qualitatively explained on the basis of hopping of electrons.

2. Results and Discussion
The dielectric properties of materials, namely permittivity, are typically measured as a function of frequency and are called dielectric/ impedance spectroscopy. The permittivity values show the interaction of an external field with the electric dipole moment of the sample (Griffiths 1999, Baker-Jarvis, et al. 2010, Yaw 2012). Dielectric measurement is an important tool to understand the material behaviour especially at high frequencies because it can provide the electrical or magnetic characteristics of the materials, which is a critical parameter required to implement the material in many applications.

Measurement of dielectric properties involves measurements of the complex relative permittivity ($\varepsilon'$), which consists of a real part and an imaginary part. The real part of the complex permittivity, also known as the dielectric constant is a measure of the amount of energy from an external electrical field stored in the material. The imaginary part is zero for lossless materials and is also known as loss factor. It is a measure of the amount of energy loss from the material due to an external electric field. The dielectric parameters were evaluated by measuring equivalent parallel capacitance $C_p$ and dissipation factor $\tan\delta$ by using the equation,

$$\varepsilon' = \frac{C_p}{\varepsilon_0}$$

or

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

The term $\tan\delta$ is called loss tangent and it represents the ratio of the imaginary part to the real part of the complex permittivity. Where $\varepsilon_0$ is the geometrical capacitance of vacuum of the same dimensions as the sample. $A$ and $t$ are the area and thickness of the sample respectively and $f$ the measuring frequency. $C_p$ is the capacitance measured, $\varepsilon'$ the real dielectric constant and $\varepsilon''$ the imaginary dielectric constant.
2.1 Dielectric Constant:
Figure-1 shows the variation of dielectric constant ($\varepsilon'$) as a function of frequency for polyaniline. The dielectric constant decreases as frequency increased over measured range 1KHz-1MHz. Figure-2 is the frequency dependent PANI-TiO$_2$ composite with different content of TiO$_2$ in the polyaniline. It is clear from the plot that, the dielectric constant is dependent of frequency and content of TiO$_2$ in the polymer. In all the cases it is observed that, the dielectric constant is quite high at low frequency and decreases with increase in applied frequency. The observed behavior may be due to the Debye relaxation mechanism taking place in these materials. Figure-3 represents the variation of $\varepsilon'$ as a function of wt% of TiO$_2$ at room temperature and at two different frequencies. It is observed that the values of dielectric constant decreases as the content of TiO$_2$ increased in the polyaniline (10%, 20%, 30%, 40% & 50%). The observed behavior may be due to the distribution of TiO$_2$ particles in the polyaniline are responsible for the decrease in the dielectric constant. All these results go in accordance with the conductivity behavior.
2.2 Dielectric loss:
Figure-4 shows the variation of dielectric loss as a function of frequency for PANI and PANI/TiO₂ composites. For polyaniline, the imaginary part of the dielectric constant has value of about 15.1 at 1KHz and decreases with increasing frequency, reaching the value of about 1.61 at 1MHz. It is observed that, dielectric loss is dependent of composition i.e, the value of e'' is lower for composites as compared to polyaniline in low frequency & higher frequency range. Figure-5 is the variation of dielectric loss (ε'') as function of composition at 1KHz and 1MHz frequency. It is observed that the values of dielectric loss decreases as the content of TiO₂ increased in the polyaniline (10%, 20%, 30%, 40% & 50%). The observed behavior may be due to the distribution of TiO₂ particles in the polyaniline are responsible for the decrease in the dielectric constant.

![Figure-4: Dielectric loss of PANI & PANI/TiO₂](image1)

![Figure-5: Dielectric loss as function of composition](image2)

2.3 Dissipation factor:
Figure-6 shows the variation of dielectric loss tangent (tanδ) as a function of frequency for PANI and PANI/TiO₂ composites. The loss tangent for polyaniline has a value of 0.41 at 1KHz, which decreases with increasing frequency, reaching a value of 0.058 at 1 MHz. It is observed from the figure that, high dielectric loss at low frequency in all the composites may be attributed to the high resistivity caused by grain boundary. Figure-7 shows the variation of dielectric loss tangent (tanδ) as a function of composition at 1 KHz & 1 MHz frequency. It is observed form plots that, the value of tanδ decreases as frequency increased and compared to polyaniline, the composites 10%, 20%, 30%, 40% & 50% have lower value of tanδ. The lower value of tanδ responsible for distribution of TiO₂ in polyaniline. The dependence of tanδ with frequency can be classified into two stages. In first stage, the value of tanδ decreases with increasing frequency within the frequency range 10 KHz to 200 KHz. In second stage, from 300 KHz to 1 MHz frequency, the value of tanδ is almost constant in the order 10⁻². Previously reported that i.e., the values of tanδ of polyaniline found to be 0.24 at room temperature for 1 KHz and 0.0305 for 500 KHz [16].
3. Conclusion:
Dielectric characterization demonstrated that TiO$_2$ particles exhibit a strong effect on the dielectric properties of resultant PANI/ TiO$_2$ composites. The dielectric constant is attributed to the formation of a better charge transport network in the relatively insulating polyaniline matrix. Dielectric measurements revealed about the strong interactions between PANI and TiO$_2$ particles causing a beneficial effect on stability of the composites. Also considered to be improved due to the addition of TiO$_2$, which can improve the formation of a more efficient network for charge transport mechanism in the base polyaniline matrix.

4. References:


