The Effect of Cesium Chloride on Thermal Properties of Poly (Vinyl Alcohol)

Nadia Azeez Betti
Materials Engineering Department, University of Technology/Baghdad
Email:chemistforever3@gmail.com

Received on:4/4/2016 & Accepted on:22/6/2016

ABSTRACT

Poly (vinyl alcohol), PVA for short, films doped with different concentrations of cesium chloride (CsCl) (0% , 2% , 4% , 6% , 8% , 10% , 12% , 14% ,16%) were prepared by solution casting method to study the effect of this salt on thermal properties of PVA by using thermogravimetric analysis (TGA) .It was found that the doped PVA films with concentrations (14% and 16%) of CsCl are more thermal stable than PVA while doped PVA films with concentrations (4% and 6%) of CsCl are less thermal stable than PVA and the doped PVA films with concentration of (2% , 8% , 10% and 12%) are almost as thermal stable as PVA. Fourier transform infrared spectroscopy (FTIR) was also used to investigate complexation between CsCl and PVA and was found that the doped PVA films with concentration (2% , 4% , 6% and 8%) of CsCl show no significant shifts in wave numbers of the characteristic bands of PVA while doped PVA films with concentrations (10%, 12% ,14% and 16%) of CsCl show a significant shifts to a higher values in wave number of stretching vibration of (-OH) comparing to PVA indicating well complexation between CsCl and PVA.

Keywords : Poly vinyl alcohol , Cesium chloride, TGA, FTIR , Thermal stability.

INTRODUCTION

In recent decades synthetic polymers have rapidly replaced traditional construction materials such as steel and non ferrous metals. synthetic polymers have many industrial applications due to its unique physical properties. One weak aspect that drawback polymers is susceptibility to high elevated temperatures in comparison with metals ,so design engineers should have well understanding of thermal response of materials including polymers[1]. The properties of polymers may be improved by adding suitable dopant[2]. PVA has many applications in biomedical fields due to its solubility in water and being a biodegradable polymer[3].

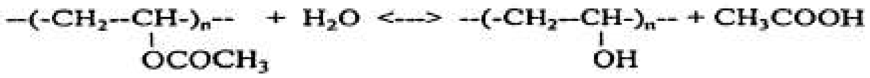
PVA has the following structure:

scheme(1):chemical structure of PVA

The hydroxyl groups of PVA are highly interconnected by H- bonding leading to high glass transition and melting temperature.

PVA is synthesized by hydrolysis of poly vinyl acetate :

https://doi.org/10.30684/etj.34.12A.3
2412-0758/University of Technology-Iraq, Baghdad, Iraq



$$--(-CH_2--\underset{OCOCH_3}{CH}-)_n-- \;+\; H_2O \;\longleftrightarrow\; --(-CH_2--\underset{OH}{CH}-)_n-- \;+\; CH_3COOH$$

Hydrolysis degree and acetate group affect crystallinity of PVA and hence its physical and thermal properties[4].Salts as dopent can modify optical ,electrical and thermal properties of PVA [5,6]. CsCl is alkali metal salt with high solubility in water and low toxicity and widely used in nuclear medicine application, manufacturing of electrically conducting glass, screen of cathode ray tubes and manufacturing of mineral water. Singh R. *et al* [7] studied thermal decomposition behavior of nano composite synthesized by embedding transition metal salts in PVA and they found according to TGA that these composites exhibit an increase in thermal stability and shift in the decomposition temperature of PVA. Nouh S. A. et al [8] found that PVA doped with $NiCL_2$ decomposes in one main break down stage and also found that $NiCL_2$ increases thermal stability of PVA if the concentration of this salts is(8% and up to 20%). Ahad N. et al[9] studied thermal stability of PVA doped with sodium salicylate and they found that the thermal stability increased with addition of sodium salicylate.

In this research we focus on the role of cesium chloride in modifying thermal properties of PVA since the latter is good hosting materials due to its chemical resistance and good film forming ability.

Experimental part

Preparation:

PVA from(barcelona assay 99.9%) and CsCl from fluka were used to prepare thin films of PVA with different concentrations of this salt (0%, 2%, 4%, 6% ,10% , 12%, 14% and 16%) denoted as(a, b, c, d, e, f, g, h and i) respectively. PVA film was prepared by dissolving a certain amount of PVA powder in distilled water and stirred vigorously at 85 ^{0}C . Doped PVA films were prepared as the way of preparing PVA film except adding a solution of CsCl of certain concentration drop by drop to PVA solution at 85^{0}C with vigorous stirring to form the wanted concentration of doped PVA films . After fine mixing ,the solutions were poured into petri dishes and left for (14) days to dry and then peeled off to be characterized.

Characterization:

a)Fourier transform infrared (FTIR):

The spectra of PVA and doped PVA films were investigated by employing (Tensor - 27 Bruker) in the range (4000 - 400 cm^{-1}) .

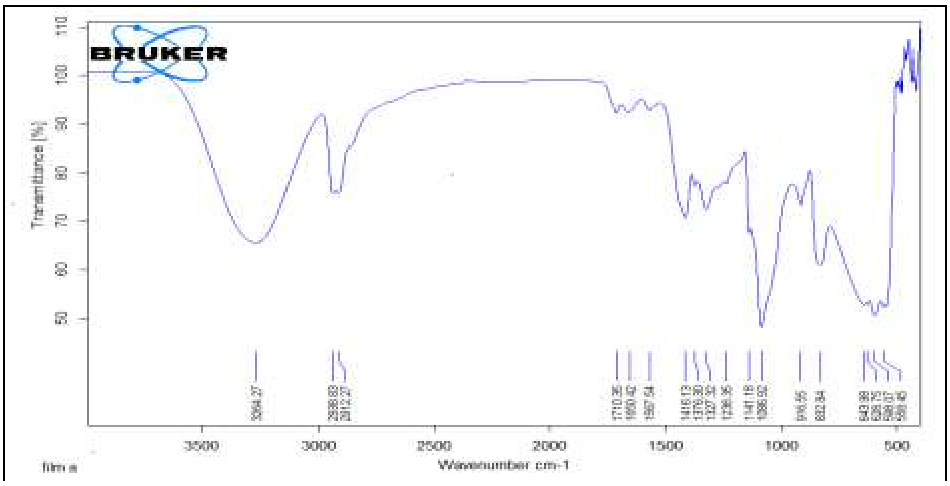
b)Thermogravimetric analysis(TGA) :

Thermal stability of PVA and doped PVA films were investigated by employing(STA PT - 1000 linseis) .The temperature range was from ambient temperature to 600 ^{0}C at heating rate of 10^{0}C /min under helium stream.

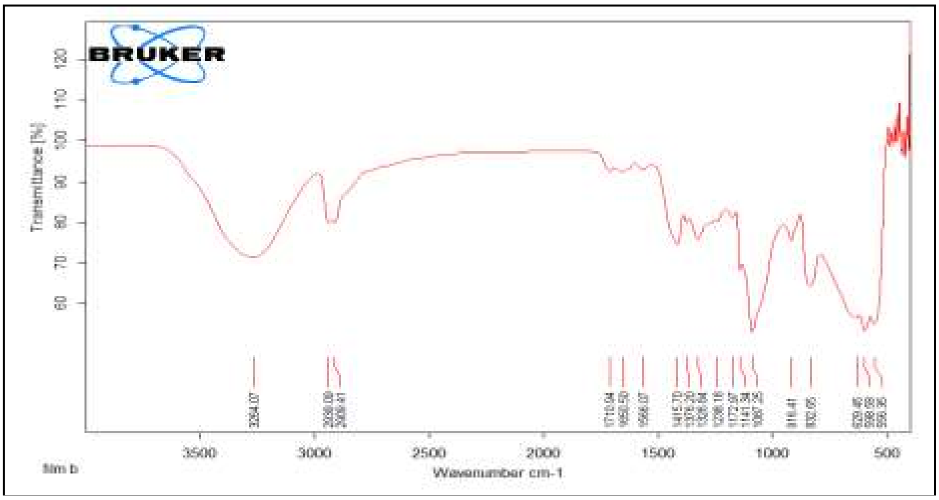
Results and Discussion

1)FTIR absorption spectra:

FTIR absorption spectra were used to investigate the complexation between PVA and CsCl. Figures (1-9) show FTIR spectra of PVA and doped PVA films :



Figure(1): Film a



Figure(2) : Film b

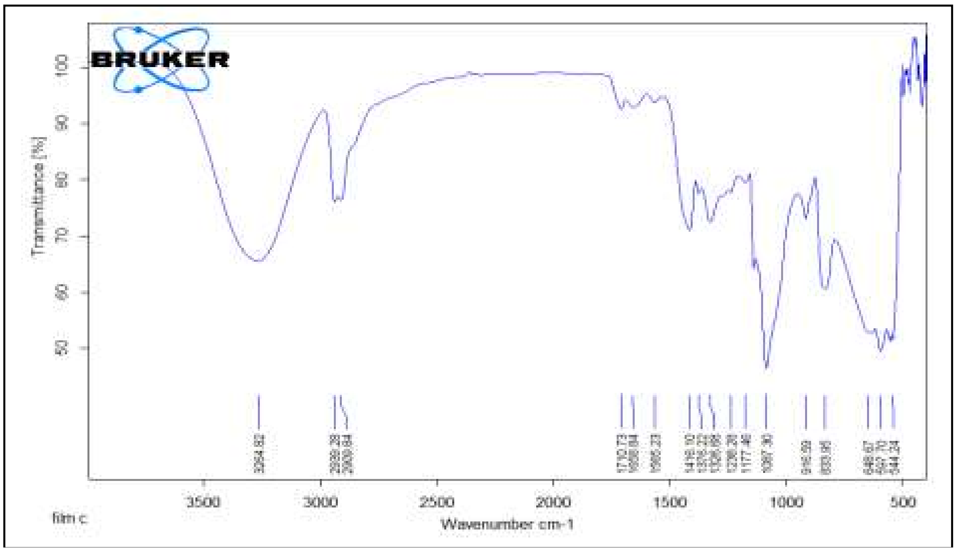
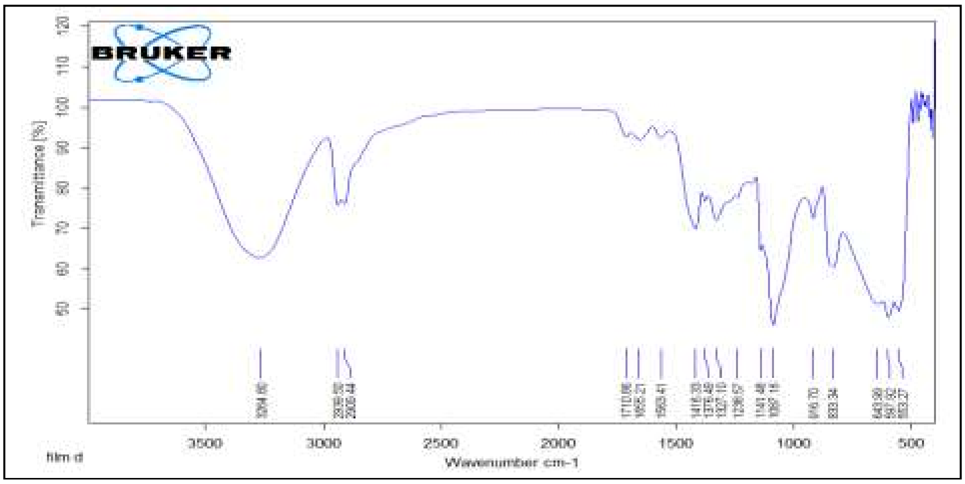
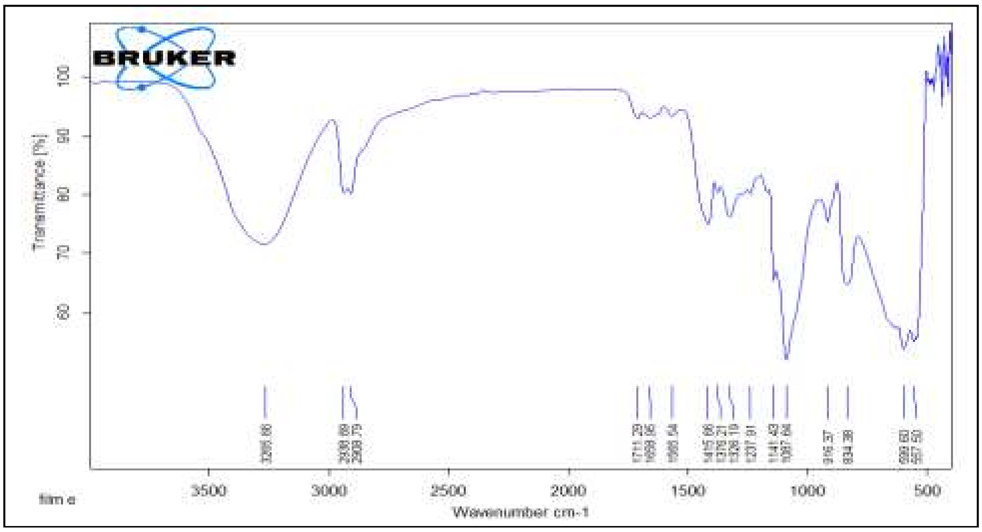


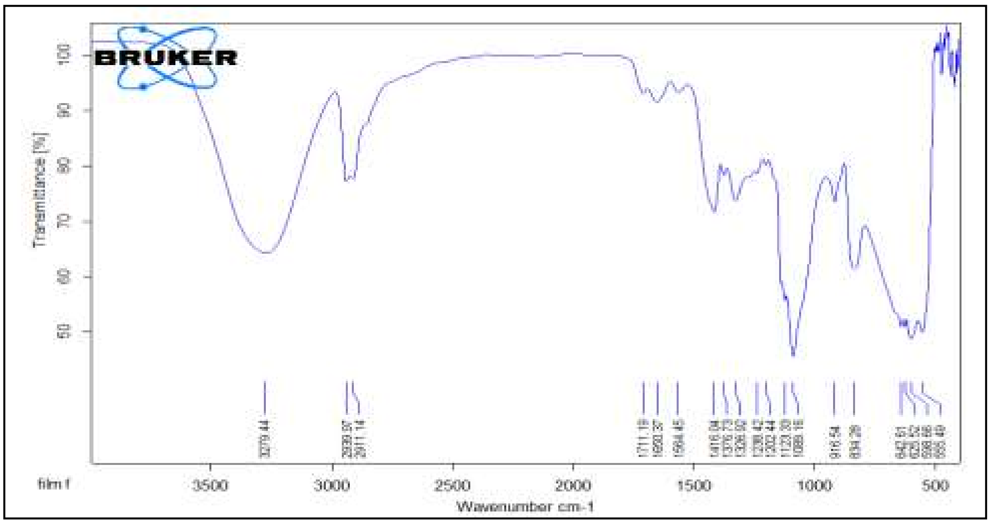
Figure (3): Film c



Figure(4): Film d



Figure(5): Film e



Figure(6): Film f

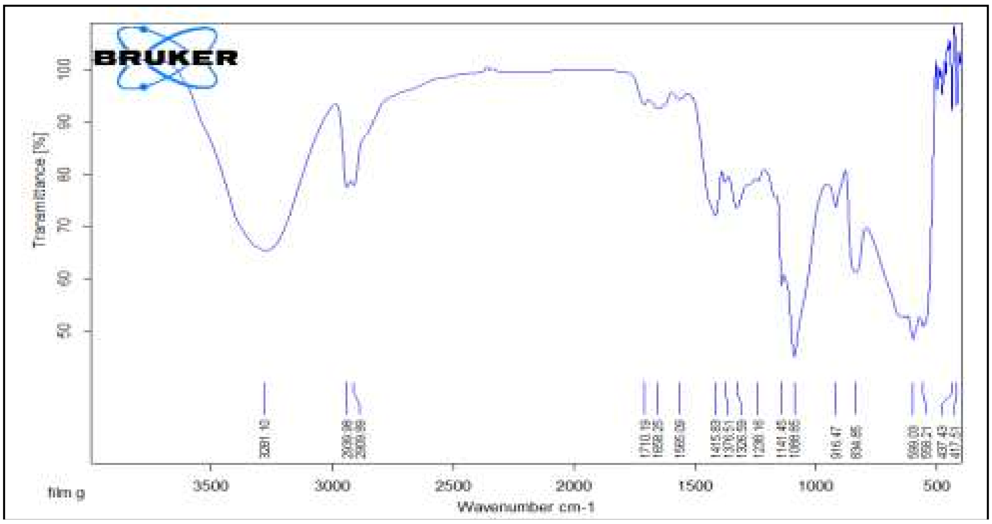
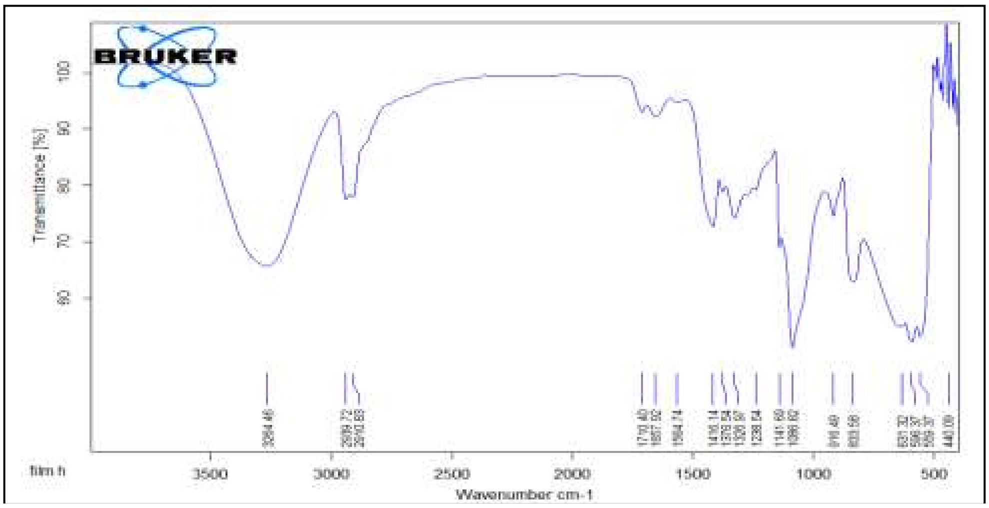
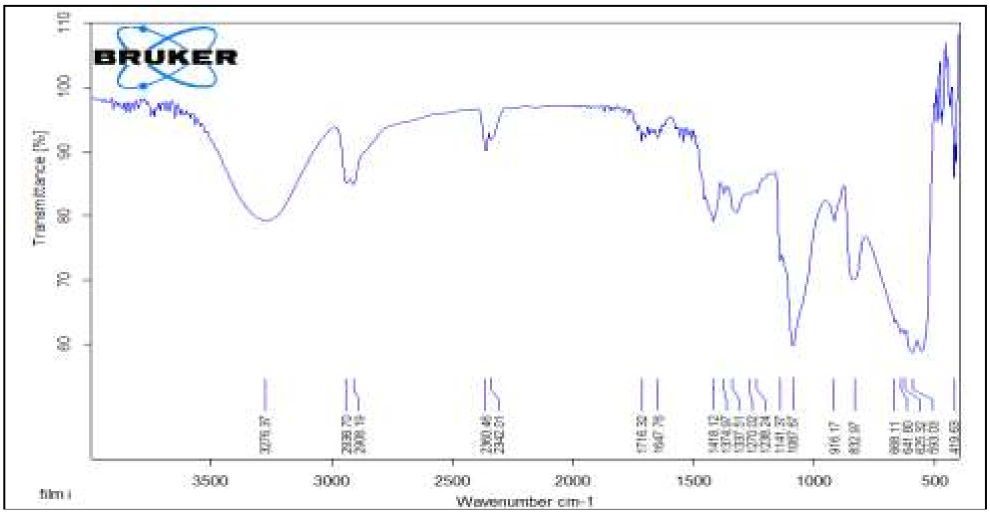


Figure (7): Film g



Figure(8): Film h



Figure(9): Film i

FTIR absorption spectra of PVA exhibit band at 3264 cm^{-1} which assigned to stretching vibration of (-OH) while the two bands at 2938 and 2912 cm^{-1} are assigned to asymmetric and symmetric stretching vibration of ($-CH_2$) respectively. The bands at 1710 and 1567 cm^{-1} represent the absorption of (-C = O) of residual acetate group since PVA is prepare by hydrolysis of poly vinyl acetate as mentioned earlier . The band at 1650 cm^{-1} is assigned to absorbed HOH [10].The band at 1416 cm^{-1} is assigned to symmetric bending mode of ($-CH_2$)or to inner face bending of (-OH). The bands at 1376 is assigned to wagging vibration of ($-CH_2$) and 1238 cm^{-1} is attributed to symmetric twisting of ($-CH_2$)[11].The band at 1141cm^{-1} commonly named crystallization sensitive band of PVA that used to measure the degree of crystallization[12] .The band at 1080 cm^{-1}C is assigned to (C-O)stretching vibration of ether group while the bands at 916 , 832 and 643 $cm^{-1}$are assigned to rocking vibration of ($-CH_2$),stretching vibration of (C-C)and out of plane bending of (O-H)respectively[13].

Table(1) FTIR bands assignments and its wave numbers of PVA and doped PVA films

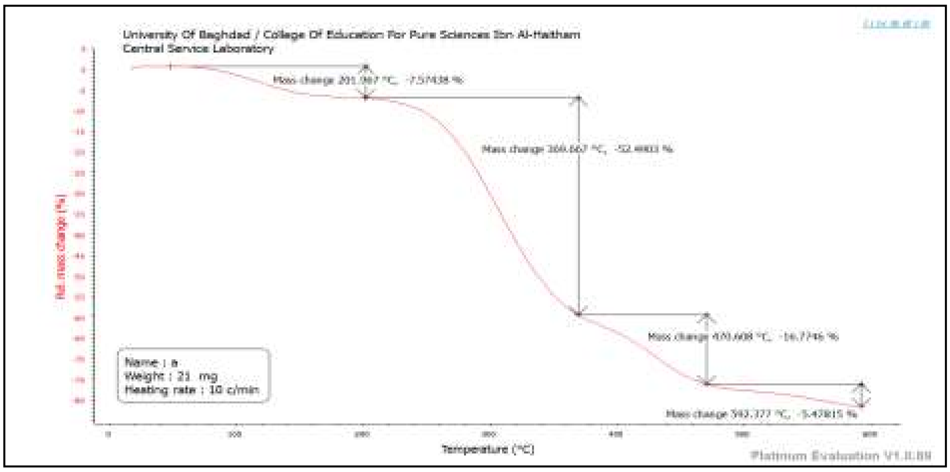
Flm	Str.vib. of O-H	Asy.str.of-CH_2	Sym.str. of -CH_2	Str.vib.of C= O	Absorbed HOH	Bending(-CH_2)	Wag. of - CH_2	Sym.twis.of -CH_2	Cry.sens.band	Str.vib.of C-O-C	Rock.vib. of -CH_2	Str.vib. of C-C	Out of plane bending of -OH
a	3264	2938	2912	1710 1567	1650	1416	1376 1327	1238	1141	1086	916	832	643 628 598
b	3264	2939	2909	1710 1566	1650	1415	1376 1326	1238	1141	1087	916	832	629 598
c	3264	2939	2909	1710 1565	1658	1416	1376 1326	1238	_	1087	916	832	648 597
d	3264	2939	2912	1712 1574	1652	1416	1376 1327	1238	1141	1087	916	832	630 598
e	3265	2938	2908	1711 1565	1658	1415	1376 1326	1237	1141	1087	916	834	599 557
f	3281	2939	2912	1713 1567	1650	1415	1376 1326	1238	1141	1086	916	833	590 556
g	3281	2939	2909	1710 1565	1658	1415	1376 1326	1238	1141	1088	916	834	558
h	3281	2940	2914	1709 1563	1649	1415	1377 1326	1238	1141	1088	916	832	598
i	3280	2940	2911	1713 1565	1648	1415	1376 1326	1238	1141	1087	916	834	641 597

Films(f, g, h, i) show shifts in wave numbers of(-OH) stretching band to higher values comparing to PVA film which affirm well complexation between Cs ion and hydroxyl group of PVA [7,14] while other doped PVA films show almost the same FTIR spectra of PVA film may be due to the concentrations of CsCl were not enough to incorporate any shifts .

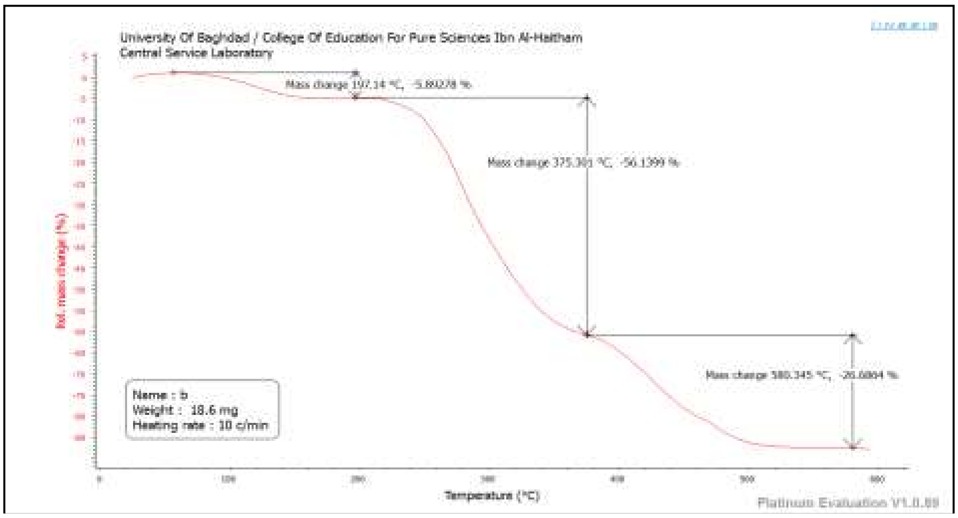
2)Thermo gravimetric analysis (TGA):

Is a useful analytical technique to asses thermal stability of materials including polymers by recording weight loss of a sample as a function of temperature[15] .

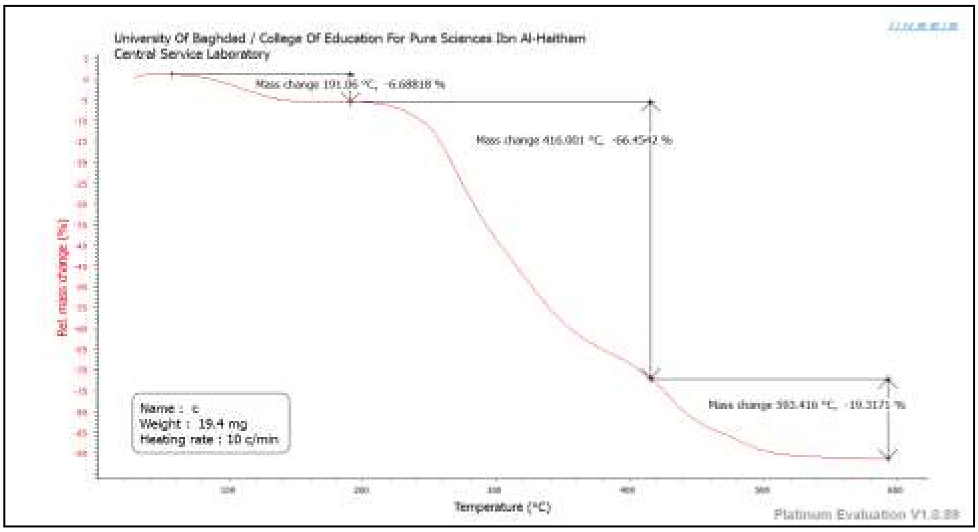
TGA thermograms for of PVA and doped PVA films are shown in figures(10-18) :



Figure(10): Film a



Figure(11): Film b



Figure(12): Film c

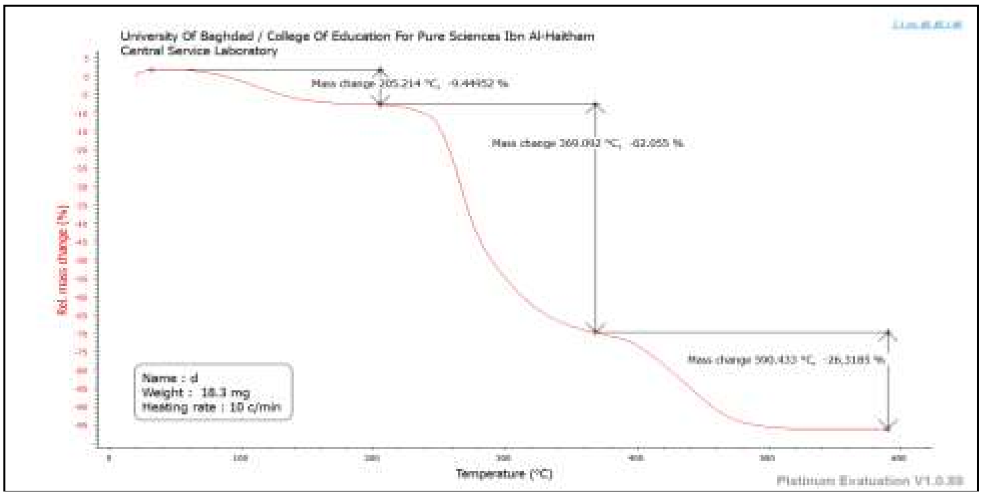
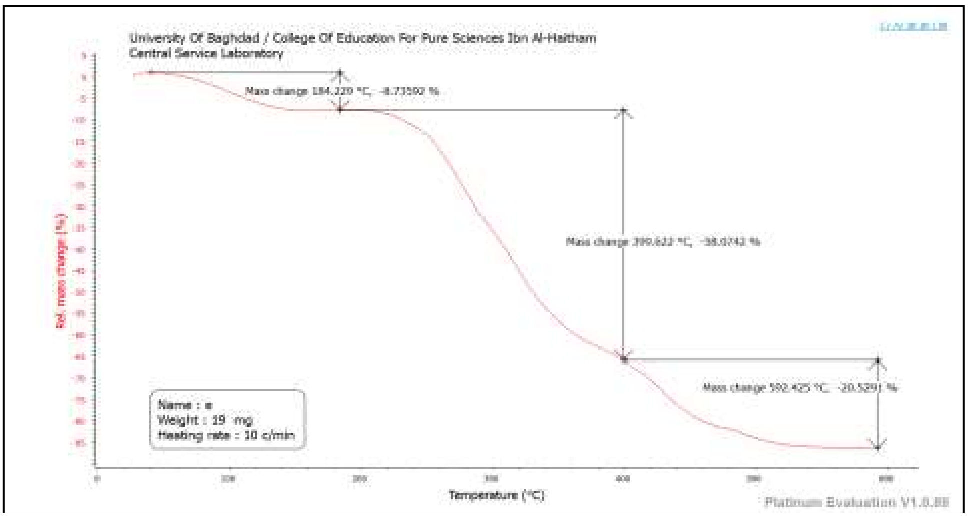
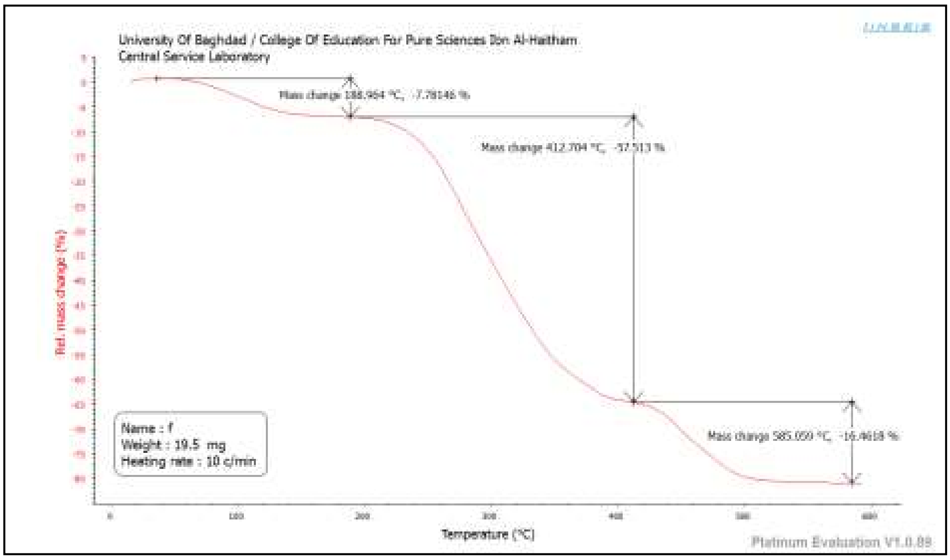


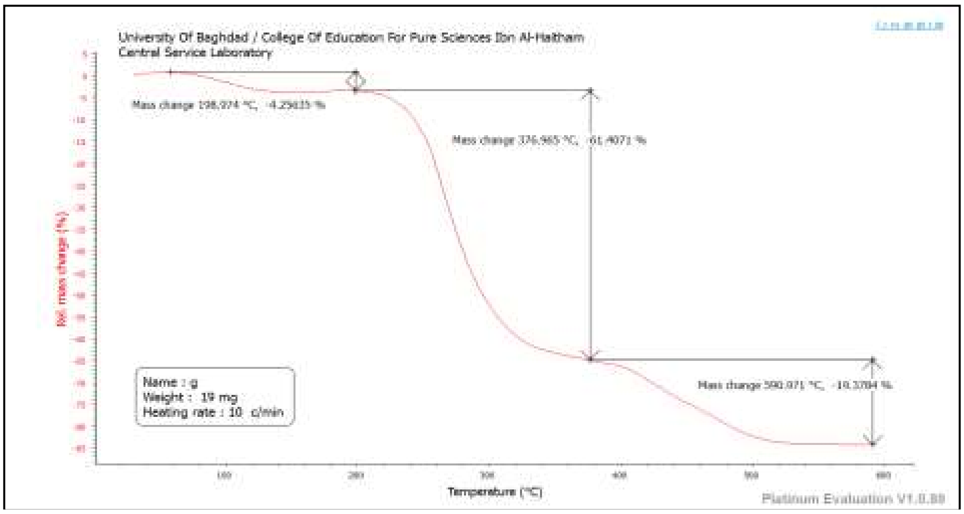
Figure (13): Film d



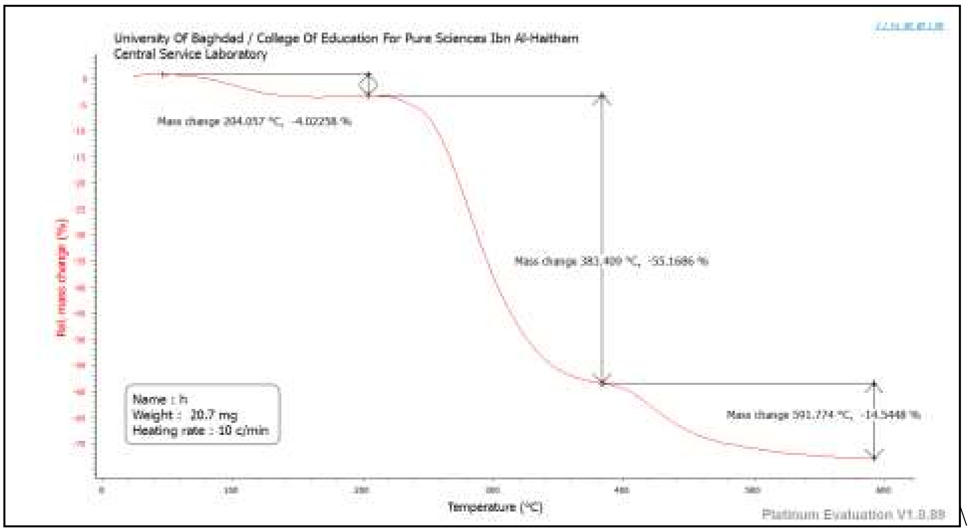
Figure(14): Film e



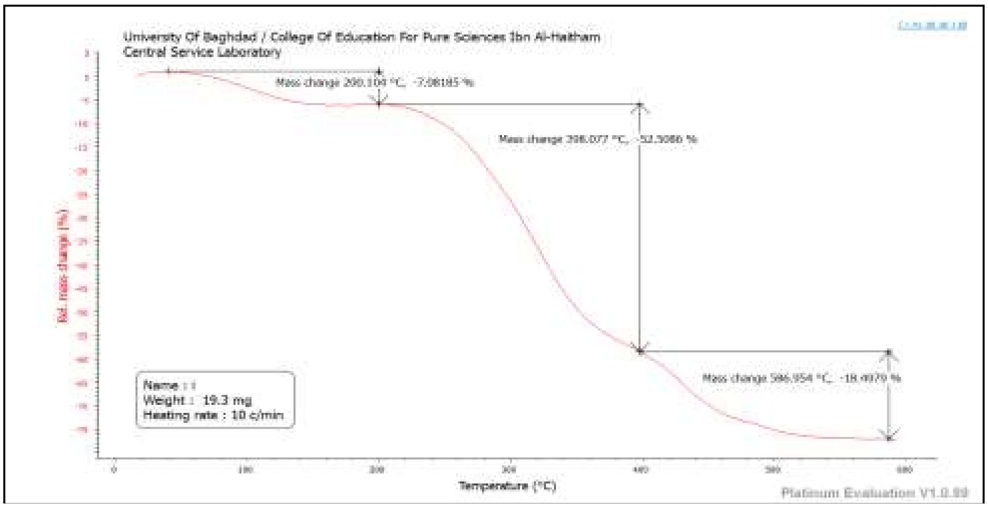
Figure(15): Film f



Figure(16): Film g



Figure(17): Film h



Figure(18): Film i

The onset and end set temperatures at which a single decomposition step occurs can be determined by drawing tangents to the curve of TGA.

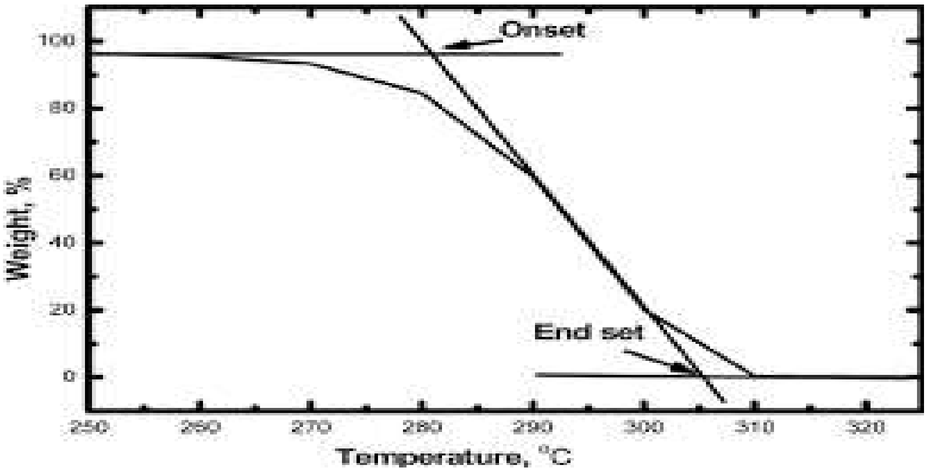


Figure (19): Determination of onset and end set temperatures of a single decomposition step in TGA curve

Table (2) summarizes data deduce from TGA thermograms for PVA and doped PVA films:

Table(2):TGA data of PVA and doped PVA films

Film	CsCl/PVA %	Step of Decomposition	Temperature(^{0}C)		Weight loss(%)	
			Onset	End set	Partial	Total
a	0%	١st	80	160	7.57	82.30
		2nd	260	350	52.49	
		3d	370	470	16.77	
		4th	500	600	5.47	
b	2%	1st	80	150	5.89	88.70
		2nd	240	330	56.13	
		3d	390	490	26.68	
c	4%	1st	75	130	6.68	92.44
		2nd	240	350	66.45	
		3d	420	500	19.31	
d	6%	1st	70	150	9.44	97.75
		2nd	250	310	62	
		3d	390	480	26.31	
e	8%	1st	50	140	8.73	87.25
		2nd	240	360	58	
		3d	400	480	20.52	
f	10%	1st	60	140	7.78	81.75
		2nd	230	360	57.51	
		3d	420	490	16.46	
g	12%	1st	70	130	4.25	85.02
		2nd	230	310	61.40	
		3d	400	510	19.37	
h	14%	1st	70	130	4	73.70
		2nd	240	330	55.16	
		3d	390	480	14.54	
i	16%	1st	60	140	7	77.99
		2nd	250	370	52.5	
		3d	400	490	18.49	

It is important to mention that the semi flat lines after each decomposition step in the curves of TGA thermograms represent thermal stable step since no weight loss is observed.

According to figure(10) PVA undergoes four decomposition steps that comprise weight losses of about (7.57%) , (52.49%) ,(16.77%) and (5.47%) at first, second ,third and fourth decomposition steps respectively. The temperature ranges at which the first , second , third and fourth decomposition steps take place are (80 - 160^{0}C) , (260 - 350^{0}C) , (370 - 470^{0}C) and (500 - 600^{0}C) respectively. The first decomposition step represents the loss of solvent [16] while the second represents the degradation of side group (-OH) to give polyene [17] . The third decomposition step represents the cleavage of (C - C) in the main chain of PVA that called carbocation [9] while the fourth decomposition step represents the completion of PVA degredation{[18].

According to figures(11-18) all doped PVA films undergo three decomposition steps showing the lowest weight loss at first decomposition step that represents the loss of solvent[16] and the major weight loss at the second decomposition step that represents the degradation of side group (-OH) to give polyene [17] while the medium weight loss occur at the third decomposition step that represents carbocation of PVA [9].

According to figure (11) film (b) has weight losses at first, second and third decomposition steps of about (5.89%) , (56.13%) and (26.68%) respectively .The temperature ranges of first, second and third decomposition steps are (80 -150^{0}C) , (240-330^{0}C) and (390 - 490^{0}C) respectively . Comparing to PVA film (b) that represents the concentration (2%) reduces slightly the loss of solvent and increases slightly the degradation of side group (-OH), but increases significantly the carbocation. The temperature ranges of the second and third decomposition steps shifts to a lower and higher values respectively comparing to PVA while the first never affected greatly.

According to figure(12) film (c) has weight losses at first, second and third decomposition steps of about (6.68%), (66.45%) and (19.31%) respectively. The temperature ranges of the first , second and the third decomposition steps are (75- 130^{0}C), (240-350 ^{0}C) and (420 -500^{0}C) respectively. Comparing to PVA film (c) that represents the concentration (4%) reduces slightly and increases slightly the solvent loss and carbocation respectively but increases significantly the degradation of side group (-OH).The temperature ranges of the first and second decomposition steps shifts to a lower values while the third shifts to a higher values comparing to PVA.

According to figure(13) film (d) has weight losses at first, second and third decomposition steps of about (9.44%) , (62%) and (26.31%) respectively. The temperature ranges of the first , second and the third decomposition steps are(70- 150^{0}C) , (250-310^{0}C) and (390 - 480^{0}C) respectively. Comparing to PVA film (d) that represents the concentration (6%) increases slightly solvent loss but increases significantly the degradation of side group (- OH) and the carbocation. The temperature ranges of the first and second decomposition steps shifts to a lower values while the third shifts to a higher values comparing to PVA.

According to figure(14) film (e) has weight losses at first, second and third decomposition steps of about (8.73%) ,(58%) and (20.52%) respectively. The temperature ranges of the first , second and the third decomposition steps are (50- 140^{0}C) , (240-360 ^{0}C) and (400 - 480^{0}C) respectively. Comparing to PVA film (e) that represents the concentration (8%) increases slightly the solvent loss , degradation of side group (-OH) and carbocation . The temperature ranges of the first and third decomposition steps shifts to a lower and higher values respectively comparing to PVA while the second starts at lower value but ends at slightly higher values comparing to PVA.

According to figure(15) film (f) has weight losses at first, second and third decomposition steps of about (7.78%) , (57.51%) and (16.46%) respectively. The temperature ranges of the first , second and the third decomposition steps are (60- 140^{0}C) , (230-360 ^{0}C) and (420 - 490^{0}C) respectively .Comparing to PVA film (f) that represents the concentration (10%) has no significant effect on solvent loss and carbocation but increases slightly the degradation of side group (-OH). The temperature ranges of the first and third decomposition steps shifts to a lower and higher values respectively. comparing to PVA while the second starts at lower value but ends at slightly higher values comparing to PVA.

According to figure(16) film (g) has weight losses at first, second and third decomposition step of about (4.25%), (61.4%) and (19.37%) respectively .The temperature ranges of the first , second and the third decomposition steps are (70- 130^{0}C), (230-310^{0}C) and (400 - 510^{0}C) respectively. Comparing to PVA film (g) that represents the concentration (12%) reduces significantly the solvent loss and increases significantly the degradation of side group (-OH) but increases slightly the carbocation. The temperature ranges of the first and second decomposition steps shifts to a lower values while the third shifts to a higher values comparing to PVA.

According to figure(17) film (h) has weight losses at first, second and third decomposition steps of about (4%) ,(55.16%) and (14.54%) respectively. The temperature ranges of the first , second and the third decomposition steps are (70- 130^{0}C), (240-330 ^{0}C) and (390 - 480^{0}C) respectively. Comparing to PVA film (h) that represents the concentration (14%) reduces significantly the solvent loss and increases slightly the degradation of side group (-OH) but decreases slightly the carbocation .The temperature ranges of the first and second decomposition steps shifts to a lower values while the third shifts to a higher values comparing to PVA.

According to figure(18) film (i) has weight losses at first, second and third decomposition steps of about (7%) , (52.5%) and (18.49%) respectively .The temperature ranges of the first , second and the third decomposition steps are (60- 140^{0}C), (250-370^{0}C) and (400 - 490^{0}C) respectively. Comparing to PVA the concentration (16%) has no significant effect on solvent loss and the degradation of side group (-OH) but increases slightly the carbocation .The temperature ranges of the first and third decomposition steps shifts to a lower and higher values respectively comparing to PVA while the second starts at lower value but ends at higher values comparing to PVA.

It is to be noted that the temperature ranges at which the solvent evaporates from doped PVA films shift to a lower values comparing to PVA film and this may be due to complexation between Cs ions with hydroxyl group of PVA [7] instead of solvent molecules and hence solvent molecules be more free to evaporate.

The starting temperature at which the second decomposition step of each doped PVA films occurs shifts to a lower values comparing to PVA film which means accelerating slightly the degradation of side group (-OH) .

It is obvious that weight loss at second decomposition step of each doped PVA films has no linear relationship with concentration of CsCl . Some doped PVA films like(c , d and g) have higher weight loss at second decomposition step comparing to PVA and some doped PVA films like (b , e ,f ,h and i) have almost the same weight loss at second decomposition step comparing to PVA .

It is also obvious that weight loss at third decomposition step of each doped PVA films has no linear relationship with concentration of CsCl . Film (f) have almost same carbocation degree of PVA while film (h) have the lowest carbocation degree while (b and d)have the highest degree of carbocation comparing to PVA . The temperature range at which third decomposition step of each doped PVA films occurs shifts to a higher values comparing to PVA film which revealed the effect of CsCl in hindering carbocation comparing to PVA and this may be due to reducing mobility of the PVA chains by the entrapment of metal salt that leads to form a complex with the hydroxyl group of the PVA chains and thus decreasing heat transfer process for decomposition of polymer composites [19].

According to total weight loss films(h and i) have the lowest values comparing to (PVA and the rest of doped PVA films) which means have the highest thermal stability while films(c and d)have the highest values comparing to(PVA and the rest of doped PVA films) which means have the lowest thermal stability but films(b ,e ,f and g)have total weight loss not greatly different from PVA which means have almost same thermal stability of PVA.

CONCLUSION

FTIR absorption spectra show that doped PVA films with concentration (2% , 4% ,6% and 8%) of CsCl have same absorption spectra of PVA while films with concentrations (10% , 12% , 14% and 16%) show some shifts in wave number of stretching vibration of (-OH) which reveal some complexation between CsCl with PVA**.** TGA show that CsCl affect thermal stability of PVA depending on its concentration. According to total weight loss doped PVA films with concentrations (14% and 16%) of CsCl have more thermal stability than the pure PVA while the concentrations (4% and 6%) are significantly less thermal stable than the PVA .The concentrations (2% , 8% , 10% and 12%) are almost as thermal stable as PVA

REFERENCES

[1]William D. Callister ,JR. David G.Rethwisch,"Fundamentals of Materials Science and Engineering:an Integrated Approach" ,John Wiley and Sons,2012 [2] Aliyah A. M. Shehab, EnasY. Abid and Seham H. Salman," Studying The Structural and Optical Properties of PVA Doped With CuO and FeCl 3 Composites Films",Eng.&Tech.Journal, Vol.33, Part (B), No.9, 2015,PP.1712-1722

[3] Suaad S. S. and .Najim A.A ," Antimicrobials Nano-Fiber PVA Pure and PVA: TiO2 for Filtration Applications", Eng. &Tech.Journal, Vol.33,Part (B), No.4, 2015,PP.753-760

[4]Veeran G.K. and Guru V.B.,"Water Soluble Polymers for Pharmaceutical Applications", Polymers: Vol.3 PP.1972-2009,2011.

[5] Abdallh H. H. M., and Yousif E. ,"Studying The Influence of Cobalt Chloride on The Optical Properties of Poly(Vinyl Alcohol) Films"Journal of Al-Nahrain University Vol.15(1),2012,PP.40-45.

[6]. Babu J.R , Kumar K.V. ,"Studies on Structural and Electrical Properties of $NaHCO_3$ Doped PVA Films for Electrochemical Cell Applications",International Journal of Chem- Tech Research ,Vol.7,No.1, 2014-2015 ,PP. 171-180

[7] Singh R. , Kulkarni S. G. , and Naik N. H. ," Effect of Nano Sized Transition Metal Salts and Metals on Thermal Decomposition Behavior of Polyvinyl Alcohol**",** Adv. Mat. Lett. ,Vol. 4 , No.1,2013,PP. 82-88

[8] Nouh S. A. , Said A. F., Abdel-Megeed K. and Hafez F. M.," Effect of Nickel Chloride Concentration and Gamma Radiation on The Thermal Properties of Poly(Vinyl Alcohol)", Radiation Effects & Defects in Solids, Vol. 161, No. 1, 2006,PP. 23–30

[9] Eliassaion N. A., and Gharibshahi E. ,"Structural,Thermal and Electrical Properties of PVA-Sodium Salicylate Solid Composite Polymer Electrolyte",Journal of Nano Materials ,Vol. 2012,Articale ID 857569.

[10].Shehap A.M ,"Thermal and Spectroscopic Studies of PolyVinyl Alcohol/Sodium Carboxy Methyl Cellulose Blends"Egypt J.Solids,Vol.(31),No.(1),PP. 75 - 91(2008). [11]. Oraby A.H , Hezma AM , Elashmawi I.S. and Alluheebe M.A. ,"Verification of The Changes In The Structural and Optical Properties of PVA/PEO Embeded by Lithium Chloride " RJPBCS**,**Vol.6.No. 5,2015 ,PP.724-734

[12]. Tadokoro H ,"Crystallization Sensetive Band of Poly Vinyl Alcohol", Bulletin of The Chemical Society of Japan,Vol.32,No.12,PP. 1334-1339 , 1959.

[13] Coats J. ,"Interpretation of Infrared Spectra,a Practical Approach "John wiley and Sons LTd.Chichester,2000.

[14] Meikhail M.S., Oraby A.H., Farea M.O. , and Abdelghany A.M.."Spectroscopic Studies of PVA/PEO Hydrogel Filled With Cesium Chloride",RJPBCS,Vol5 ,No.6 ,2014 ,PP.976-983

[15] Hatakeyama T. and Quinn F.X. ,"Thermal Analysis Fundamentals and Applications to Polymer Science",Second Edition,Jhon wiley and Sons ,1999.

[16].El-Sayed,.Mahmoud S. K..H ,.fatah A.A ,.Hssen A ,"DSC,TGA and Dielectric Properties of Carboxymethyl Cellulose/Polyvinyl Alcohol Blends",Physica B :406,p.p.4068-4076,2011

[17] Gilman J. W. , Vanderhart D. L. and Kashiwagi T. ,"Thermal Decomposition Chemistry of Poly(Vinyl Alcohol)",IN:Fire and polymersII:materials and test for hazard prevention ,american chemical society,ACS Symposium series 599,August 21-26,1994.

[18] Hemalatha K.S. , Parvatikar N. , Rukmani K. ," Influence of ZnO Nanoparticles on Thermal Behavior of Poly Vinyl Alcohol Films",International Journal of Advanced Scientific and Technical Research ,Issue 5, volume 5, 2015 ,PP.106 -115

[19] Hegazy D. E. , Eid M. and Madani M. ," Effect of Ni Nano Particles on Thermal, Optical and Electrical Behaviour of Irradiated PVA/AAc Films" Arab Journal of Nuclear Science and Applications,No. 47 ,Vol.1, 2014,PP. 41-52