RESEARCH PAPER

Study Effect KPF_6 Salt and TiO_2 Nanocomposite on the Characteristics of PVP Polymer Electrolyte

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ABSTRACT

Polymer poly vinyl pyrrolidone (PVP) was doped with Potassium hexafluoro phosphate (KPF_6) and TiO_2 nanomaterials for different weight ratio (0, 10, 20) % were prepared by cast solution method to produced thin films of PVP/KPF_6, PVP/TiO_2 and PVP/KPF_6-TiO_2. The characterization of thin films such as TGA analysis and the absorption spectra of thin films at the range wave number (300-800) nm were studied. It is found that the weight loss for polymer PVP was decreased with increase of weight ratio for added KPF_6 but it has no effect with increase TiO_2 nanocomposite. For absorption spectra we see that adding TiO_2 nanocomposite to the polymer PVP is better than of KPF6 salt. And the energy gap for thin films decreases with increases nanocomposite and salt, the best result was for adding mixing of KPF_6 salt with TiO_2 nanocomposite to polymer PVP which was equal to 1.1eV for the weight ratio 20% of PVP/KPF_6-TiO_2 thin films.

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INTRODUCTION

In general Polymer materials are the materials of the new era have important properties as light weight, low cost and easy processibilty. These polymeric materials can be used as a polymer electrolyte in rechargeable batteries or solid state devices [1], in super capacitors [2], smart windows [3], gas sensors [4], etc. The polymer can be blended with another polymer or a dopant so as to improve its properties. Studies on optical properties of these polymers have attracted much attention in different application in optical and electronic devices [5, 6]. Adding the materials as doping to polymers leads to change and improves their optical properties by charge transport of doped polymer electrolyte films [7].

The polymer poly vinyl pyrrolidone (PVP) is soluble in water and other solvents, Chemical formula was $(C_6H_9NO)_n$, melting point equal to 150°C and the density is 1.2 g/cm^3. It is a light flaky hygroscopic as a dry powder, readily absorbing up to 40% of its weight in atmospheric water. In solution, can be used it as a coating or an additive to coatings because of it has excellent wetting properties and readily forms films [8]. The electrical properties of polymer PVP can be improved with the incorporation of cupric sulphate (CuSO), as it has the capacity to significantly modify the electrical and optical properties of a material. The ionic nature of CuSO causes it to dissociate into Cu^{2+}, and SO^{2-} ions in aqueous solution and these ions are responsible for the conductivity of the host polymer [9].

The aim of project was study the effect of KPF_6 salt and TiO_2 nanomaterials on the polymer PVP as thin films polymers. This study was represented by

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determine TGA analysis and the energy gap from the optical properties for thin films polymers.

MATERIALS AND METHODS

The electrolyte solution of polymer PVP were prepared by dissolving PVP with each of KPF_6 and TiO_2 in distal water for different weight ratio (0, 10, 20) %. This solution was mixing using hotplate stirrer for 120 min with 600rpm at room temperature. After that thin film for different weight ratio was then prepared on glass substrate (1.5 X 2.5) cm^2 by cast Solution method and put at room temperature for (24 h.) to get polymerized homogeneous solid films of doped polymer PVP. The solid thin films were put on hot plate for 30 min to do annealing for it at 70°C. To measure thickness of the films was that by using (digital thickness gauge meter) where the films put on the stainless steel substrate, table 1 describe the weight ratio with thickness for all types of thin films. The optical measurements were recorded at room temperature using (T80-uv/vis. Spectrophotometer) in wavelength range from (300-800) nm

RESULTS AND DISCUSSION

Thermal gravimetric analysis (TGA):

A thermal gravimetric analysis of polymer thin

Table 1. show the weight ratio for prepared thin films.

No.	PVP	KPF_6	TiO_2	W%	d(μm)	symple
1	1	0	0	0%	0.67	A
2	0.09	0.01	0	10%	0.77	B
3	0.09	0	0.01	10%	0.74	C
4	0.08	0.02	0	20%	0.56	D
5	0.08	0	0.02	20%	0.6	E
6	0.08	0.01	0.01	20%	0.65	F

Table 2. TGA analysis for polymeric films.

No.	films	W%	Decomposition	Temperature range (°C)		Weight loss%	
				start	end	partial	Total
1	PVP	0%	1st	40	165.38	6.997	
			2nd	165.38	522.09	80.668	91.502
			3rd	522.09	900	3.837	
2	PVP/KPF_6	10%	1st	40.02	167.15	7.391	
			2nd	167.15	516.8	73.307	90.981
			3rd	516.8	900	10.283	
3	PVP/TiO_2	10%	1st	40	170.68	7.412	
			2nd	170.68	513.26	68.595	81.544
			3rd	513.26	900	5.537	
4	PVP/KPF_6	20%	1st	40	239.55	23.837	
			2nd	239.55	515.03	54.641	85.879
			3rd	515.03	900	7.401	
5	PVP/TiO_2	20%	1st	40.48	179.51	7.464	
			2nd	179.51	506.20	58.031	81.337
			3rd	506.20	900	15.842	
6	PVP/KPF_6-TiO_2	20%	1st	40	175.98	6.194	
			2nd	175.98	518.56	75.688	89.333
			3rd	518.56	900	7.451	

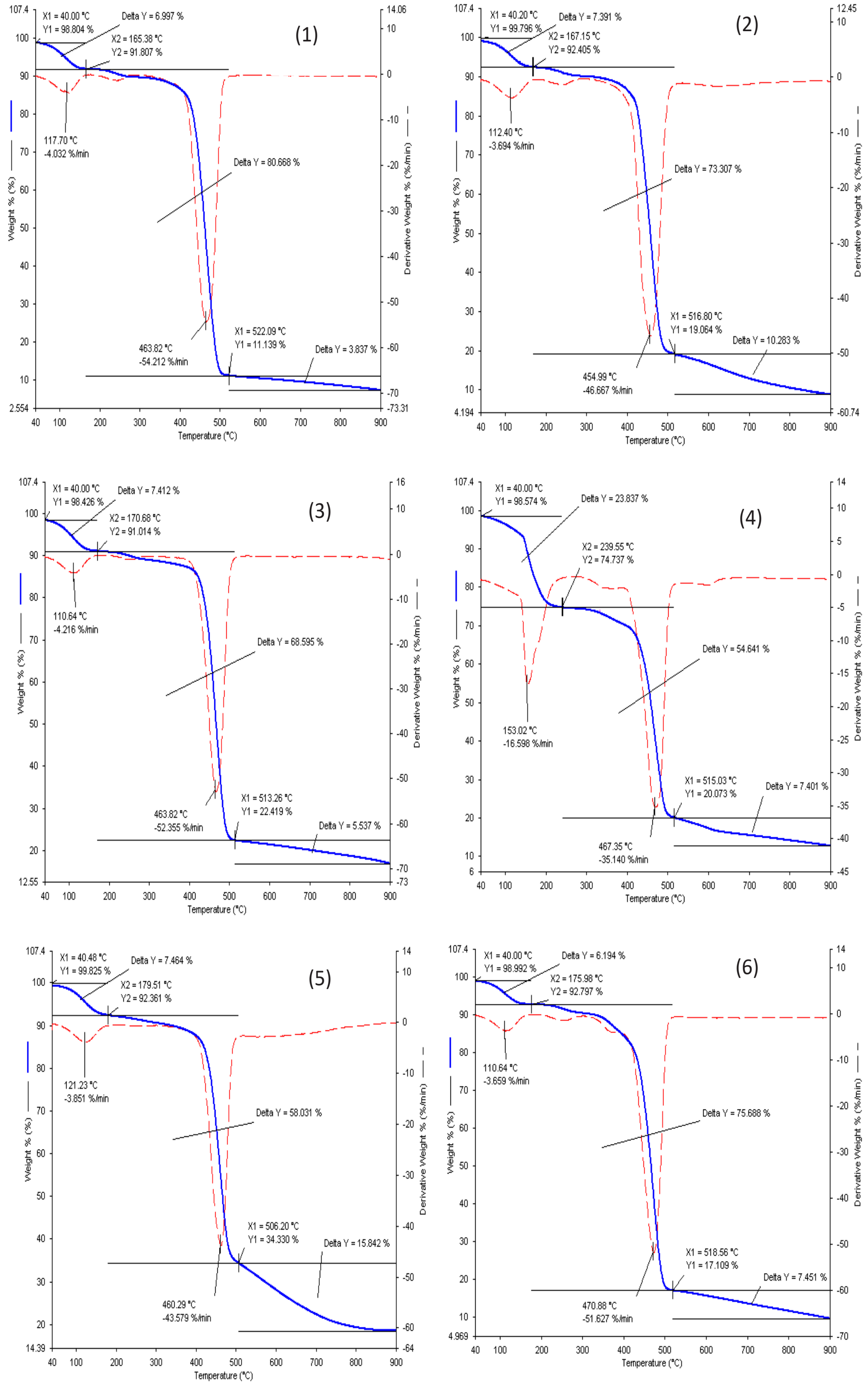
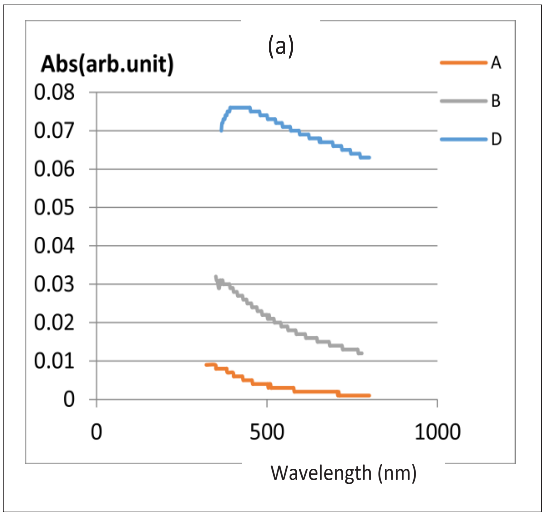


Fig. 2. Fig. 1. show TGA thermogram of polymers thin films



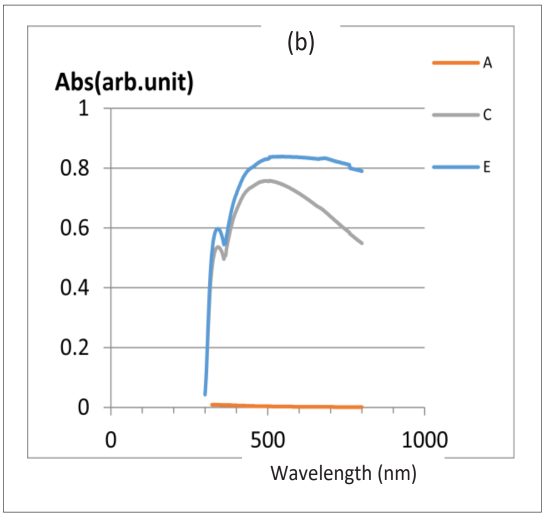


Fig. 2. show the relationship between the Absorption spectra as a function of the wavelength: a) for PVP/KPF_6 , b) PVP/TiO_2.

films of PVP/KPF_6, PVP/TiO_2 and PVP/KPF_6-TiO_2 were done by Perkin Elmer (TGA4000) under nitrogen atmosphere, 20ml/min gas flow rate and 20^{o}C/min. In this case TGA is a useful analytical technique to asses thermal stability of materials thin films by recording weight loss of a sample as a function of temperature [10, 11]. Fig. 1 show TGA thermogram of polymers thin films, from Fig. 1 we see that PVP undergoes two decomposition steps ,the first occurs at temperature range of (40-165.38)^{o}C with weight loss of 6.997% that represents the loss of residual solvent and low molecular weight oligomers. The second decomposition step occurs at temperature range of (463 – 522.09) ^{o}C with weight loss of 80.668% that represents the decomposition of PVP. Also for all thin films can be insert the effect KPF_6 and TiO_2 on polymer PVP in table 2, If we compared between PVP and all films that containing on KPF_6 and TiO_2 for different weight ratio we see that the

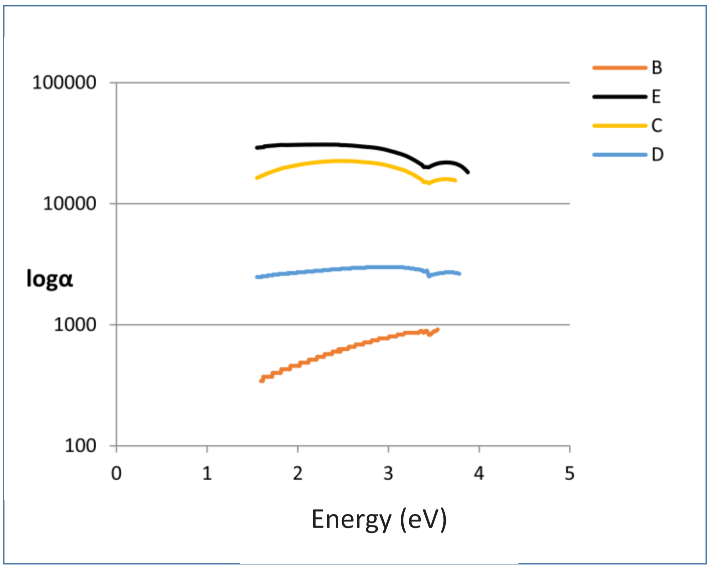


Fig. 3. show the relationship between the Absorption coefficients as a function of the energy.

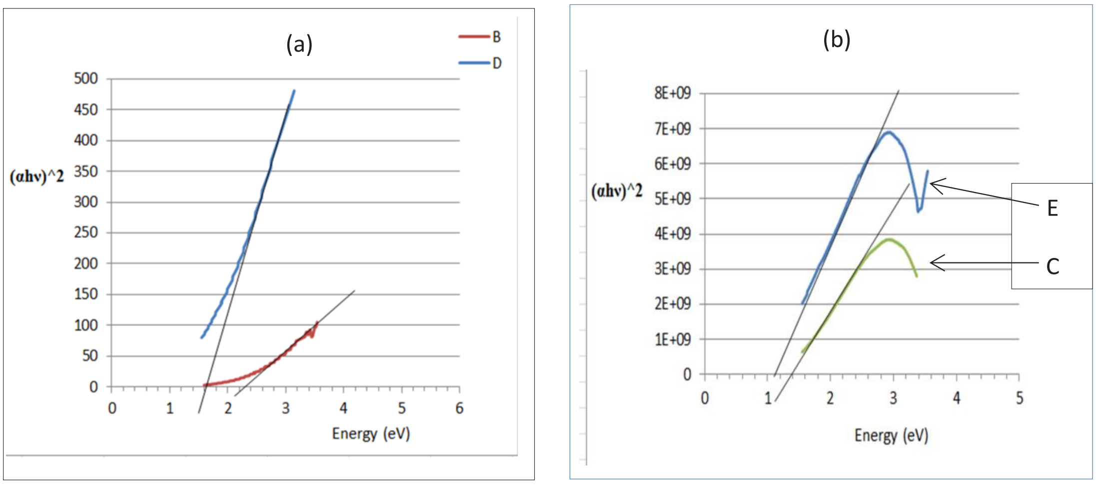


Fig. 4. Show the relationship between $(\alpha h\nu)^2$ as a function of the energy for: a) PVP/KPF_6 , b) PVP/TiO_2.

Table 3. show the energy gap for PVP/KPF_6 and PVP/TiO_2.

symple	W%	Type	Eg(eV)	Ref.
A	0%	PVP	3.88	[15]
B	10%	PVP/ KPF_6	2.3	Current work
C	10%	PVP/ TiO_2	1.4	Current work
D	20%	PVP/ KPF_6	1.6	Current work
E	20%	PVP/ TiO_2	1.1	Current work

weight loss was decreases with increase of weight ratio for added KPF_6 but it's don't effect with increase TiO_2 nanocomposite.

Optical Properties

The Absorption spectra of thin films at the range wave number (300-800) nm were studies using spectrophotometer type (T80 UV/Vis Spectrometer). Fig. 2 show the relationship between the Absorption spectra as a function of the wavelength for PVP after adding KPF_6 salt and TiO_2 nanocomposite for it. From Fig.2a we see that decreases in the absorption spectra with increase wavelength for all ratios, but its increases with increase the ratio of KPF_6 from (0.008) at the wavelength (354) nm to (0.076) at the wavelength (442) nm. And when replaced KPF_6 with TiO2 nanocomposite as Fig. 2b, we get on better result represented by increases in the absorption spectra with increase weight ratio of added, the maximum absorption was (0.838) at the wavelength (556)nm. The materials can be crystalline and amorphous and having energy band gap (BG) that can be determined using the optical absorption spectrum. The electrons will be excited from the VB to the CB by the absorption spectrum to tackle the nature and quantification of the energy (BG). In this case the absorption coefficient (α) can be determined using the relation [12, 13]:

$$\alpha = \frac{2.303}{d} A \qquad (1)$$

Where: d is the film thickness and A is the optical Absorbance.

Fig. 3 represent the relationship between Log(α) as a function of energy, The data of absorption coefficient lead to obtain on the energy band gap which is depend on the theory of Bardeen et all[14]:

$$\alpha = B\frac{(h\upsilon - Eg)^{r}}{h\upsilon} \quad (2)$$

Where, r is equal to (1/2, 2/3, 2 or 3) and ,Eg, is the optical energy band gap. The plot of $(\alpha h\nu)^2$ versus the energy (photon energy) are shown in Fig. 4, from figure we determine the energy gap by intercept with x-axis and its increases with increase the weight ratio each of KPF_6 and TiO_2 nanocomposite (Table 3). From table we see that the added of TiO_2 nanocomposite to polymer PVP was better than added KPF_6 salt as thin films that clear in value of the energy gap.

CONCLUSION

For study TGA, If we compared between PVP and all films that containing on KPF_6 and TiO_2 for different weight ratio we see that the weight loss was decreases with increase of weight ratio for added KPF_6 but it's don't effect with increase TiO_2 nanocomposite. For study Absorption spectra, we see that the best result was for added TiO_2 nanocomposite to polymer PVP if we compared it with KPF_6 salt, where the maximum absorption was (0.838) for added TiO_2 nanocomposite but for added KPF_6 salt the absorption value was (0.076).

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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