Investigation of Optical and Dielectric properties of $Mg(ClO_4)_2$ based PVC+ZnO Nanocomposite Polymer Electrolytes

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Abstract:
Nanocompistie polymer electrolytes of PVC+ZnO+$Mg(ClO_4)_2$ were synthesized by solution casting and studied using UV-visible spectroscopy and AC conductivity. The electrolytes had varying amounts of $Mg(ClO_4)_2$. Based on the findings of the UV visible spectroscopy, the sample with x=50 wt.% $Mg(ClO_4)_2$ had the best direct and indirect band gap values, suggesting that the interaction between the polymer, ZnO nanofiller, and $Mg(ClO_4)_2$ salt improved its optical properties. In terms of dielectric constant and ion dissociation, the sample with x=75 wt.% $Mg(ClO_4)_2$ performed the best out of all of the samples tested. polymer electrolyte with frequency-dependently high dielectric constant values is perfect for cutting-edge applications.

Key words: polymer electrolyte, solution casting, UV -visible spectroscopy, AC conductivity, dielectric constant.

1. Introduction:

Research into polymers seeks, among other things, to create polymeric systems that exhibit high ionic conductivity. This is due to their capacity to serve as an electrolyte in solid-state batteries [1]. Numerous advantages are associated with polymer batteries, such as their great ionic conductivity, low weight, solvent-free environment, extended electrochemical stability window, and leak-proof design. According to ionic conduction in polymer electrolytes is often controlled by the amorphous elastomeric phase [2]. An efficient method of creating materials with varying properties is to blend polymers. Both in the scientific community and the corporate world, polymer mixes like PVC rank high [3]. For salt and ionic liquid [4], PVC is an excellent solvent because the chlorine atom in it has one pair of electrons. Chlorine and hydrogen atoms' dipole-dipole interaction may stiffen the polymer backbone, which aids in the mechanical stability of the electrolyte [5]. One way to tell whether a material has dipoles is to look at its dielectric permittivity. The conductivity of polymer electrolytes may be better understood via studies of dielectric behavior. Electrochemical device manufacturers want to better understand the manufacturing, optical, and electrical conductivity of PVC and ZnO nanocomposite polymer electrolytes based on magnesium.

2. Materials and Experimental Techniques:

The components employed in the synthesis method include PVC (Polyvinyl Chloride—Main polymer) (M.W ~99,000), ZnO (Zinc Oxide) nanoparticle powder, and $Mg(ClO_4)_2$ (Magnesium per chlorate) salt (Purity 99%), all of which were acquired from Sigma Aldrich. The Merck firm supplied the THF (Tetrahydrofuran) solvent and EMPARTA (AR Grade). To dissolve the PVC polymer and ZnO nanopowder, 30 milliliters of THF solution was poured to a glass beaker after they were weighed according to the necessary ratios. The solution was homogeneous after 12 hours of stirring at room temperature using a magnetic stirrer. Then, $Mg(ClO_4)_2$ salt was added to the mixture in different weight ratios and stirred for a further 12 hours. Finally, the homogeneous mixture was moved to a glass petri dish and allowed to evaporate at room temperature. During the transfer from the petri dish to the polythene cover, a desiccator was used to ensure that the thin films remained dry. The labeling and tabulation of the prepared PVC+ZnO+ $Mg(ClO_4)_2$ nanocomposite films can be found 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, UV-visible spectroscopy and AC conductivity were used to characterize the prepared polymer composite electrolytes.

3. Results and discussion:

3.1 UV-visible spectroscopy:

The optical band gap and variations in band structure were determined by measuring the samples' UV-Visible absorption [6]. At room temperature, we recorded the infrared spectra of each sample. Figure 1 displays the optical properties of nanocomposite polymer electrolyte thin films made of PVC/ZnO and $Mg(ClO_4)_2$, where x=25 wt.%, 50 wt.%, and 75 wt.%. Research has shown that the absorbance spectra of the PVC polymer electrolyte sheet shift to longer wavelengths when the quantity of $Mg(ClO_4)_2$ is increased. It seems that the absorption edge intensity decreased as the $Mg(ClO_4)_2$ concentration rose, indicating that the inclusion of $Mg(ClO_4)_2$ induced interactions between all components. The unsaturated bond source of the π-π* transition is C=O and C=C.

An adequate understanding of solid band structures may be gleaned via optical absorption experiments. Based on their band gap, insulator and semiconductor materials are fundamentally categorized as either direct or indirect band gap materials. The valence and conduction bands of a material with a direct band gap share the same wave vector. In materials with an indirect band gap, the wave vector does not coincide with the lowest point of the conduction band. In materials with an indirect band gap, a phonon with the appropriate crystal momentum must always accompany the transition from the valence band to the conduction band [7]. The optical band gap was analysed by the following relationship [8, 9]

$$(\alpha h v) = B(hv - E_g)^n \qquad \text{--------(1)}$$

Where the variables E_g, α, h, v, and n denote the energy gap, an energy-independent constant, Planck's constant, incoming wave frequency, and kinds of transition, respectively.

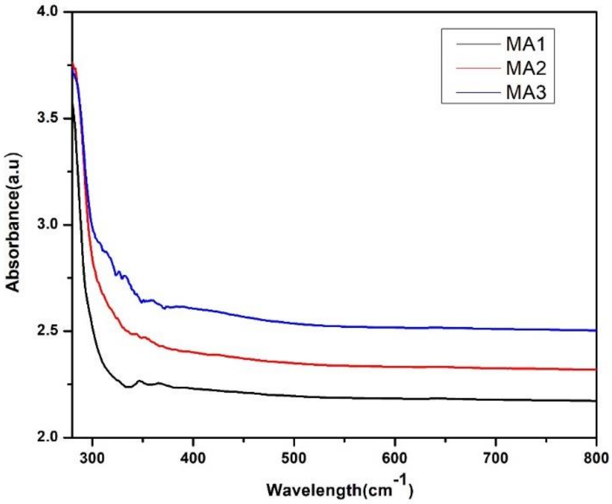

Figure 1: UV-visible absorption spectra of $Mg(ClO_4)_2$ salt added PVC/ZnO nanocomposite polymer electrolytes

Figure 2 (a&b) illustrates two graphs that were used to find the values of the direct band gap and indirect energy gap. One graph had E=hv(eV) on the x-axis and $(\alpha hv)^2$ on the y-axis, while the other had E=hv (eV) on the x-axis and $(\alpha hv)^{1/2}$ on the y-axis. Figure 2 (a&b) shows that in order to get a good estimate of the energy band gap from the plots, the linear part of the curve has to be extended until it intersects the x-axis of the photon energy (hυ). We can see from Table 2 that the Eg values drop when the $Mg(ClO_4)_2$ salt concentration in the PVC/ZnO nanocomposite polymer goes up from 25 wt.% to 75 wt.%. This holds true for both the direct and indirect energy gap values. According to predictions, the direct and indirect band gaps between salt and polymer will decrease due to salt aggregation. The samples show the lowest direct and indirect energy gap values because the PVC polymer and the $Mg(ClO_4)_2$ salt interact optimally.

Table 2: Direct, indirect bandgap values of $Mg(ClO_4)_2$ salt added PVC/ZnO nanocomposite polymer electrolytes.

Sample Code	Direct band gap values	Indirect band gap values
MA1	3.98	3.62
MA2	3.87	3.43
MA3	3.82	3.37

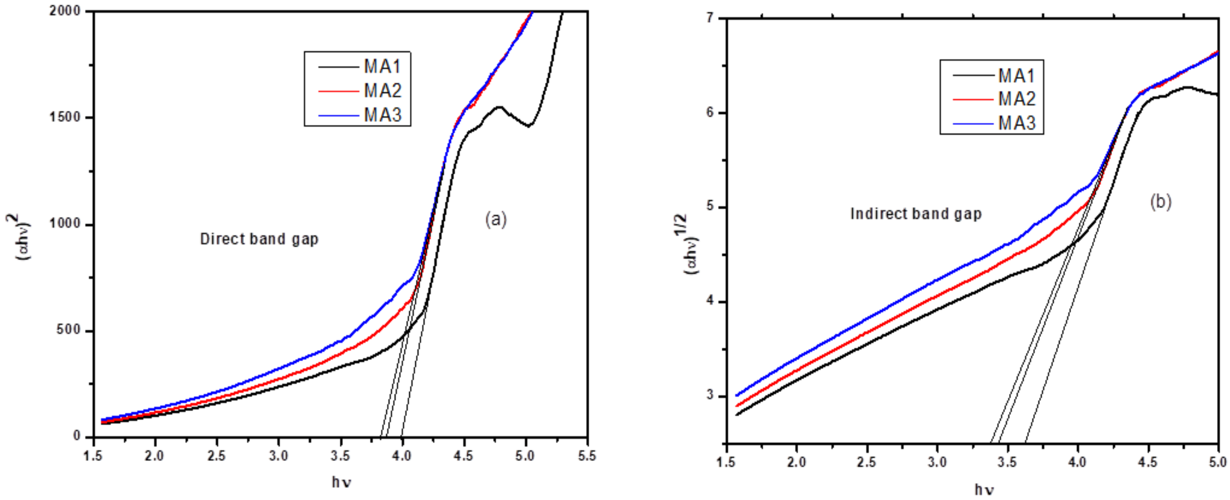

Figure 2 (a&b): Direct and indirect bandgap plots of $Mg(ClO_4)_2$ salt added PVC/ZnO nanocomposite polymer electrolytes

3.2 AC conductivity studies:

3.2.1 Real part of frequency dependent electric Modulus:

An important physical characteristic, the electrical modulus shows how a material's electric field relaxes with a constant electric displacement. The frequency-dependent characteristics of the real (M′) and imaginary (M″) components of the electrical modulus are excellent instruments for analyzing relaxation [10]. Figure 3 displays the real component of the electric modulus (M′) at room temperature against frequency for MA1, MA2, and MA3 samples. We may infer that the electrical characteristics of the materials are frequency-independent as M′ approaches zero at low frequencies, indicating that electrode polarization has a little influence. However, M′ is more significant at higher frequencies. The dispersion at high frequencies might be caused by the relaxation of conductivity [11–13]. As the concentration of $Mg(ClO_4)_2$ salts in PVC/ZnO nanocomposite polymer electrolytes increases, the M′ value remains almost constant with frequency, suggesting that the produced sample remains stable with frequency.

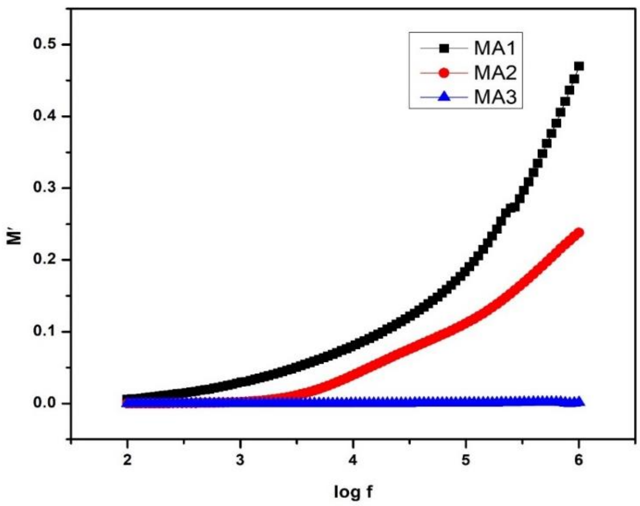

Figure 3: Frequency vs. real part of electric modulus of $Mg(ClO_4)_2$ salt added PVC/ZnO nanocomposite polymer electrolytes

3.2.2 Real part of frequency dependent electric Modulus:

Figure 4 displays the MA1, MA2, and MA3 samples' imaginary parts of the electric modulus (M″) at room temperature vs frequency. While studying the imaginary electric modulus (M") versus frequency logf at ambient temperature, many studies highlight the importance of electric modulus and dielectric relaxation in polymer systems. The electric modulus technique has the potential to provide light on the relaxation dynamics and conduction mechanisms of these materials. The fact that M″ is almost negligible at low frequencies suggests that the electrical properties of the materials are frequency independent, meaning that electrode polarization has no effect on them. In contrast, M″ becomes increasingly important as the frequency increases. Conductivity relaxation is one possible explanation for the dispersion at high frequencies [14]. In PVC/ZnO nanocomposite polymer electrolytes, the M″ value increases with frequency as the concentration of $Mg(ClO_4)_2$ salt increases. The manufactured sample exhibits superior conductivity with respect to frequency, as seen by its lower M″ compared to other samples.

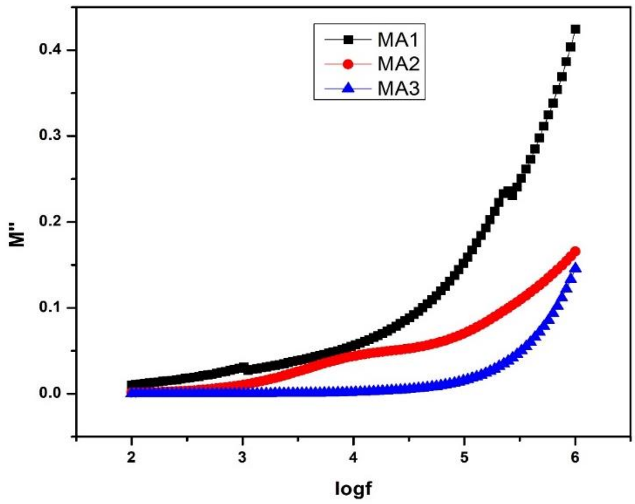

Figure 4: Frequency vs. imaginary part of electric modulus of $Mg(ClO_4)_2$ salt added PVC/ZnO nanocomposite polymer electrolytes

3.2.3 Frequency dependent conductivity:

As seen in Figure 5, the MA3 sample has a high gram-based conductivity, whereas the MA1 and MA2 nanocomposite polymer electrolytes exhibit an increasing conductivity with frequency. The ions in the sample have a higher reactivity to high-frequency electric fields and may travel along the polymer chain via more segmental pathways, which contributes to this. Additionally, considerable ion conductivity may be seen due to the presence of ZnO nanofiller in MA3 polymer electrolyte, which implies a substantial segmental motion of the polymer chain and ion moment across all frequency ranges [15]. Polymer electrolytes with high ionic mobility across all frequencies are ideal for cutting-edge uses.

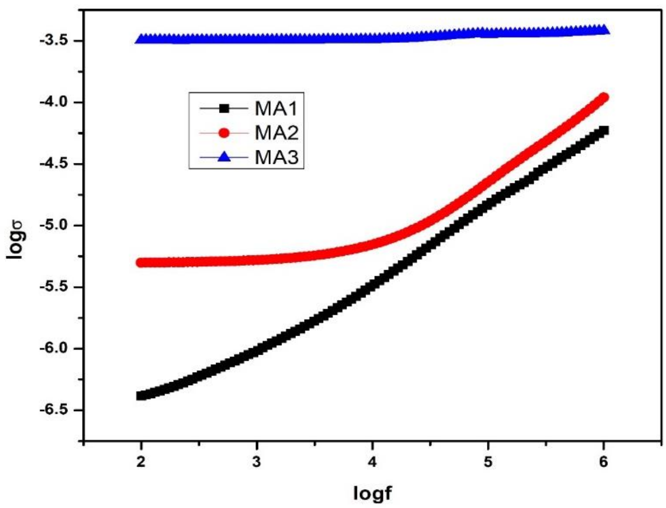

Figure 5: log f vs. log □ of $Mg(ClO_4)_2$ salt added PVC/ZnO nanocomposite polymer electrolytes

3.2.4 Dielectric studies:

The real part of the dielectric constant represents the storage capacity of the battery. High dielectric constant polymer electrolytes can store a lot of energy for applications like RF frequency and batteries [16]. An essential step in creating the ideal polymer electrolyte is increasing the salt concentration, since the dielectric constant in a PVC/ZnO/x$Mg(ClO_4)_2$ polymer electrolyte is proportional to the concentration of $Mg(ClO_4)_2$. Consequently, adding more salt causes the ZnO nanofiller concentration to rise in tandem. Figure 6 shows that out of all the samples, the MA3 sample exhibited the best ion dissociation and the greatest dielectric constant. Due to its frequency dependent high dielectric constant values, MA3 is supposedly the perfect polymer electrolyte for cutting-edge applications.

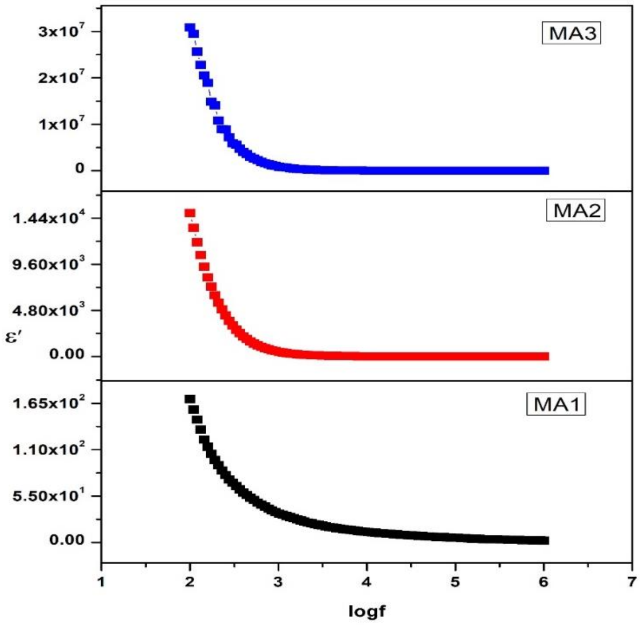

Figure 6: log f vs. □' of $Mg(ClO_4)_2$ salt added PVC/ZnO nanocomposite polymer electrolytes

Based on the frequency dependency behavior, it seems that the polymer electrolyte samples could have an extremely high value for the imaginary component of the dielectric constant, denoted as ε''. This would indicate that the electrical energy loss is much higher at lower frequencies. At lower frequencies, it becomes clear that the polymer is becoming more polarized and creating structural obstacles for the ion moment. The polymer electrolyte, as seen in Figure 7, is a very sensitive material with outstanding conducting capabilities; it may display little dielectric loss in the mid- to high-frequency range. Across many frequency ranges, the figure clearly shows that the MA3 sample shows negligible energy dissipation caused by the polymer electrolyte, as shown by the low imaginary component of the dielectric constant.

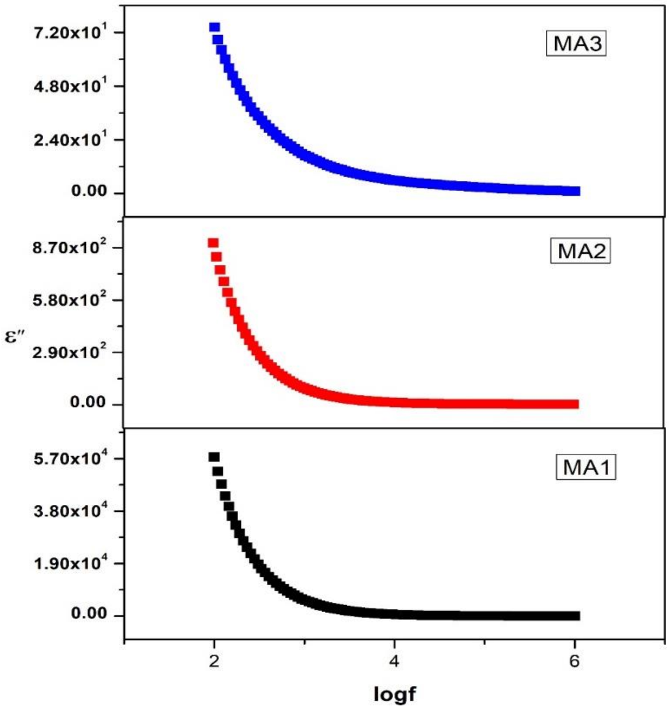

Figure 7: log f vs. □" of $Mg(ClO_4)_2$ salt added PVC/ZnO nanocomposite polymer electrolytes

4. Conclusions:

Nanocompistie polymer electrolytes of $PVC+ZnO+Mg(ClO_4)_2$ were synthesized by solution casting. The interaction between the polymer, the ZnO nanofiller, and the $Mg(ClO_4)_2$ salt in sample MA2 resulted in the best direct and indirect band gap values, suggesting that the material had high optical enhanced properties. As $Mg(ClO_4)_2$ salt concentration increases in PVC/ZnO nanocomposite polymer electrolytes, M′ stays practically constant with frequency, indicating the sample is stable. MA3, the produced sample, has a lower M″ than the others, implying conductivity rises with frequency. The optimal polymer electrolyte requires raising the salt concentration since the dielectric constant in a $PVC/ZnO/xMg(ClO_4)_2$ polymer electrolyte is proportional to Mg concentration. The ZnO nanofiller concentration rises with salt addition. Thus, MA3 had the highest dielectric constant and ion dissociation. MA3 is recommended for cutting-edge polymer electrolytes because to its frequency-dependent high dielectric constant values. Results show MA3 has good conductivity.

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