Influence of prepared chloropenta amine cobalt (III) chloride nanoparticles on the dielectric properties of PVA Film

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ABSTRACT

Chloropenta amine Cobalt (III) Chloride [Co(NH$_2$)$_5$Cl]Cl$_2$ was prepared then characterized XRD. The obtained results indicated the formation of Orthorhombic [Co(NH$_2$)$_5$Cl]Cl$_2$-nano particles of $\approx$ 28.75 nm size. Polymeric films based on polyvinyl alcohol PVA doped with Chloropenta amine Cobalt (III) Chloride [Co(NH$_2$)$_5$Cl]Cl$_2$ at different weight percent ratios were prepared using the solvent cast technique. The structural properties of these polymeric films are examined by SEM. The complexation of the additive with the polymer was confirmed by SEM studies. The AC electrical properties have been measured by LCR meter with frequencies range (100 - 5*10$^5$) Hz.

It was observed that, the dielectric behaviors of polymer matrix strongly depend on frequency and additive content. The dielectric behaviors such as: dielectric constant ($\varepsilon$) and dielectric loss ($\delta$) increases with increase in [Co(NH$_2$)$_5$Cl]Cl$_2$ nano particle concentration, but decreases with increase in frequency. AC conductivity ($\sigma_{ac}$) of PVA/[Co(NH$_2$)$_5$Cl]Cl$_2$ nano composites increases with increasing frequency following the universal dielectric response law.

INTRODUCTION

Studies of the dielectric properties of polymers have increased importance because it provide an understanding to movement of molecular chains and its applications in electrical and electronic engineering (Elimat, Z.M et al., 2008).

Polymers have received much experimental attention in an attempt to synthesize organic polymers alternative to conventional inorganic materials, due to their unique properties, such as low density, ability to form intricate shapes, versatile electrical properties and low manufacturing cost. The electrical resistivity of polymers such as polyvinyl alcohol, polyvinyl chloride, polystyrene and polyethylene would normally be classified as insulators possessing specific resistivities of the order $10^{15}$ or greater (OmedGh. Abdullah, et al., 2012).

Polymeric materials have special interest because, in combination with suitable metal salts, they give complexes which are useful for the development of advanced high energy electrochemical devices, e.g. batteries, fuel cells, electrochemical display devices, and photo electrochemical cells with ease of fabrication into desirable sizes (Abdelrazek, E.M., et al., 2010). The electrical conductivity of the selected polymer can be controllably modified owing to the type of the filler used, its concentration and the way in which it penetrates and interacts with the chains of the polymer. Detailed studies of polymer filled with different filling levels of a certain filler allow the possibility of choice of the desired properties (OmedGh. Abdullah, et al., 2012). The composites not only combine the advantageous properties of dopant and polymers but also exhibit many new properties that single-phase materials do not have (OmedGh. Abdullah, et al., 2012).

Polymers are used in an amazing number of applications. More recently, significant developments have occurred in the area of flexible electronic devices based on the useful piezoelectric, semiconducting, optical and electro-optical properties seen in some polymers (Donald, R., et al., 2010). Development of dielectric materials for applications in communication systems such as substrates, cellular phone, etc. has been rapidly progressing in the past few years (Archanj Nigrawal, Navin Chand, 2013).

Polyvinyl alcohol (PVA) is a semi crystalline polymer whose hydroxyl groups produce inter-
intra-molecular hydrogen bonding (Song fe Song, ByoungChul Kim, 2001). Over recent years polyvinyl alcohol (PVA) polymers have attracted attention due to their variety of applications. PVA is a potential material having high dielectric strength, good charges to rage capacity and do pant-dependent electrical and optical properties. It has carbon chain backbone with hydroxyl groups attached to methane carbons/these OH groups can be a source of hydrogen bonding and hence assist the formation of polymer complexes (Abdelaziz, M., Magdy M. Ghannam, 2010).

Coordination compounds or metal complex are metal ions surrounded by ligands. Ligands are either anions or molecules that can donate electrons into the d-orbitals of the metal ion and form a bond. An example of common ligands is chloride ion. The metal ions that form coordination compounds are from a group of metals known as transition metals. These metals have more than one oxidation state. This property allows the transition metals to act as Lewis acids (Gary Wulfsberg, 2000). The metal complex used in this paper is Chloropentammine cobalt (III) chloride. It decomposes upon heating above 150 °C. Its solubility is 0.4 g per 100 ml at 25 °C (Young Tyree S. Jr., 1967).

In this paper an effort has been made to study the effect of addition of [Co(NH₃)₅Cl]Cl₂ on electrical and optical properties. It has been analyzed and discussed.

Experimental work:
Preparation of chloropenta amine cobalt (III) chloride [Co(NH₃)₅Cl]Cl₂:
Chloropenta amine Cobalt (III) Chloride [Co(NH₃)₅Cl]Cl₂ was prepared by the procedure reported in literature according the chemical reaction equation (1) (Theodore Brown et al., 2002). All chemicals used in Preparation of chloropenta amine cobalt (III) chloride were purchased from Sigma – Aldrich.

\[
2\text{CoCl}_2\cdot6\text{H}_2\text{O(s)}+2\text{NH}_3\text{Cl(s)}+8\text{NH}_3\text{(aq)}+\text{H}_2\text{O}_2\text{(aq)}+3\text{H}_2\text{O}_2\text{(l)}\rightarrow 2[\text{Co(NH}_3)_5\text{Cl}]\text{Cl}_2\text{(s)}+\frac{1}{2}\text{O}_2\text{(g)}
\]

Sample preparation:
Polyvinyl alcohol (PVA) with molecular weight (30,000-70,000) was purchased from Aldrich. The PVA/ [Co(NH₃)₅Cl]Cl₂ composites films were fabricated by the solvent casting technique. At first a PVASolution was prepared by adding distilled water to solid PVA (–C₆H₄O₆) then stirred by magnetic stirrer for 2 h. under 70°C. The necessary weight fractions of [Co(NH₃)₅Cl]Cl₂ were first dispersed in distilled water with a magnetic stirrer for 1 h and then added gradually into the polymeric emulsion with continuous stirring and kept under string for 1 h.

Finally, the solution was poured onto cleaned Petri dishes and allowed to evaporate slowly at room temperature for a week. After drying, the films were peeled from Petri dishes and kept in vacuum desiccators until use. The thickness of the obtained films was in the range of ≈120–150 µm.

Theory:
The electrical measurement (dielectric permittivity (\(\varepsilon\)), dielectric loss (\(\varepsilon^\prime\)) and conductivity (\(\sigma_{ac}\)) for PVA/(0,3,6 and 9) wt% [Co(NH₃)₅Cl]Cl₂ composites films were obtained at frequency range (100- 5*10⁵) Hz. By LCR meter type HIOKI 3532-50 LCR HI TESTER, the values of the equivalent parallel capacitance \(C_p\) and parallel equivalent resistance \(R_p\) were recorded at the selected frequency range f. dielectric parameters have been calculated using the following equations (Ravikiran, Y.T., et al., 2006):

\[
\varepsilon = \frac{C_p}{\varepsilon_0}
\]

\[
\varepsilon = \frac{1}{\alpha R_p C_p}
\]

Where \((C_p= 0.0885\frac{\Lambda}{\pi})\) pf is the geometrical capacitance of vacuum of the same dimensions as that of the sample; A and d are the area and thickness of the sample, respectively; \(C_p\) is the capacitance measured in pf; and \(\alpha=2\pi f\).

The dissipated power in the insulator is represented by the existence of alternating potential as a function of the alternating conductivity \(\sigma_{ac}\) can be calculated according to the following equation (Muheisin, A., 2009):

\[
\sigma_{ac}= \alpha \varepsilon^\prime \varepsilon_0
\]

\(\sigma_{ac}\) is a measurement for the generated temperature in the insulating material resulting from the rotation of the dipoles in their positions, (or the vibration of the charges) as a result of the alternating of the field (Muheisin, A., 2009).

\(\varepsilon\) and \(\varepsilon^\prime\) are the real and the imaginary parts of the complex dielectric constant (Ravikiran, Y.T., et al., 2006).

\[
\varepsilon = \varepsilon(f) + i\varepsilon^\prime(f)
\]

RESULTS AND DISCUSSION

X-ray diffraction (XRD):
A typical XRD pattern for [Co(NH₃)₅Cl]Cl₂ is shown in Figure 1. It can be seen that many sharp peaks were observed in the X-ray profile. The crystalline nature of synthesized [Co(NH₃)₅Cl]Cl₂ was observed by the various sharp crystalline peaks in the XRD pattern. It shows diffraction peaks at 15.8313°, 25.6011°, 32.6249° and 34.8279° corresponding to the (011), (211), (122) and (040) planes [Co(NH₃)₅Cl]Cl₂ which could be indexed to Orthorhombic structure which were consistent with the literature data of Materials...
The average particle size can be calculated using the first sphere approximation of Debye–Scherrer formula (Sheha, E., et al., 2011):

\[ D = \frac{0.9 \lambda}{B \cos \theta} \]  

(6)

where \( D \) is the average diameter of the crystals, \( \lambda \) is the wavelength of X-ray radiation, and \( B \) is the full width at half maximum intensity of the peak (FWHM). The obtained particle size of \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) which is around 28.75 nm. The structural parameter such as diffraction angle \( 2\theta \) (deg.), interplanar d (\( \text{A}^° \)), relative intensity \( (I/I_0) \) and full width at half maximum FWHM (deg.) are presented in table 1.

Table 1: Diffraction angle \( 2\theta \) (deg.), interplaner d (\( \text{A}^° \)), relative intensity \( (I/I_0) \) and full width at half maximum FWHM (deg.).

<table>
<thead>
<tr>
<th>Material</th>
<th>( 2\theta ) (deg.)</th>
<th>d (( \text{A}^° ))</th>
<th>( I/I_0 )</th>
<th>FWHM (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2)</td>
<td>15.7313</td>
<td>5.59343</td>
<td>100</td>
<td>0.2763</td>
</tr>
<tr>
<td></td>
<td>25.6011</td>
<td>3.47674</td>
<td>60</td>
<td>0.2046</td>
</tr>
<tr>
<td></td>
<td>33.4837</td>
<td>2.6741</td>
<td>36</td>
<td>0.2359</td>
</tr>
<tr>
<td></td>
<td>34.7279</td>
<td>2.5739</td>
<td>43</td>
<td>0.2143</td>
</tr>
</tbody>
</table>

4.2 Scanning electron microscope (SEM):

Depending on the amount of \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) present in the polymer matrix, the morphology of the PVA/[\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) composite will vary and greatly influence its properties. Scanning electron micrographs of pure PVA, and PVA/(3,6,9) wt.% of \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) composites are given in Figure 5 (a,b,c and d) respectively. Very distinguishable changes have been observed from pure PVA, to low, intermediate and high concentrations of \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\). Pure PVA shows smooth surface of the PVA film. Tiny and very few agglomeration of \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) particles was observed in Figure 5 (b), which contain 3 wt.% of \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\), thus suggesting that \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) particle can be well dispersed in PVA matrix and the fabricated film can be considered as homogenous and dense with no obvious phase separation. With 6 wt.% concentration of \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) (figure 5 c), an agglomerations with different size (about 4.2-1.8 \( \mu \text{m} \)) are appeared , while in PVA/ 9wt.% of \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) prepared samples (figure 5d) there are some semi-tori (with different sizes in the range of about 0.178–0.625\( \mu \text{m} \)) appeared as bright spots in all of them with different degree of roughness. These observed uniform distributed bright spots on the backscattered images shown in the figure seem to be agglomerates of \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) particles, which increase with increasing the concentration of \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\). The degree of roughness of the film surface increases with increase of the content of \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\). This indicates segregation of the filler in the host matrix and this may be confirmed the interaction and complexation between the additive and the polymer (Kirk, S., et al., 2000) also it may refers to growth of \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) particles in PVA matrix (Kirk, S., et al., 2000).
Fig 5: SEM photographs for PVA/ [Co(NH$_3$)$_5$Cl]Cl$_2$ composite films with different concentration of [Co(NH$_3$)$_5$Cl]Cl$_2$: (a) 0 wt.%,(b) 3wt.%, (c) 6wt.% and (d) 9wt.%.

**Ac electrical properties results And discussion:**

Figure 1 shows the dielectric constant of PVA / (0,3,6 and 9) wt.% of [Co(NH$_3$)$_5$Cl]Cl$_2$ composite films as a function of frequency. The dielectric constant $\varepsilon'$ of composite film, calculated from equation (2), is decreases with increase in frequency. The dielectric behavior of the composites films is due to different types of polarizations present in the composites. It is well known that composite material contains enormous number of interfaces, and the large number of defects present at these interfaces can causes a change of positive or negative space charge distribution. When an electric field is applied these charges move and trapped by these defects, resulting in the formation of dipole moments. This called space charge polarization or interfacial polarization. When exposed to an electric field, these dipoles are rotate, giving a resultant dipole moment in the direction of the applied field. This is called rotation of polarization direction. Thus high value of dielectric constant at low frequencies is mainly due to the space charge polarization (interfacial polarization) and rotation of polarization direction.

However, at the high frequency range ($1 \times 10^3$ to $1 \times 10^7$ Hz), the decreasing trend seems not too sharp as compared to lower frequency region. It could be explained by the inability of the dipole to become oriented in a rapidly varying electric field (Abdelaziz, M., 2012). Similar behavior of the dielectric constant has been reported by various workers (Kungumadevi, L., et al., 2010; Mohan, V.M., et al., 2010). Also the dielectric constant of the composites increased with the increase of [Co(NH$_3$)$_5$Cl]Cl$_2$ content in PVA polymer matrix. The enhancement in dielectric constant is attributed to the interfacial polarization effect which is a phenomenon that appears in a heterogeneous system consisting of phases with different dielectric permittivities and conductivities, attributed to the accumulation of charges at the interfaces (Chandrakala, H.N., et al., 2013). In other words, the number of particles per unit volume is large; hence the dipole moment per unit volume increases, and so the dielectric constant increases (Jana, S., et al., 2008).
Figure 1: Dielectric constant as a function of frequency for PVA / [Co(NH$_3$)$_5$Cl]Cl$_2$ composites films.

Figure 2 shows the variation of dielectric constant at certain frequency, 100 Hz, for different content of [Co(NH$_3$)$_5$Cl]Cl$_2$ in PVA matrix. The dielectric constant increased monotonically with increasing additive content. As [Co(NH$_3$)$_5$Cl]Cl$_2$ content increases the number of the defects existing at grain boundaries, dangling bonds, and vacancies will increased. These defects will generate more and more dipole moments. Therefore the increase in the dipole moment will increase the dielectric constant of the composites (Abdelaziz, M., 2012).

The imaginary part of permittivity $\varepsilon''$ is called the dielectric loss and is a measure of how dissipative or lossy a material to an external electric field. The dielectric loss $\varepsilon''$ is always greater than zero and is usually smaller than $\varepsilon'$. From equation (3), dielectric loss was calculated. Figure 3 shows the plot of dielectric loss as a function of frequency for PVA / [Co(NH$_3$)$_5$Cl]Cl$_2$ composites films with different additive concentrations. The dielectric loss increases with increase in additive concentrations. The increase in dielectric loss with increasing additive contents may be attributed to the interfacial polarization mechanism of the heterogeneous system (Chandrakala, H.N., et al., 2013). The interfacial polarization in polymer having structural inhomogeneties can be identified by low frequency dielectric measurement based on Maxwell–Wagner–Sillars polarization (Ku, C., R. Liepins, 1987). Maxwell–Wagner–Sillars polarization occurs either at inner dielectric boundary layers on a mesoscopic scale, or at the external electrode-sample interface on a macroscopic scale. In both cases this leads to a separation of charges. The charges are often separated over a considerable distance (relative to the atomic and molecular sizes), and the contribution to dielectric loss can therefore be orders of magnitude larger than the dielectric response due to molecular fluctuations (Kremer, F., and A. Schönhals (Eds.), 2003). Also the larger value of dielectric loss at the lower frequency range could be due to the mobile charges within the polymer backbone (Chandrakala, H.N., et al., 2013). Furthermore it can be noted that the values of dielectric loss decrease with increasing the applied frequency. This behavior is may be due to the fact that at lower frequencies the dipoles or ionic charges have sufficient time to align with the
field before it changes its direction (Chandrakala, H.N., et al., 2013). It is obvious that the composite with 9 wt.% [Co(NH\textsubscript{3})\textsubscript{5}Cl]\textsubscript{2} has a much more interfacial polarization than the lower [Co(NH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} content loaded.

**Fig. 3:** Dielectric loss as a function of frequency for PVA / [Co(NH\textsubscript{3})\textsubscript{5}Cl]\textsubscript{2} composites films.

Figure 4 shows the variation of dielectric loss at certain frequency, 100 Hz, for different content of [Co(NH\textsubscript{3})\textsubscript{5}Cl]\textsubscript{2} in PVA polymer matrix.

**Fig. 4:** Concentration dependence of dielectric loss at 100 Hz for PVA / [Co(NH\textsubscript{3})\textsubscript{5}Cl]\textsubscript{2} composite films.

Figure 5 shows Ac conductivity as a function of frequency for PVA / (0,3,6,9) wt.% [Co(NH\textsubscript{3})\textsubscript{5}Cl]\textsubscript{2}. The Ac conductivity, calculated from equation (4), is increases with increase of the frequency. The rise of conductivity upon increasing the frequency is a common response for polymeric and semiconductor samples. It is due to the tremendous increase in the mobility of charge carriers in the composite systems (Chandrakala, H.N., et al., 2012). As the additive concentration is increased, the additive molecules start bridging the gap separating the two localized state and lowering the potential barrier between them, thereby facilitating the transfer of charge carrier between two localized states (Sangawar, V.S., et al., 2007). Also the segmental movement of the polymer facilitates the translational ionic motion. From this, it is clear that the ionic motion is due to translational motion/hopping facilitated by the dynamic segmental motion of the polymer leads to the increase of charge carrier mobility. Conductivity enhancement due to increase in additive concentration is reported by many authors for different composite systems (Abdelaziz, M., 2012; Choudhury, A., 2010).
**Fig. 5:** frequency dependence AC conductivity for PVA / [Co(NH$_3$)$_5$Cl]$^2$Cl$_2$ composites films.

Figure 6 shows the variation of AC conductivity at certain frequency, 100 Hz, for different content of [Co(NH$_3$)$_5$Cl]$^2$ in PVA polymer matrix.

**Fig. 6:** concentration dependence of AC conductivity at 100 Hz for PVA / [Co(NH$_3$)$_5$Cl]$^2$Cl$_2$ composite films.

The AC conductivity of Chloropenta amine cobalt(III) chloride might be attributed to the nature of the complex and the electron configuration of the metal ion in the complexes. Below is the orbital electron configuration of Co and Co$^{2+}$ and the complex ion [Co(NH$_3$)$_5$Cl]$^{3+}$:

\[
egin{align*}
\text{Co} & : 1s^22s^22p^63s^23p^64s^23d^7 \\
\text{Co}^{2+} & : 3d^74s^2 \\
[\text{Co(NH}_3\text{)}_5\text{Cl}]^{3+} & : \text{d}^{sp^3} \\
\text{NH}_3 & : \text{NH}_3 & \text{NH}_3 & \text{NH}_3 & \text{NH}_3 & \text{Cl}
\end{align*}
\]

The electron configuration explained that $\text{Co}^{2+}$ and the complex ion [Co(NH$_3$)$_5$Cl]$^{3+}$ has good coordination ability. Therefore the presence of the complex in PVA matrix shows higher AC conductivity than the polymer matrix.
Conclusion:
The of PVA / (0,3,6 and 9) wt.% of [Co(NH$_3$)$_2$Cl]Cl$_2$ composite films were prepared by solution casting technique. The effect of different amounts of [Co(NH$_3$)$_2$Cl]Cl$_2$ on dielectrical properties of the PVA polymer matrix was studied. Dielectric behaviors of polymer matrix strongly depend on frequency and additive content. As [Co(NH$_3$)$_2$Cl]Cl$_2$ content increases, the dielectric constant, dielectric loss, and AC conductivity of PVA polymer host increases.

Summarizing, the measurements of dielectric properties indicate that the [Co(NH$_3$)$_2$Cl]Cl$_2$ is useful additive to simultaneously increase dielectric constant of polymer composites. As a result, the PVA/9 wt.% of [Co(NH$_3$)$_2$Cl]Cl$_2$ composite film shows dramatic changes in dielectric properties.

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REFERENCES

