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The Effect of Doping Cr^{3+} Ions on Thermal, Structural and Morphological, Properties of PVP Polymer Electrolytes

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Abstract: — In this work, the method of solution casting were used for the PVP polymer films doped with Cr^{3+} ions at various concentrations (1 to 5 mol%). The TGA, XRD and SEM Characterizations was explained for the structural, thermic and morphology properties of pure and PVP polymer films doped with Cr^{3+}. The thermal stability improvement and three different stages of weight losses of the investigated samples were shows dTG data. The X-ray diffraction explains for the increasing amorphousness of the PVP polymer film due to doping. The morphological studies of PVP polymer films doped with Cr^{3+} is nearly bumpy compared to pure film, suggesting the amorphous description.

Keywords: polymer electrolytes, PVP, TGA, XRD, and SEM

1. Introduction

In electrochemical devices plays a crucial role in the present trends like electrochromic devices, supercapacitors, and energy storage batteries [1-5]. Equated to usual liquid onetime, solid polymer electrolytes can be simple manufactured with many benefits such as security, no leakage, mere cost and simple of synthesis into adjustable shapes [6-8] and reasonable connection at the interelectrode interface in various electronic apparatus [9, 10]. Ionic conductivity at room temperature is a decisive equity of polymer electrolytes for realizing its high-tech uses [5]. Thus, intensive work for directed two from a basic view point to knowledge about a transposition of ions, and also from the view point of applications to improve the key performance indicator on polymer electrolytes. Some other advantage of PVP is acceptable ionic conductivity, flexibility, processability and dimensional stability under environment conditions. These requirements used for various preparation methods.

a synthetic biodegradable polymer of Polyvinylpyrrolidone (PVP) having good characteristics such as optoelectronic devices, excellent solubility in various solvents, resistivity, high charge transfer mechanism, moderate electrical conductivity, thermal stability, and low manufacturing cost of solid polymers batteries and dielectric constant. It is also a high amorphous conjugated polymer that can provide higher ion mobility than other semi-crystalline polymers. The increased dielectric properties of low scattering losses, and predominance of an amorphous nature are due to carbonyl groups (C=O), which leads to a noticeable character of Lewis bases in the side chain of PVP, which leads to the formation of various complexes with various inorganic salts [11]. A high Tg with excellent environmental resistance of PVP. Moreover, it exits outstanding mechanical strength, thermal stability, and high ionic conductivity. The low loss of light scattering due to the amorphous nature of PVP is the justification for the best outcomes in numerous optical usages [3].

Given the significance and pertinence of the PVP polymer as a capable matrix, transition metal ions can be used as a dopant to raise its electrical conductivity and optical absorption. In addition, it should be noted that the extension of transition metal particles within the polymer system contributes to a change in various applications, such as laser systems, integral waveguides, electromagnetic shielding photo electronics, various flexible elements for resistive heating, solid-state Ionics, optical lenses, optical data storage and microelectronics [12-15]. The Cr^{3+} ions provide the superior packing efficiency of the original PVP, which in turn affects the thermal properties of the polymer. Though, to the elegant of our wisdom, there have been no reports on the thermal, structural, and morphological properties of PVP films doped with Cr^{3+} ions. Therefore, the authors undertook the present study. The research aims to develop solid polymer electrolytes based on the significance and relevance of the PVP polymer as a suitable matrix and doped transition metal ions as a promising application in electrochemical devices.

2. Experimental

2.1. Preparation of Electrolytes

The molecular weight of PVP (Aldrich) 3,60,000 was used and $Cr_2 (SO_4)_3. nH_2O$. The prepared samples were using solution casting technique in which double distilled water was used as a solvent. Stock solutions of 5% PVP and various concentrations (1, 2, 3, 4, and 5 mol %) of $Cr_2 (SO_4)_3. nH_2O$ were prepared separately. Wide solutions were continuously stirred individually at room temperature using a magnetic stirrer for one hour until complete dissolution. The aqueous solutions of pure PVP and one of the various concentrations of $Cr_2 (SO_4)_3. nH_2O$ was added and then create a homogeneous and clear solution. Then the mixed solutions were poured into plastic Petri dishes and evaporated at room temperature until polymer films were formed on the bottom of the dishes. The thickness of the prepared sample was obtained by the capacitive method and amounted to about 150 μm.

2.2. Characterization of Electrolytes

Thermal properties of polymer electrolytes were determined using thermogravimetric analysis (TGA). SEIKO thermal analysis system (TGA-20) was used to measure the thermal properties carried out from 30 to 600°C at a heating rate of 10°C/min in the presence of a nitrogen atmosphere. Siemens D5000 diffractometer used to studied in X-ray diffraction (XRD) patterns of the pure and Cr^{3+} ions doped PVP polymer electrolytes. prepared samples were examined under glancing angles in the range of 5° to 80° with a step size of 0.02 using CuKα radiation. Gaussian approximation of the observed wide XRD peaks was done using origin pro 8.0 commercial software packages to estimate the values of 2θ, β, d, and D. The surface morphology of the films observed by Scanning electron microscopy (SEM) was done using JOEL JSM 840A electron microscope with scanning attachment.

3. Results and Discussion

3.1. Thermogravimetric studies

Thermogravimetric analysis revealed the thermal stability and degradability of the prepared samples [16]. The shape of the curve mainly depends upon the order of reaction (n) and activation energy (E). The values of these parameters are essential in estimating samples thermal stability [17]. Figure 1 shows dTG thermograms of pure and different molar concentrations of PVP polymer films doped with Cr^{3+} at a heating rate of 10°C/min in the temperature range from room temperature to 600°C. Fig.2 shows the TGA/dTG curves of 5 mol % of Cr^{3+} doped polymer film. The dTG and TGA curves of the polymer electrolytes of the present invention showed that the thermal stability completed the degradation process in three main phases of weight loss. The first decomposition was accompanied by a slight weight loss (6-9%) in the range of 47-135°C, which is due to the fact that the water has completely evaporated or has undergone a dehydration process in this area. The moisture content of the samples affects the percentage of initial weight loss. Saadiah et al. [18] and Ahmad and Isa [19] reported a similar observation where the first phase corresponds to a decrease in sample moisture due to evaporation and dehydration, which contributes to the initial weight loss.

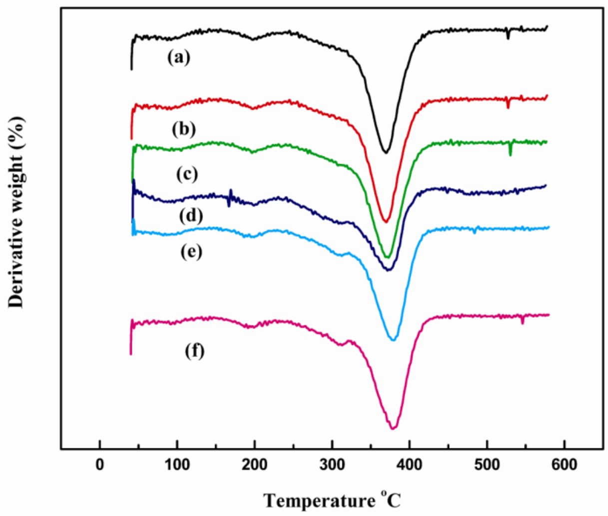

Fig.1. thermograms of dTG (a) pure and (b) 1 mol%, (c) 2 mol%, (d) 3 mol%, (e) 4 mol% and (f) 5 mol% PVP polymer films doped with Cr^{3+}.

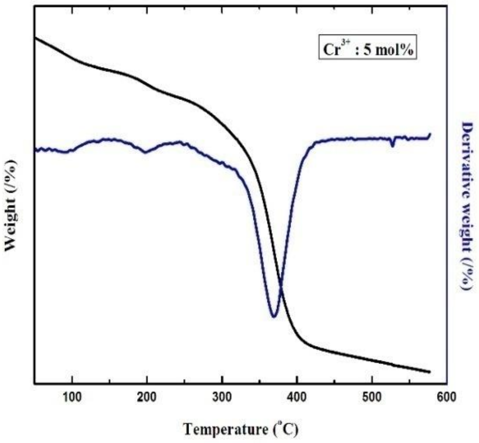

Fig.2.The curve of TGA/dTG in 5 mol% PVP polymer films doped with Cr^{3+}.

The second weight loss happens in the range from 153 to 237°C, with a weight loss of 5-15%, including the melting temperatures of the host polymer and decline temperatures [20]. The third significant weight loss (49-67%) was observed in the range of 307 to 443°C for the prepared samples. CO_2 from the carboxylate groups (C=O) in the PVP backbone is degraded, resulting in a dramatic drop in weight loss [3]. The decrease in weight loss shows that when Cr^{3+} ions are added to this system, the decomposition temperature for the entire system begins to increase, which may correspond to the structural decomposition of the polymer and their complexes upon addition of Cr^{3+} to the PVP film. The decomposition steps of all the samples and the percentage of weight loss of pure and PVP polymer films doped with Cr^{3+} were given in Table 1.

Table 1. Degradation stages and percent weight loss for pure and various concentrations (1.0, 2.0, 3.0, 4.0 and 5.0 mol %) of PVP polymer films doped with Cr^{3+}.

Concentration in mol% Cr^{3+}: PVP	Temperature (°C)			Weight loss (%)	
	Start	End	T_P	Partial	Total
Pure PVP	55	109	90	8.0	83.4
	176	227	198	8.6	
	322	418	368	66.8	
1	47	128	91	8.8	81.3
	165	236	198	15.0	
	319	422	369	57.6	
2	50	135	101	9.2	77.6
	153	228	198	11.5	
	307	432	372	56.1	
3	48	121	89	9.1	74.2
	169	231	196	8.6	

	323	**420**	**373**	**49.8**	
4	**50**	**118**	**97**	**8.8**	**72.6**
	157	**227**	**198**	**8.5**	
	325	**428**	**381**	**48.6**	
5	**48**	**128**	**94**	**6.3**	**70.3**
	160	**237**	**196**	**4.5**	
	333	**443**	**376**	**59.0**	

It is observed that the peak temperature of the final decomposition step of pure and doped samples varies from 368°C to 381°C. It is believed that there was a breakdown of the bond break in the main PVP chain. It has been established that the value of the total weight loss decreases with an increase in the dopant concentration from 1 to 5 mol.%, which indicates an increase in thermal stability. XRD phase analysis also confirms that the amorphous nature results in an increase in the flexibility of polymer electrolytes, which facilitates ion transport.

2. study of X-ray diffraction

X-ray diffraction investigations were carried out to study the crystallinity of the prepared electrolytes. Figure 3 shows X-ray diffraction patterns of pure and various concentrations of PVP polymer films doped with Cr^{3+}. In Fig.3, two weak peaks at about $2\theta = 11.87°$ and 16.37° are observed for pure and doped films. Aboud and Mahmoud reported weak diffraction peaks of the amorphous nature of PVP polymer at $2\theta = 11.87°$ and 16.37°, which is similar to the peaks present in our studies [21].

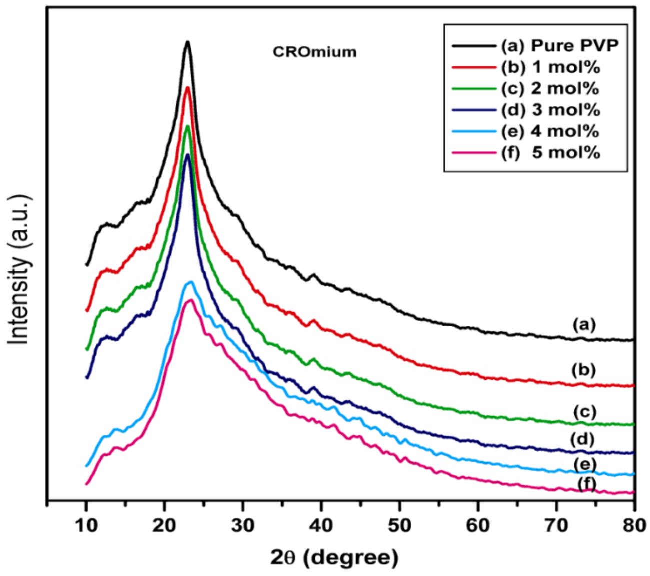

Fig. 3. XRD shows (a) pure and (b) 1 mol%, (c) 2 mol%, (d) 3 mol%, (e) 4 mol% and (f) 5 mol% PVP polymer films doped with Cr^{3+}.

A suggestive peak at 2θ = 22.84°, which is relatively sharp, denotes the semi-crystalline character of polymer films. This result is in good consensus with the already report by Rajesh et al. [22] on the polymer CMC with the main diffraction peak of a semi-crystalline nature at 2θ = 21.5°. X-ray diffraction patterns of these amalgams containing Cr^{3+} ions showed a noticeable reduction in intensity compared to pure PVP polymer.

The changes might be due to the polymer and dopant interaction, which increases the amorphous phase of the polymer electrolyte system [23]. The PVP polymer creates free volume space and a chance for ions relocation when more with a dopant. The decrease in polymer film crystallinity with increasing dopant concentrations may be due to the interaction of Cr^{3+} ions with the end chain of the polymer [24]. Most of the literature reported the continual rise in the conductivity of polymer films with the incorporation of dopant [25], which indicates the decrease in the degree of crystallinity.

Interplanar spacing (d) between planes and average crystallite size (D) of the crystalline phase of samples can be assessed using the Bragg law [26] and the Scherrer equation [27], respectively, where λ indicates wavelength of X-ray radiation, θ indicates the angle of diffraction and β indicates the full width at half maximum (FWHM) in radians unit.

$$2d \sin\theta = n\lambda \qquad \ldots\ldots \qquad (1)$$

$$D = \frac{0.94\,\lambda}{\beta \cos\theta} \qquad \ldots\ldots \qquad (2)$$

Using a Gaussian fit of the followed broad XRD peaks (Fig. 3), the assessed values of 2θ, β, d and D for pure and Cr^{3+} doped PVP composites are presented in Table 2. The crystallite size D of the spherulites of the samples doped with Cr^{3+} turned out to be considerably smaller than that of pure PVP. A decrease in the coherent length convincingly indicates a decrease in the degree of crystallinity due to the dislocation of the size of pure PVP spherulites due to its complexation with Cr^{3+} ions in their composites in an amorphous structure. From these diffractograms, the coherence length was calculated using Eq. (2). The results showed that with increasing dopant concentration, the coherent length decreases, i.e., the amorphous nature of the sample increases due to the length decreases [28].

Table 2. Full-width Half maximum (FWHM) (β) and Bragg's angle (2θ) and also d spacing and crystallite size (D) of pure and PVP polymer films doped with Cr^{3+}.

PVP: Cr^{3+} concentration (mol%)	2θ°	β (rad)	d (nm)	D (nm)
pure	22.94	0.046	0.388	3.046
1	22.96	0.0457	0.386	3.100
2	22.94	0.046	0.388	3.046
3	22.95	0.0469	0.3871	3.08

4	23.38	0.149	0.381	0.950
5	23.46	0.1510	0.3793	0.937

3. Morphological studies

The scanning electron microscope (SEM) is an instrument that creates magnified images that reveal microscopic-scale information on the size, shape, composition, and other physical and chemical properties of a specimen. Morphological studies of the pure and PVP polymer films doped with Cr^{3+} (1.0, 2.0, 3.0, 4.0, and 5.0 mol %) considered by the SEM approach is exhibited in Fig. 4 (a-f). The pure PVP surface was a soft and uniform smooth surface, as shown in Fig. 4 (a). The extension of Cr^{3+} ions cause a significant change in the surface morphology of the polymer film, as shown in Fig. 4 (b-f). When Cr^{3+} ions are added to the PVP, surface roughness is improved, and the modified surface is observed. This indicates that the Cr^{3+} ions disperse in the soft-segment phase with little influence on the microphage separation and mixing of the hard and soft segments.

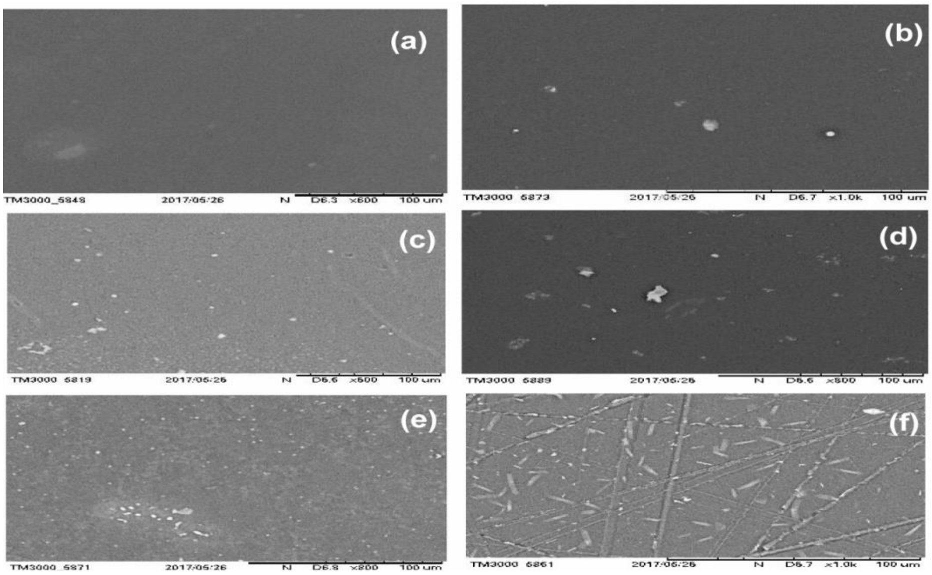

Fig. 4. images of SEM (a) pure and (b) 1 mol%, (c) 2 mol%, (d) 3 mol%, (e) 4 mol% and (f) 5 mol% PVP polymer films doped with Cr^{3+}.

From Figures 4(b), 4(c), 4(d), 4(e) and 4(f), the extension of Cr^{3+} ions generate significant change in the morphological studies of the tested polymer films is due to the agglomerates of Cr^{3+} ions, which increases with raising the concentration of Cr^{3+} ions. Also, the Cr^{3+} ions are dispersed consistently with no aggregation (Figures 4(b-d)), and a low degree of aggregation of Cr^{3+} ions show the roughness of the film increases with the increase of the content of Cr^{3+} ions (Figures (4e and 4f)). This indicates the segregation of Cr^{3+} ions in the host matrix, which may confirm the interaction and complexation between the additive and the polymer [29]. The increase of Cr^{3+} ions in the polymer film leads to a more amorphous phase in the system and make the polymer film more flexible [30]. These morphological changes are indicative of the interaction of the microparticles with the polymer, depicting excellent compatibility between transition metal ions in the micro composite samples.

3.4. Conclusions:

The effect of doping Cr^{3+} ions on PVP polymer electrolytes obtained by a method of solution casting technique shows that the dTG curve of the thermal stability was improved after adding Cr3+ ions to the pure PVP. All the prepared films show three different stages of weight loss, due to the loss of adsorbed water, the side chain decomposition, and the decomposition of main chain carboxylate groups. In the X-ray diffraction, two weak peaks at about 2θ = 11.87° and 16.37° are observed and a significant peak at 2θ = 22.84°, which is moderately sharp, indicates the semi-crystalline nature of polymer films. The XRD pattern showed a broadening of the peaks with increasing dopant concentration reveals the increase of amorphous fraction. The SEM images of doping Cr^{3+} ions on PVP polymer electrolytes disclosed the presence of structural reorganization of polymer films. This indicates that the Cr3+ ions doped PVP polymer electrolytes are considered the potential materials for the fabrication of electrochemical devices and solid-state batteries.

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