Spectral Studies on Impact of Alkali Perchlorate (Li/Na/K-ClO$_4$) Salts on the Properties of PVA-Ag-Cr$^{3+}$ Polymer Nanocomposite Films

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Abstract. Poly (Vinyl alcohol) metal (PVA-Ag-Cr) nanocomposites were prepared by a slow evaporation method with the help of a refluxing procedure. The effect of alkali perchlorate (Li/Na/K-ClO$_4$) salts embedded in PVA-metal nanocomposites were analysed with SEM, XRD, EPR, and optical techniques. The surface structure and topology of the synthesized composites were studied using scanning electron microscopy. The crystallinity of the prepared polymer films has been determined using the X-ray diffraction pattern. Existing changes in some diffraction angle with the alkali salts results the fluctuations in the degree of crystallinity. EPR studies reveal the ‘g’ values at 1.96, 1.93, and 1.98 due to the oxidation exchange-coupled pair. The observed absorption spectra of Cr$^{3+}$ ions corresponding to Li, Na & KClO$_4$ salts in PVA-AgSe polymer films revealed the band positions centered at 220, 275, 480, 535, and 1030 nm of all the alkali chlorates with small shifting in-band positions. This may be due to the inter/intramolecular hydrogen bonding.

Keywords: Perchlorates, Nanocomposites, Refluxing, Chemical stability, and Crystallinity.

1. Introduction

Nanotechnology is an important tool to improve the properties of advanced materials. It covers the preparation, characterization, and structures of devices having at least one dimension about 1-100 nm in length. Nanomaterials are beneficial to improving the mechanical and barrier properties of packing food materials. They enhance the innovative structures for active and smart packing applications [1]. In recent years, metal base nanocomposites are widely investigated in research because of their potential applications in physics and chemistry. They have many advantages along with polymers such as dielectric materials and excellent host matrices to encapsulating the metal nanoparticles like silver, gold, etc. Due to the improvement in optical, mechanical, and electrical properties, metal nanoparticles attract the attention of many researchers [2].

In the present work, polyvinyl alcohol (PVA) was taken as the host matrix/polymer due to its wider spread and biocompatibility in the bio-medical field like hemodialysis membranes, artificial skin, drug delivery system, contact lenses, and blood prosthetic devices [3]. PVA has some technological
applications in fuel cells and electrochromic devices, and addition of PVA improves the mechanical properties and ionic/electrical conduction of the materials [3]. Polyvinyl alcohol is a potential synthetic polymer to establish/improve various properties like durability, tensile strength, flexibility, and high gloss (smooth and shiny). It is a bio-compatible semi-crystalline polymer with good flexibility, highly hydrophilic, transparency and high chemical stability [4-5].

Polymer films with silver ions have the potentiality in antimicrobial devices like wound dressings, bone cement, catheters, and heart valve sewing cuffs. The incorporation of silver particles improves the mechanical and barrier properties, greatly enhances the polymer applications. Polymers filled with silver nanoparticles release more effective silver ions than the materials with silver microparticles [4-5]. The polymers act as a ligand to the metal ions when a transition metal ion induced into the polymers and improves the polymer common properties like high thermal stability, low solubility, and sensing - optical materials [6].

Selenium-contain organic materials are extremely used in synthetic organic chemistry [7] and found many applications due to their biological activity [8]. ‘Se’ was introduced into the environment by anthropogenic activities such as mining and combustion of fossil fuels [9]. Selenium also available in some food materials and bedrock, because of typical scattered property ‘Se’ was used in semiconductors, electronic-industries, solar panels, light-emitting diodes, and phase change memory chips [10]. Nano-selenium can be produced in various forms like nanoplates, nanorods, nanoribbons, nanotubes, etc. In the present work, refluxing method has been used for the synthesis of elemental selenium. The polyvinyl alcohol stabilized selenium nanoparticles can be effectively utilized to synthesis polymeric films because of its technological applications. It is an essential micronutrient and antioxidant to enhance the nano-form activity when stabilized by the suitable stabilizer [11]. Silver-selenide has several advantageous properties for super-ionic conductors and switching devices, which are present and future technological interest. Some of these applications required silver selenide to possess a good polymeric phase transition [12]. Silver selenide is a phase change material which is widely used in optical information storage devices such as DVD R/W and phase change random access memory (PRAM) devices [13].

The properties of polymer films are suitably modified by the addition of dopants and it results in a good reaction with the host polymer matrix [14]. Among all the dopants, trivalent chromium (Cr$^{3+}$) is the most stable oxidation state of chromium, which is widely used as a luminescent dopant and luminescent sensitizer to provide deep color and bright luminescence in various materials. It has various biological, chemical, and environmental impacts [15]. Chromium is essential nourishment and an alimentary element of all living organisms and it has a high tendency to form stable complexes when reacting with organic/inorganic species of negative charge [15]. Cr$^{3+}$ ions doped materials are also used in modern technologies such as tunable solid-state lasers, high-temperature sensors, and high-pressure calibrants [16]. Polymeric films doped with chromium ions possess some remarkable properties which were used in night-vision materials, fiber-optic thermometers, lasers, and photocatalysis [17]. Alkali perchlorate salt (Li/Na/K-ClO$_4$) contained polymeric films poses several challenges in the electrical, optical, mechanical, and thermal properties of the materials due to their complicated microstructure [18].

2. Experimental

In the present work all the chemicals used are of AR (analar) grade and as purchased without further purification. PVA (Li/Na/K)AgSe: Cr$^{3+}$(0.2 mol%) polymer film preparation was carried out by adopting the refluxing process in slow evaporation method. PVA-aqua solution was prepared by adding 5g of PVA powder in 100 mL de-ionized water to formulate 5 mol% PVA solution. It is heated and blended on a magnetic stirrer at 70 °C for half an hour with continuous stirring until a viscous clear solution is obtained. The metal solution at room temperature was synthesized through stirring process as reported in several articles [19-20] with required mol% of AgNO$_3$ and the desired concentration of Cr(NO$_3$)$_3$ solution (0.2 mol%). 1 mol% alkali chloride solutions of (Li/Na/K)ClO$_4$ are prepared by the addition of required amount of alkali salt (Li/Na/K) powder within 100 mL deionized water and stirred for some time to mix thoroughly. One gram of Na$_2$SO$_3$ salt powder was dissolved in 100 ml of deionized water and stirred on a magnetic stirrer for complete dilution. Sodiumselenosulfate (Na$_2$SeSO$_3$) solution
has been chosen as the selenium source prepared by the refluxing method. Various methods have been reported in literature for the preparation of Na$_2$SeSO$_3$ solution, in which refluxing process is the easy and best method for the selenium. Na$_2$SO$_3$ aqueous solution is mixed with 0.05 g of selenium powder and refluxed for 3 hours at 70°C on the stirrer. After completion of the refluxing process, the final solution was filtered and stored in dark at 60°C to prevent photo-oxidation. 2.0 mol% ammonia solution is used to control the pH of the solution and also reduce the free metal ion concentration to revolve metal ions into complex ions.

2.1 Preparation of PVA (Li/Na/K) AgSe: Cr$^{3+}$ (0.2 mol%)

In a 50 ml flask, 20 ml of the obtained PVA-aqua solution and 0.1 mol% of silver nitrate solution were mixed under constant stirring at room temperature. After few minutes (10 mins), 0.2 mol% of chromium nitrate solution and 10 ml of lithium perchlorate solution (Li/Na/K) were added to the PVA-AgNO$_3$ mixture. The pH value of the current solution is adjusted about to 10 by slowly adding 2 mol% of ammonia solution in a dropwise manner and then 5 ml of sodium selenosulfate solution (0.50 mol%) is injected into the PVA-Li-Ag-Cr complex with rapid stirring to achieve the required metal/Se ratio. The final mixture was stirred at room temperature for 3 hours. After completion of the mixing procedure the resulting film formulation was cast into glass Petri-dishes (PET). For the remaining two samples, the same procedure is repeated with NaClO$_4$ and KClO$_4$. The solution was slowly evaporated at room temperature for 7 days, the PVA(Li/Na/K)AgSe: Cr$^{3+}$(0.2 mol%) polymer composite films were peeled off from Petri dishes for characteristic measurements.

3. Results and Discussions

3.1 Scanning Electron Microscopy (SEM) Studies

Scanning electron microscope studies are used to know about the surface arrangement of the prepared composite film. The FE-SEM images of PVA (Li/Na/K)AgSe: Cr$^{3+}$ (0.2 mol%) polymer films are shown in Figure 1(a-c). In the case of ‘Li’ salts with 0.2 mol% of Cr$^{3+}$ ions, the surface morphology distributed with rod-shaped particles having a width from 95-380 nm. The length of the rods reached up to several hundred micrometers and most of the rods were inter joined with one another in different directions. The topology of the ‘Na’ contained sample also had the distribution of rods besides that some small crystalline particles with ≤ 100 nm size. An extra grain in the morphology may be due to the additional Na$_2$O atoms which are available in Na$_2$SeSO$_3$ and NaClO$_4$ components. In another magnification of Na sample, we can observe a homogeneous distribution of pits with different diameters. The obtained pits are spherical in shape and diameters ranging from 0.85-1.6 cm. The surface morphology of the K-based polymer sample was also filled with clear rod-shaped particles with width ranging from 62 to 156 nm. The gained rods were thinner and sharper than the ‘Li’ and ‘Na’ filled polymer films. The morphology for the entire series of the composites having different particles with the
alkali salts variation, which means that the induced components are successfully reacted with the host polymer matrix. From the above SEM analysis, it is observed that the entire polymer composite films have the non-homogeneous spreading of the surface.

3.2 X-ray diffraction pattern studies

Figure 2 shows the room temperature XRD pattern of PVA (Li/Na/K)AgSe: Cr$^{3+}$ (0.2 mol%) polymer samples. There are no considerable changes in band positions with alkali salt but variation in the peak intensities with slight band shifting was observed. Two diffraction peaks for PVA molecule at $2\theta$ = 19.3 and 22.7° are corresponding to (101) and (200) planes have been observed and which indicated that the prepared samples having the regions of ordering as well as random arrangements [21]. This may be due to strong inter/intramolecular hydrogen bonding between the PVA chains. The diffraction angles at 29.8°, 32°, 33°, 38°, 44°, and 64° corresponding to (112), (112), (201), (111), (200), and (220) diffraction planes respectively and these are related to ‘Ag’ crystal structure. The occurrence of above planes indicates the presence of ‘Ag’ metal ions in face-centered cubic (fcc) structure in the PVA network of the polymer films [22-24]. The diffraction angle at $2\theta$ = 29.8° and 32° were attributed to AgNO$_3$ belonging to the planes of (112) [23]. A peak was attained at 36° attributed to the formation of Cr$_2$O$_3$ nanoparticles [25]. But in the case of peak intensities, some modifications were observed as follows. The peak intensities at 19° and 32° increased for (Na/K) samples than the Li-polymer film. From this, we can conclude that the crystal arrangement was increased with ‘Na and K’ perchlorates [26]. In the case of potassium salt contained polymer film, some new peaks were appeared as shown in the figure and are attributed to the increase in the degree of crystallinity by the incorporation of potassium salt [24].

The diffraction angles and their corresponding lattice planes are given in table 1.
### Table 1: XRD Diffraction angles and their planes of PVA(Li/Na/K)AgSe: Cr$^{3+}$ (0.2 mol %) polymer films.

| Diffraction angles (2θ°) | Diffraction Planes |
|--------------------------|--------------------|
| PVALiAgSe:Cr$^{3+}$ (0.2mol%) | PVANaAgSe:Cr$^{3+}$ (0.2mol%) | PVAKAgSe:Cr$^{3+}$ (0.2mol%) |
| 19.40                     | 19.30              | 19.30              |
| 22.7                      | 22                 | 23                 |
| 29.8                      | -                  | 28                 |
| 31.3                      | 31.3               | 31.3               |
| 37                        | 37.4               | 37.4               |
| 44                        | 43.8               | 43.8               |
| 64                        | 64                 | 64                 |

![Diffraction Planes](image)

#### 3.3 Electron Paramagnetic Resonance Studies

The EPR spectra of PVA (Li/Na/K)AgSe: Cr$^{3+}$(0.2 mol%) polymer samples were studied at room temperature and is shown in Figure 3. The polymer films of ‘Li and K’ exhibit a single resonance signal whereas the ‘Na’ based polymer film having a multiple resonance signals as shown in (inset) Figure 3. Chromium ions are paramagnetic ions due to the partially filled orbits with valance states +3, +4, +5 and +6. In all these states Cr$^{3+}$ has the $d^3$ configuration with spin number $S= 3/2$ or 0 and shows a clear hyperfine structure [27]. The calculated g- factor values are 1.96, 1.93, and 1.96 of the Li, Na & K based samples respectively. The resonance signals at 1.96 and at 1.93 were due to the Cr$^{3+}$-Cr$^{3+}$ exchange-coupled pairs [28]. In PVANaAgSe: Cr$^{3+}$(0.2 mol %) polymer film we can observe multiple resonance lines as shown in inset graph. The existence of multiple resonance signals only for ‘Na’ salt contained sample is the clear indication for increasing the coordination number of Na$_2$O atoms which are available from both Na$_2$SeSO$_3$ and NaClO$_4$ components [29]. These atoms make additional weakly bound O$^-$ for each Cr$^{3+}$ ion and it results in the change in coordination around Cr$^{3+}$ ions gives the number of transitions [27]. The respective calculated Spin-Hamiltonian parameters are presented in table 2.
3.3.1 Analysis of Spin Concentration (N)

The spin concentration of PVA (Li/Na/K)AgSe: Cr\textsuperscript{3+} (0.2 mol\%) polymer composite films were calculated using the formula given in our previous papers [30]. The calculated value 0.98, 0.45 and 1.71 for Li, Na & K samples shows the non-uniform changes in the spins participating in the resonance. This may be due to the randomisation of the PVA structure [28]. The structural changes in both kinds (Na/K) of polymer composites shows that the unpaired electrons should be delocalized with several carbon atoms of PVA. The unpaired electrons are in closer analogy (comparision) to a domain wall and results the conversions in cis-to-trans isomerism [31]. The paramagnetic susceptibility (\(\chi\)) of PVA (Li/Na/K)AgSe: Cr\textsuperscript{3+} (0.2 mol \%) polymer samples at room temperature have been calculated using the formula given in our previous papers [30] and are at 1.96, 4.25, and 1.14 for the three alkali salts. From these values, we noticed that the susceptibility of sodium sample have the high value than the remaining two salts. The high susceptibility may cause the increase in coordination number of Na\textsubscript{2}O atom and results the change in coordination around Cr\textsuperscript{3+} ions to attain more transitions [27].

Table 2: Calculated spin Hamiltonian Parameters of PVA(Li/Na/K)AgSe: Cr\textsuperscript{3+}(0.2 mol \%) polymer films.

| Sample Name                  | g-factor | spin – Hamilton Parameters | \(\chi\times10^6\) |
|------------------------------|----------|----------------------------|-----------------|
| PVALiAgSe:Cr\textsuperscript{3+}(0.2 mol \%) | 1.96     | 0.98                       | 1.96            |
| PVANaAgSe:Cr\textsuperscript{3+}(0.2 mol \%) | 1.95     | 0.45                       | 4.25            |
| PVAKAgSe:Cr\textsuperscript{3+}(0.2 mol \%) | 1.93     | 1.71                       | 1.14            |
3.4 **UV-VIS-NIR spectra studies**

The UV-VIS absorption spectra of PVA (Li/Na/K)AgSe:Cr\(^{3+}\) (0.2 mol %) composites loaded with different alkali chlorate (Li/Na/K) salts are shown in Figure 4. The spectra of all the alkali chlorates exhibit five-band positions around 220, 275, 480, 535, and 1030 nm. In that, the band locations below 300 nm belong to n-π\(^*\) and π-π\(^*\) transitions and the band near to 600 nm belongs to \(^4\)A\(_{2g}\)(F) → \(^4\)T\(_{1g}\)(F) and \(^4\)A\(_{2g}\)(F) → \(^4\)T\(_{2g}\)(F). The optical edge at 220 nm shows the presence of unsaturated C=O/C=C in the tail-head of PVA and the absorption peak at 275 nm was the CT (charge-transfer) band of Cr\(^{6+}\) and Ag-O [32-33]. The bands centered at 480 and 535 nm were attained the presence/existence of Cr\(^{3+}\) ions in the six-coordinate binding sites [34-35]. A single peak in the NIR region at 1030 nm of all the salts was attributed Cr\(^{4+}\) ions in either tetra/octahedral coordination and also due to the Cr\(^{3+}\) to Cr\(^{4+}\) partial oxidation present in the samples [32]. Existing of small shiftings/changes in the band locations when varying alkali salts were due to the formation of inter/intramolecular hydrogen bonding and these results are supported by the XRD studies [33]. The obtained band positions and their band transitions are placed in table 3.

![Figure 4. Uv-Vis-NIR plots of PVA(Li/Na/K)AgSe:Cr\(^{3+}\)(0.2 mol %) polymer films.](image-url)
Optical constants (direct, indirect & urbach energies) of all the chlorate salts were drawn in Fig. 5(a-b) and calculated values are in table 3. In direct bandgap, the energy values for ‘Na & K’ samples are less than the ‘Li’ samples. The indirect bandgap value of ‘K’ salt was significantly decreased when compared with Li & Na salts. The variations in $E_g$ (bandgap) value is a consequence of new energy level generation which was due to the formation of disorder in the PVA(Li/Na/K)AgSe: Cr$^{3+}$(0.2 mol%) polymer films [36]. This leads to an increase in the density of the localized states of the host varied polymer films. The calculated Urbach energy values are 0.81, 3.04, and 2.83 for Li, Na, and K contained composite polymer films. High urbach value of Na and K salts shows the presence of additional defects causes the localized states to overlap and also to extend mobility gap [31]. The above result was supported by the EPR studies.

**Table 3.** Optical band positions and calculated band energy values of PVA(Li/Na/K)AgSe: Cr$^{3+}$(0.2 mol %) polymer films.

| Sample Name | Band Position(nm) | Bandgap Energies(eV) |
|-------------|-------------------|----------------------|
|             | Direct band gap    | Indirect band gap    | Urbach energy |
| PVALiAgSe:Cr$^{3+}$(0.2 mol %) | 220 276 477 537 1024 | 4.46 2.48   | 0.81 |
| PVANaAgSe:Cr$^{3+}$(0.2 mol %) | 219 279 478 533 1027 | 4.23 2.73   | 3.04 |
| PVAKAgSe:Cr$^{3+}$(0.2 mol %) | 215 279 478 533 1027 | 4.20 1.64   | 2.83 |

**3.5 Conclusion**
In the present work, PVA (Li/Na/K)AgSe: Cr$^{3+}$(0.2 mol%) polymer nanocomposites were synthesized through the solution-casting technique with the help of the refluxing procedure. The SEM images reveal that gained particles (rods) size of present polymer composites was ≤ 100 nm. From XRD studies, several diffraction angles observed for PVA (Li/Na/K)AgSe: Cr$^{3+}$(0.2 mol%) polymer films. This shows
the crystallinity of the present polymer films. New planes in XRD are attained may be the increase the degree of crystallinity by the doping salts. In EPR studies, a single broad resonant signal shows for Li and K samples and multiple resonance signals were observed for the Na sample. Cr$^{3+}$ ions with spin 3/2 or 0 shows the single resonance signal and existence of multiple lines may be the increasing coordination number of Na$_2$O atoms available in Na$_2$SeSO$_3$ and NaClO$_4$ components. In-room temperature optical absorption studies, five absorption band positions and there is an effect in band locations with varying alkali salts. Band shifting was due to the incorporation of Cr$^{3+}$ ions with adjacent OH groups.

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