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Investigation of Structural and Thermal Properties of $Mg(ClO_4)_2$ Based PVC + ZnO Nanocomposite Polymer Electrolytes

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Abstract:

PVC+ZnO+$Mg(ClO_4)_2$ nanocompistie polymer electrolyte of differnet concentrations of $Mg(ClO_4)_2$ electrolytes were prepared using solution casting technique and further characterized using XRD, FTIR and TGA & DTA. The results of XRD suggests that the high amorphous of the PVC/ZnO nanocomposite with x=50 wt.% $Mg(ClO_4)_2$. As it due to high amorphous nature it can show a good ionic conductivity. The FTIR peaks shifting may also representing change of bond length and attaining good amorphous nature. The high heat resistance for all the sample can notice for DGA-DTA.

Key word: polymer electrolyte, XRD, FTIR, TGA & DTA, Nanofiller

1. Introduction:

Polymer research aims, among other things, to develop polymeric systems with strong ionic conductivity. The reason for this is because they have the ability to be used as an electrolyte in solid state batteries [1]. The benefits of a polymer battery include a high energy density, a low weight, a large electrochemical stability window, a solvent-free environment, a leak-proof construction, and a strong ionic conductivity. The amorphous elastomeric phase often controls ionic conduction in polymer electrolytes [2,3]. Blending polymers is a practical way of producing materials with diverse characteristics. From a scientific and business perspective, polymer blends including poly (vinyl chloride) (PVC) are among the most significant [4]. The chlorine atom in PVC possesses one pair of electrons, making it a good solvent for salt and ionic liquid [5]. The mechanical stability of the polymer electrolyte may be provided, among other things, by the dipole-dipole interaction between chlorine and hydrogen atoms, which can stiffen the polymer backbone [6]. The presence of dipoles in the bulk material may be shown by the dielectric permittivity. One advantage of researching dielectric behavior is that it helps us understand how polymer electrolytes conduct. This study aimed to understand the electrical conductivity of magnesium-based PVC and ZnO nanocomposite polymer electrolytes for use in electrochemical devices by discussing their production, structural and thermal characteristics.

2. Materials and Experimental Techniques:

PVC (Polyvinyl Chloride-(Main polymer) (M.W ~99,000) ZnO (Zinc Oxide) nano particles powder and $Mg(ClO_4)_2$ (Magnesium per chlorate) salt (Purity 99%) purchased from Sigma Aldrich company and these materials are used in synthesis process without furification. THF (Tetrahydrofuran) solvent, EMPARTA (AR Grade) purchased from Merck company. After weighing the PVC polymer and the ZnO nanopowder according to the specified ratios, they were transferred to a glass beaker and 30 milliliters of THF solution was added to dissolve them. After a 12-hour period of stirring on a magnetic stirrer at room temperature, the solution was homogenous. Next, $Mg(ClO_4)_2$ salt was added in varying weight ratios, and the mixture was agitated again for another 12-hour period. In addition, the uniform solution was transferred to a petri dish made of glass and let to evaporate at room temperature. A desiccator was used to keep the thin films dry when they were transferred from the petri dish to the polythene cover. Prepared PVC+ZnO+ $Mg(ClO_4)_2$ nanocompistie polymer electrolyte films were labled and tabulated in Table 1.

Table 1: Weight ratios of PVC, ZnO and $Mg(ClO_4)_2$ Nanocmposite Polymer Electrolyte System

S.No	Sample Code	PVC weight mg	ZnO Weight mg	Mg $(ClO_4)_2$ Weight mg
1	MA1	1000	40	250
2	MA2	1000	40	500
3	MA3	1000	40	750

For this investigation, XRD, FTIR, and TGA&DTA were used to characterize the prepared nanocomposite polym er electrolytes.

3. Results and discussion:

3.1 X-ray Diffraction:

The X-ray diffraction examinations were used to examine the nanocomposite polymer complexation and the crystallinity of the produced electrolyte films of polymer [7]. These nanocomposite polymer electrolyte thin films are shown in Figure 4.1 as XRD data for PVC/ZnO/x$Mg(ClO_4)_2$, where x=25 wt.%, 50 wt.%, and 75 wt.%. There were no noticeable peaks in the diffraction patterns of the PVC/ZnO nanocomposite containing 25 wt.% or 50 wt.% $Mg(ClO_4)_2$, indicating that the structure is completely amorphous. Differences in intensity and the lack of distinct peaks are indicators of the polymer electrolytes' amorphous nature [8]. Because it is not perfectly solid, it has excellent ionic conductivity and enhanced ionic diffusion.

The existence of small crystalline peaks at x=75 wt.% at $2\theta=27^0$ indicates a higher concentration of $Mg(ClO_4)_2$. This might be because of an excess of salt or because the side chains of the PVdF-HFP copolymer are coordinated with $Mg(ClO_4)_2$. You can tell whether the polymer membrane is amorphous or not by looking at the correlation

that Hodge et al. [9, 10] found between peak height and degree of crystallinity. It is clear that the salt has fully dissociated from the matrix since the polymer electrolytes display ionic conductivity; this was confirmed by the absence of peaks associated with $Mg(ClO_4)_2$ in the polymer complexes. Results like this suggest that the high amorphicity of the PVC/ZnO nanocomposite with x=50 wt.% $Mg(ClO_4)_2$ can lead to new applications.

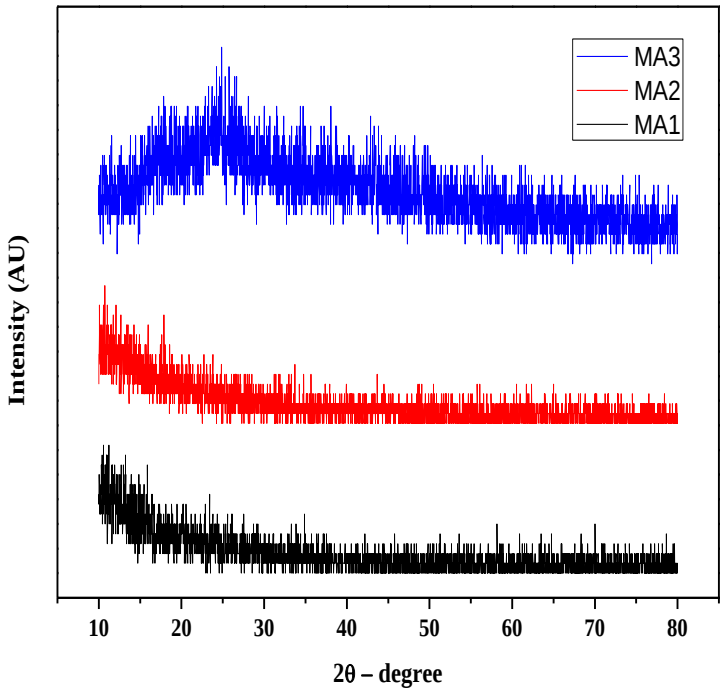

Figure 1: XRD plots of $Mg(ClO_4)_2$ salt added PVC/ZnO nanocomposite polymer electrolytes.

3.2 FTIR:

Fourier transform infrared spectroscopy are the assessment of samples for the presence of functional groups and the identification of vibrational transitions in organic molecules [11, 12]. Figure 2 shows the Fourier transform infrared spectra of thin films of PVC/ZnO/x$Mg(ClO_4)_2$ nanocomposite polymer electrolyte, where x=25 wt.%, 50 wt.%, and 75 wt.%. From 400 to 4000 cm^{-1} is the range of the spectra. A band at around 3410 cm^{-1} is caused by the stretching of the O-H bonds in the PVC. It is at 1622 cm^{-1} that the C=O stretching of the aldehyde carbonyl group is rooted. A peak at 1065 cm^{-1} is ascribed to the stretching of the C-O-C bonds, whereas the absorption peak at 1135 cm^{-1} is generated by the ceto group stretching. We may infer that the peak at 631 cm^{-1} is caused by bending vibrations of -CF_2. The bands move to lower wavenumbers when the phase is amorphous. Increasing the $Mg(ClO_4)_2$ wt.% in a nanocomposite polymer causes a noticeable change in the FTIR spectra's band locations, which strongly suggests salt complexation and interaction [13,14]. Peaks at 620 and 951 cm^{-1}, which are believed to be sensitive to anion-cation interaction, remain unchanged when the salt concentration in polymer complex systems rises, assuming no ion association. The findings prove that the elaborate construction is genuine.

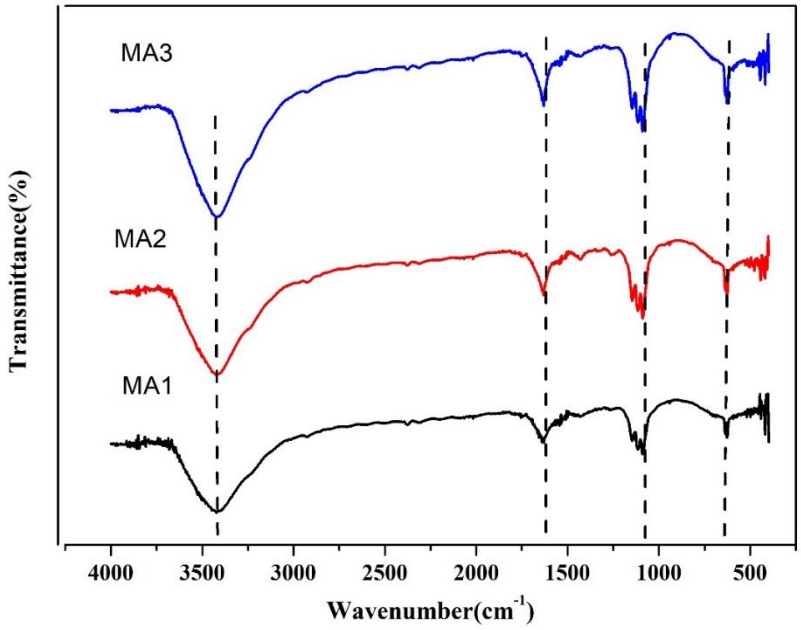

Figure 2: FTIR spectra of $Mg(ClO_4)_2$ salt added PVC/ZnO nanocomposite polymer electrolytes.

3.3 TGA-DTA analysis:

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to ascertain the thermal characteristics of the prepared samples. Thermogravimetric analysis (TGA) is a method for determining a material's thermal stability and volatile component percentage by monitoring the weight change that occurs to a sample as it is heated [15]. A temperature-gradient thermogram (TGA) of weight loss from room temperature to 200^0C is shown in Figure 3(a) for each of the produced nanocomposite polymer electrolytes [16]. During the temperature range of 80–120°C, the samples may have evaporated because of the solvent or water molecules, leading to a 2.2%-2.8% loss of mass for each sample (Figure 4.3a). Figure 3(b) shows the DTA exothermic peaks for the $xMg(ClO_4)_2$ samples at 121°C, 101°C, and 92°C, where x=25 wt.%. The modest weight loss with temperature (average 2.5%) makes all of the samples more heat resistant, as evidenced by TGA data. This little mass loss emphasizes the difference in the films' electrical properties, optical features, conductivity, and crystallinity level.

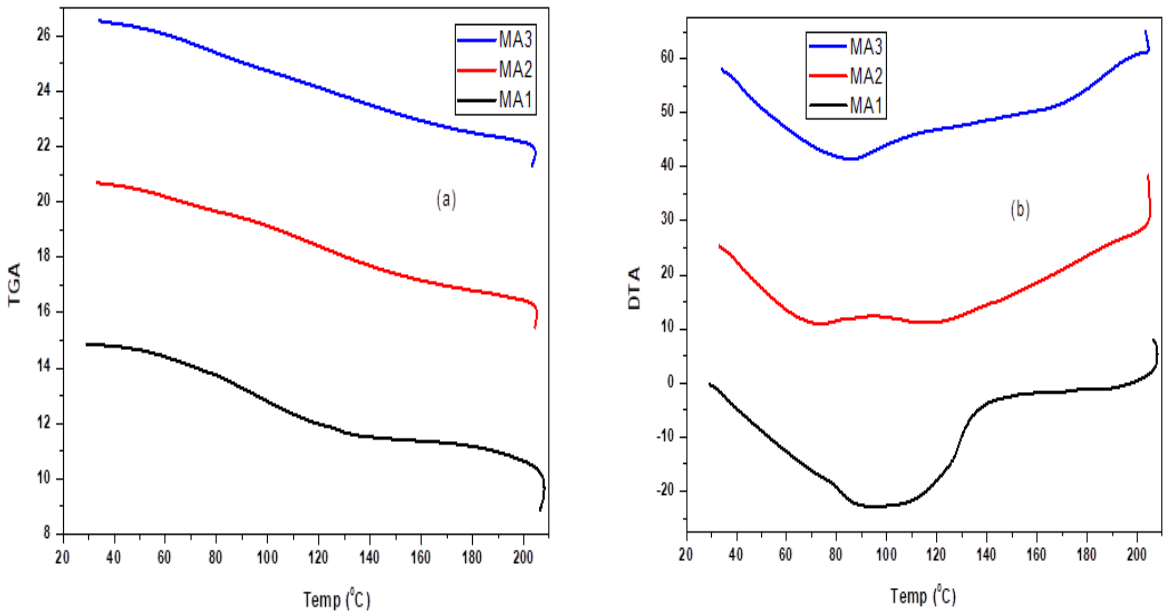

Figure 3(a&b): TGA-DTA curves of $Mg(ClO_4)_2$ salt added PVC/ZnO nanocomposite polymer electrolytes.

Conclusions:

PVC/ZnO/$Mg(ClO_4)_2$ nanocompistie polymer electrolyte films were prepared using solution cast technique. Based on the results of the XRD analysis, the PVC/ZnO nanocomposite with x=50 wt.% $Mg(ClO_4)_2$ might have further applications because of its high amorphicity. According to the FTIR data, the bands are at lower wavenumbers in the amorphous phase. It is very suggestive of salt complexation and interaction with the nanocomposite polymer when the band locations move in the FTIR spectra. All of the samples exhibit greater heat resistance as shown by TGA-DTA findings, which are based on the minimal weight loss with temperature (average 2.5%) seen in TGA data. This little mass loss emphasizes the difference in the films' electrical properties, optical features, conductivity, and crystallinity level. The results suggest that a PVC/ZnO nanocomposite electrolyte containing x=50 wt.% $Mg(ClO_4)_2$ would be useful for future research and development.

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