

## Study of Thermal Decomposition and FTIR for PVA-AlCl<sub>3</sub> Composite Films

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**Abstract:** Pure and (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt filled (with different weight ratios (1, 3, 5, 7, 9, 11, 13 and 15) wt.%) Polyvinyl Alcohol (PVA) films have been prepared using casting method. The influence of (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt on some thermal properties of PVA films was studied by Differential Scanning Calorimetry (DSC). The interaction between (PVA) and (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt was investigated by Fourier Transform Infrared (FTIR) spectroscopy. The results of TGA curves showed that pure (PVA) film underwent two stages of thermal decomposition process and total weight loss was (100%) whereas the (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt filled (PVA) films showed two and three stages of thermal decomposition process with lower total weight loss compared with pure (PVA) film. Moreover, the results of (FTIR) indicated that (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt could form interaction with the hydroxyl group on PVA chain.

**Key words:** Polyvinyl Alcohol (PVA), aluminium chloride, thermal decomposition, FTIR, composites, TGA

### INTRODUCTION

Polymers such as plastics and rubbers, pervade our lives and we come across them in many different forms and because of that, their physical properties have great importance and understanding these properties is vital for their uses in technology and engineering (Salman *et al.*, 2016).

Polyvinyl Alcohol (PVA-[CH<sub>2</sub>-CHOH]<sub>n</sub>-) is the world's largest volume synthetic polymer produced for its excellent chemical resistance, physical properties and complete biodegradability which has led to broad practical applications (Guirguis and Moselhey, 2012; Hemalatha *et al.*, 2014). PVA is a semi-crystalline polymer whose crystalline index depends on the synthetic process and the physical aging. PVA is a water-soluble polyhydroxy polymer, one of the few linear, non-halogenated aliphatic polymers. PVA has a two dimensional hydrogen-bonded network sheet structure. The physical and chemical properties of PVA depend to a great extent on its method of preparation.

PVA could be considered as a good host material due to good thermo stability, chemical resistance and film forming ability. PVA is an important material in view of its large scale applications. It is used in surgical devices, sutures, hybrid islet transplantation, implantation, blend membrane and in synthetic cartilage in reconstructive joint surgery (Guirguis and Moselhey, 2012). PVA consists of a carbon chain backbone with Hydroxyl (OH) groups attached to methane carbons, these hydroxyl groups are sources of hydrogen bonding (Abdelghang *et al.*, 2015).

Thermogravimetric analysis is a technique for measuring weight loss as a function of temperature and it is one of the most important methods used to determine the thermal stability of polymer and to determine the temperature at which it degrades. TGA is of two types: isothermal and non-isothermal in the first type, the sample is maintained at a constant temperature for a period of time and the weight loss is recorded whereas in second type, the sample is subjected to a continuous increase in temperature, usually, linear with time and the weight loss is recorded which gives more useful information because it shows the highest limit of thermal stability (Al-Adam and Aziz, 1985; Stevens, 1975).

### MATERIALS AND METHODS

#### Experimental details

**Materials and samples preparation:** Polyvinyl Alcohol (PVA) powder with a molecular weight of 14000 g/mol and (86-89) % degree of hydrolysis was provided by Central Drug House (P) Ltd., New Delhi, India. It is characterized as transparent whitish, odorless, nontoxic and soluble in distilled water.

Aluminium Chloride (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt was supplied from (Central Drug House (P) Ltd., New Delhi, India) with a molecular weight of 241.43 g/mol which is in the form of yellow powder soluble in distilled water. Films thicknesses were 40-140 µm prepared at room temperature by solution casting method. The (PVA) and (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt with different weight ratios (1, 3, 5, 7, 9, 11, 13 and 15) wt.% were completely dissolved in distilled water at (80°C)

using magnetic stirrer for 1 h. The solution is then poured in glass plates and left to dry for 24 h to remove any residual solvents.

**Differential Scanning Calorimetry (DSC) test:** Thermal behaviour of the prepared films was examined by differential scanning calorimetry model (STA. PT-1000 Linseis). The system was calibrated using (9-19) mg of alumina at a temperature increase rate of  $10^{\circ}\text{C}/\text{min}$  with the presence of argon gas.

**FTIR test:** In order to record the (FTIR) spectra of the films, (IR Affinty-1CE (FTIR) spectrophotometer, Shimadzu, Japanese company) was used.

## RESULTS AND DISCUSSION

**Thermogravimetric Analysis (TGA):** As polymers undergo with several changes when heated, they release gases and liquids which are different in their shapes, colors and molecular weights. The polymer's ability to resist these changes at high temperatures is called thermal stability. Thermogravimetric Analysis technique (TGA) can be used to test the kinetics of reactions and products in the thermal dissolution process stages using Differential Scanning Calorimetry (DSC) (Stevens, 1975; Akram, 1993). Figure 1-9 show (TGA) curves for pure and  $(\text{AlCl}_3.6\text{H}_2\text{O})$  salt filled with different weight ratios (PVA) films. Figure 1 shows the curve of (TGA) of pure (PVA) film and we can notice the presence of two stages of thermal decomposition of the weight loss process where

the temperature range of the first stage of thermal analysis process is  $242\text{-}367^{\circ}\text{C}$  with a partial weight loss of about (89%), this partial of weight loss may be due to the large (PVA) chains decomposition into small parts whereas the second stage of the thermal decomposition process is in the temperature range of  $367\text{-}431^{\circ}\text{C}$  with a partial weight loss of about (11%). The second partial weight loss is due to further decomposition of (PVA) chains yielding carbon material (Singh *et al.*, 2013). The total weight loss of the pure (PVA) film is 100%. After  $(\text{AlCl}_3.6\text{H}_2\text{O})$  salt filling, we notice that the total weight loss for all weight ratios of the added  $(\text{AlCl}_3.6\text{H}_2\text{O})$  salt decreases compared with that of pure (PVA) film except the (PVA) sample filled with 7 wt.% where it has total weight loss of 100%. The (PVA) sample filled with (9 wt.%) showed the lowest total weight loss of about (80.63%). Table 1 shows the process stages of thermal decomposition and the values of partial and total weight losses for all composite films. From the table, it can be noticed that the value of partial weight loss for the first stage of the thermal decomposition process for all weight ratios is less than the partial weight loss value of the first stage of the thermal decomposition process of the pure (PVA) film and the (PVA) samples filled with (1, 3, 9, 13 and 15) wt.% undergo two stages of thermal decomposition of the weight loss process at different temperature ranges and that the greater value of the partial weight loss was in the first stage of the thermal decomposition process for all the weight ratios of the added  $(\text{AlCl}_3.6\text{H}_2\text{O})$  salt except the (PVA) sample filled with 9 wt.%. This is possibly due to the splitting or volatilization of small molecules or evaporation of the

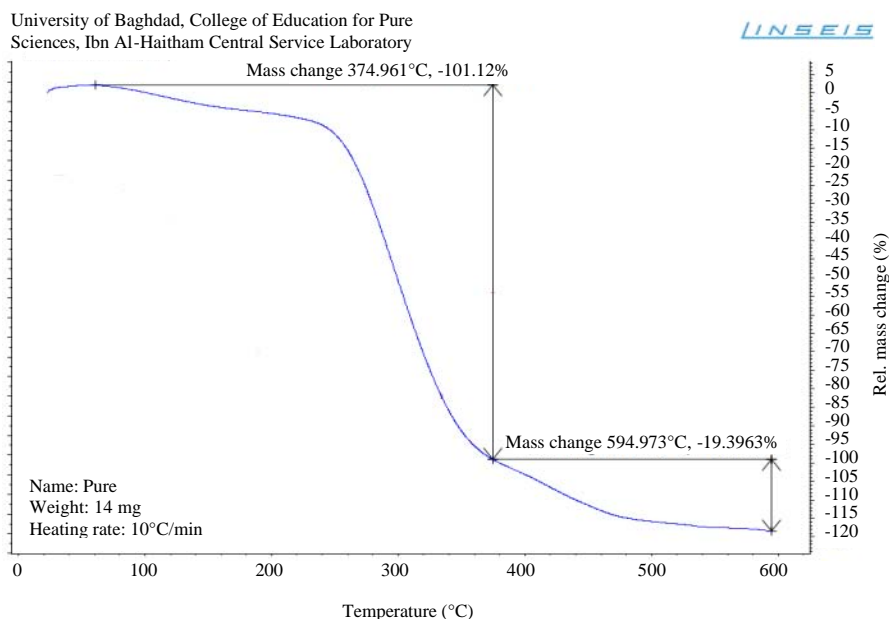


Fig. 1: Diagram of DSC thermal weight of pure (PVA) film (platinum evaluation V1.0.89)

Table 1: TGA curve values of PVA-AlCl<sub>3</sub> composite films with weight ratio of AlCl<sub>3</sub>.6H<sub>2</sub>O salt

Concentration (wt.%)	Region of decomposition	Temperature range (°C)		Weight loss (%)	
		Start	End	Partial	Total (%)
Pure	1st	242	367	89	100
	2nd	367	431	11	
1	1st	79	348	60.61	96.7
	2nd	348	595	36.09	
3	1st	80	339	49.04	89.04
	2nd	339	594	40	
5	1st	91	304	46.09	97
	2nd	304	479	28.29	
	3d	479	594	22.62	
7	1st	80	315	50	100
	2nd	315	490	29	
	3d	490	594	21	
9	1st	92	317	32.29	80.63
	2nd	317	594	48.34	
11	1st	80	236	36.57	84
	2nd	236	347	10.98	
	3d	347	594	36.45	
13	1st	60	312	48.73	97.14
	2nd	312	594	48.41	
15	1st	90	299	50.42	92.95
	2nd	299	592	42.53	

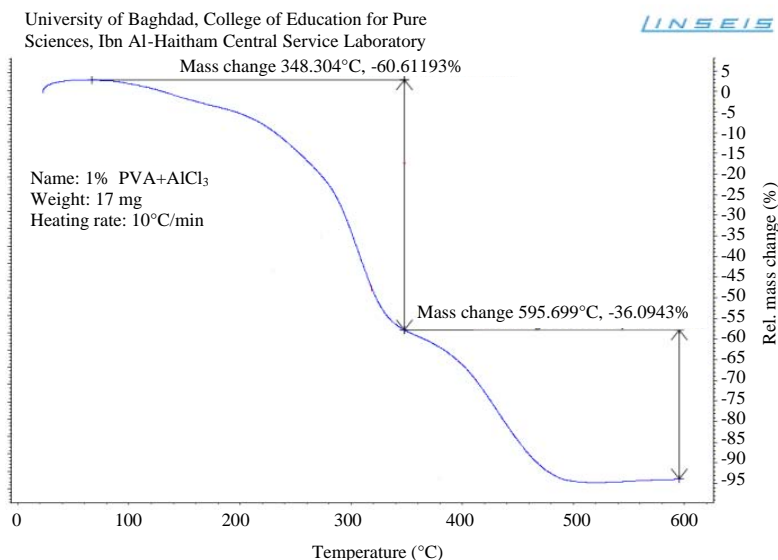


Fig. 2: Diagram of DSC thermal weight of PVA film filled with (1 wt.%) (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt (platinum evaluation V1.0.89)

remaining absorbed water. The second stage of the thermal decomposition process has a low value of partial weight loss and this indicates the existence of a chemical decay process resulting from the separation of carbonate bond (C-C) in the backbones of PVA (Shehap, 2008). While the (PVA) samples, filled with (5, 7 and 11) wt.% of (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt, undergo three stages of thermal decomposition of the weight loss process at different temperature ranges. The greatest value of the partial weight loss is in the first stage of the thermal decomposition process and this stage represents the loss

of the solvent while the (PVA) sample filled with (11 wt.%) of AlCl<sub>3</sub>.6H<sub>2</sub>O salt has the lowest value for partial weight loss at the second stage of the thermal decomposition process, this stage of the thermal analysis process represents the side hydroxyl group (-OH) decay which gives (polyneen) while the third stage of the thermal decomposition process for the partial weight loss showed that the (PVA) sample filled with (11 wt.%) of AlCl<sub>3</sub>.6H<sub>2</sub>O salt has an average value of partial weight loss. Moreover, the (PVA) samples, filled with (5 and 7) wt.% of (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt have the lowest value of the partial

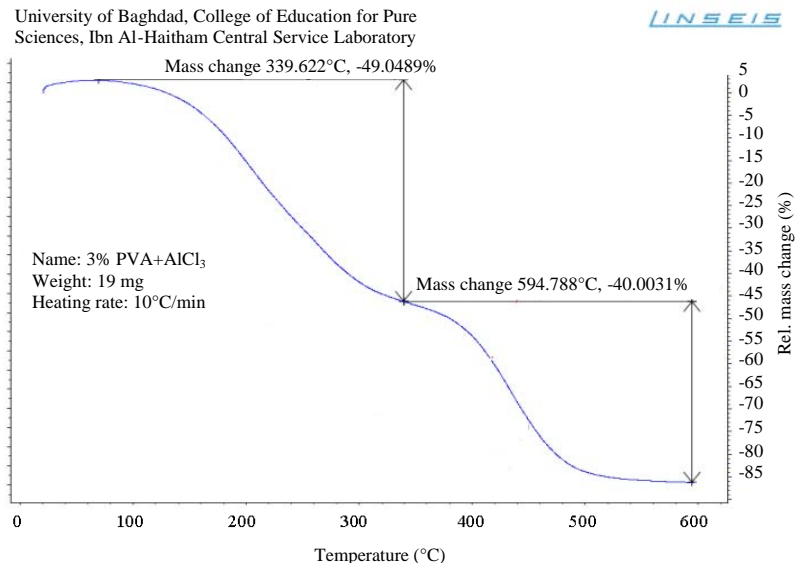


Fig. 3: Diagram of DSC thermal weight of PVA film filled with (3 wt.%) (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt (platinum evaluation V1.0.89)

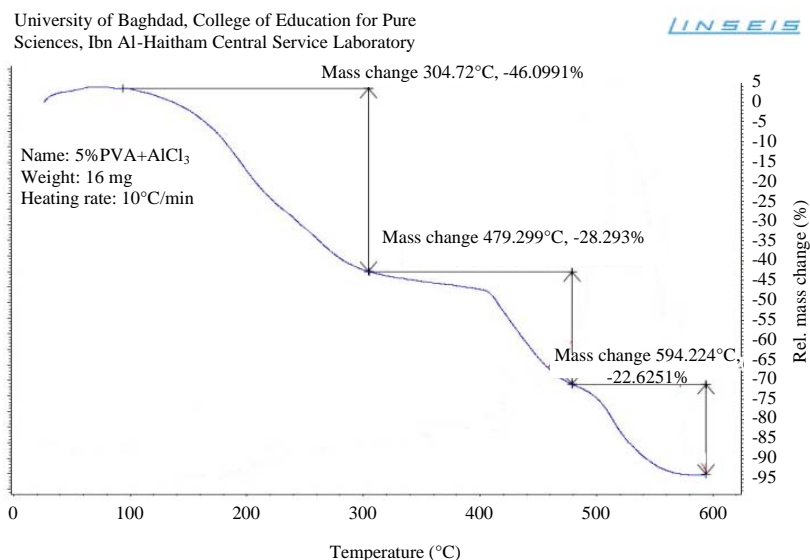


Fig. 4: Diagram of DSC thermal weight of PVA film filled with (5 wt.%) (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt (platinum evaluation V1.0.89)

weight loss at this stage of the thermal decomposition process. This stage represents the separation of carbonate bond (C-C) in the main chain of PVA (Betti, 2016).

**Fourier Transform Infrared (FTIR):** The Fourier transform spectrum of infrared radiation for pure and (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt filled with different weight ratios (PVA) films was studied by measuring transmittance spectrum as a function of wavenumber within the range of 400-4000 cm<sup>-1</sup> as shown in Fig. 10 and Table 2 which illustrate some stretching and bending of vibrational

bands of pure (PVA) film (OH, CH, C = O, C = C, CH<sub>2</sub>). From the figure, it can be observed that there is no absorption band for the hydroxyl group (-OH) at the wavenumber (3600 cm<sup>-1</sup>) of PVA. This indicates that the hydroxyl groups of PVA chains are generally linked between the molecules or inside the molecules of the hydrogen bond, also, the figure shows that the wavenumber of the absorption band of hydroxyl group (-OH) of PVA are shifted to higher values after filling with (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt. These deviations in the absorption frequency value of the hydroxyl group (-OH) of PVA with the increase in the weight ratio of the added (AlCl<sub>3</sub>.6H<sub>2</sub>O)

Table 2: Values of the wavenumbers of the absorption bands of PVA- $\text{AlCl}_3$  composite films at different weight ratios of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  salt

Vibrational bands	Wavenumbers ( $\text{cm}^{-1}$ )								
	Pure (PVA)	1 (wt.%)	3 (wt.%)	5 (wt.%)	7 (wt.%)	9 (wt.%)	11 (wt.%)	13 (wt.%)	15 (wt.%)
O-H Stretching vibration	3506	3533	3510	3523	3541	3537	3541	3527	3516
C-H asymmetric stretching	2945	2949	2945	2943	2947	2966	2970	2985	2993
C=O stretching vibration	1710	1712	1710	1708	1708	1706	1703	1686	1687
Acetylene C=C group	1664	1654	1651	1651	1651	1649	1649	1647	1647
Bending of $\text{CH}_2$ vibration	1568	1568	1567	1541	1579	1541	1543	1541	1541
Wagging of $\text{CH}_2$ vibration	1332	1330	1330	1330	1330	1330	1328	1328	1328

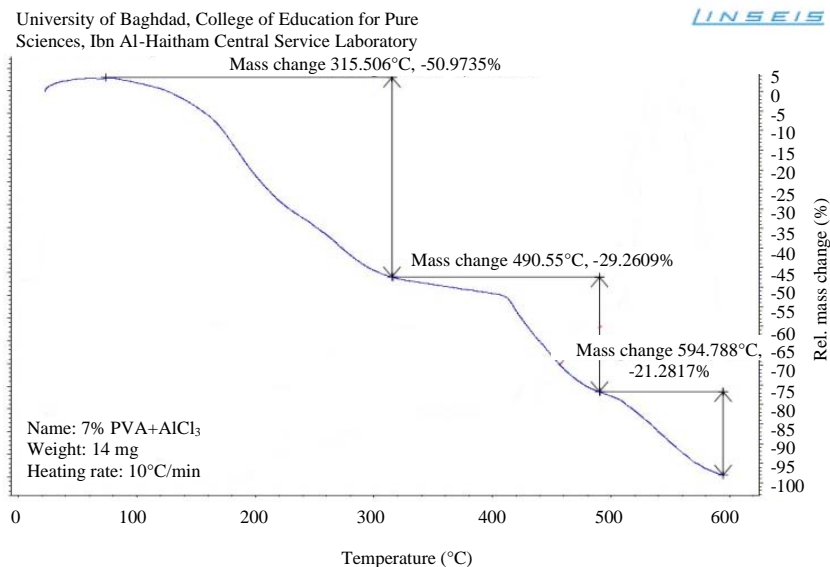


Fig. 5: Diagram of (DSC) thermal weight of PVA film filled with (7 wt.%) ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) salt (platinum evaluation V1.0.89)

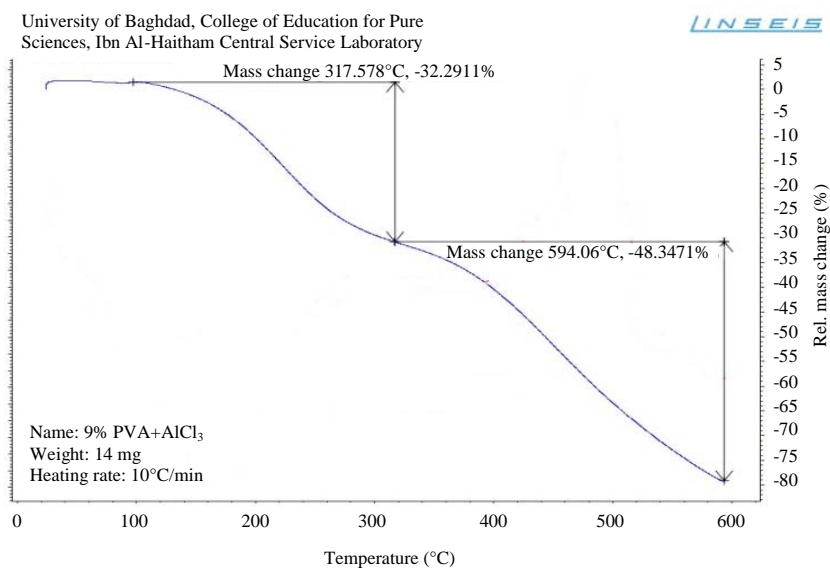


Fig. 6: Diagram of DSC thermal weight of PVA film filled with (9 wt.%) ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) salt (platinum evaluation V1.0.89)

salt indicates the interaction between (PVA) and the added ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) salt. The absorption frequency of

the hydroxyl group ( $-\text{OH}$ ) of the pure (PVA) film occurs at  $3506 \text{ cm}^{-1}$  but when filling with ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) salt, this

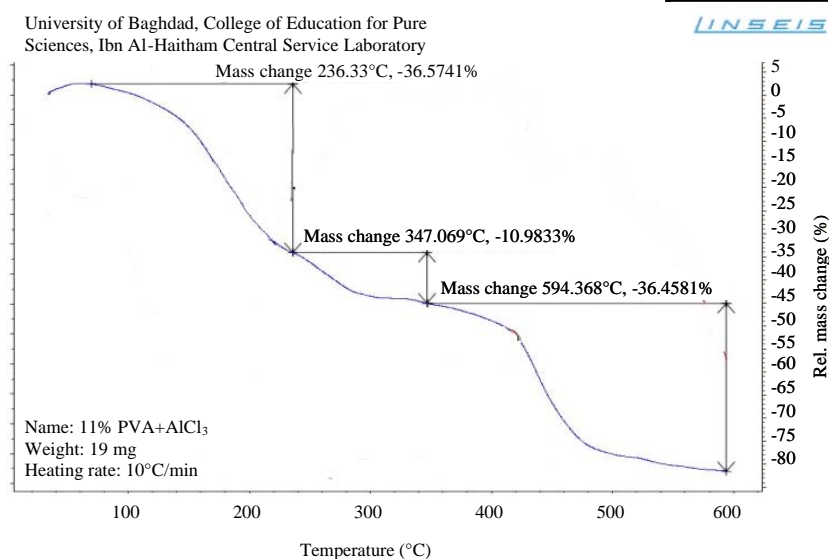


Fig. 7: Diagram of DSC thermal weight of PVA film filled with (11 wt.%) (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt (platinum evaluation V1.0.89)

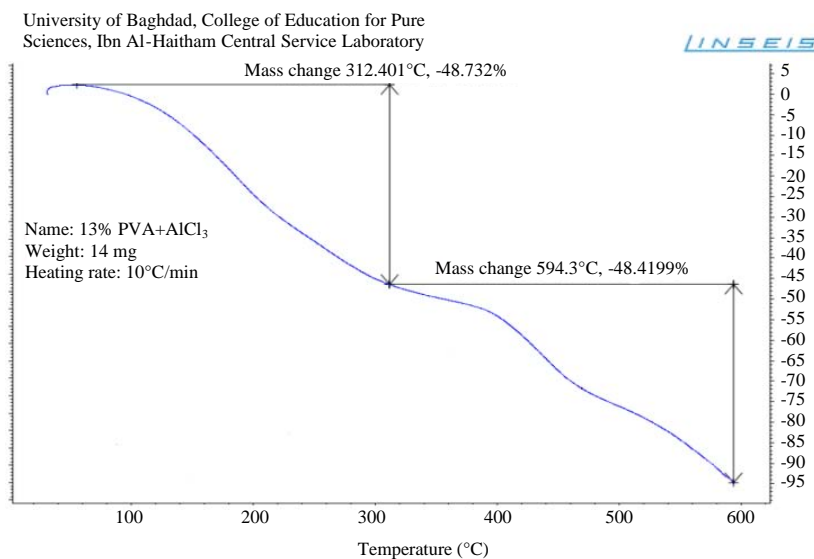


Fig. 8: Diagram of DSC thermal weight of PVA film filled with (13 wt.%) (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt (platinum evaluation V1.0.89)

absorption frequency is shifted to higher value (3541 cm<sup>-1</sup>) for the (PVA) samples filled with (7 and 11) wt.% of the (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt. This indicates that the hydrogen bond is weak when the absorption frequency shifted to higher value in other words, the addition of AlCl<sub>3</sub>.6H<sub>2</sub>O salt reduces the intensity of the hydrogen bond of PVA molecules because this salt has strong form of the hydrogen bond with (PVA) which takes the position of hydrogen bond between the hydroxyl group (-OH) of PVA molecules. As shown in the figure, the appearance of a band at the wavenumber (2945 cm<sup>-1</sup>) is related to the asymmetric stretching bond (C-H) of pure (PVA) film, after

filling with (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt the value of this wavenumber of this bond is shifted to higher value (2993 cm<sup>-1</sup>) for the (PVA) sample filled with (15 wt.%) of AlCl<sub>3</sub>.6H<sub>2</sub>O salt and we also notice two bands at the wavenumbers (1710 cm<sup>-1</sup>) and (1664 cm<sup>-1</sup>) which are attributed to the stretching vibrational bands of C = O and (C = C) bonds of pure (PVA), respectively. After filling with (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt, we notice that the value of these two wavenumbers for the bonds (C = O) and (C = C) are shifted to low values which means that the (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt also interacts with the acetate groups of phenyl acetate units of PVA. It can also be noticed the appearance of a band at

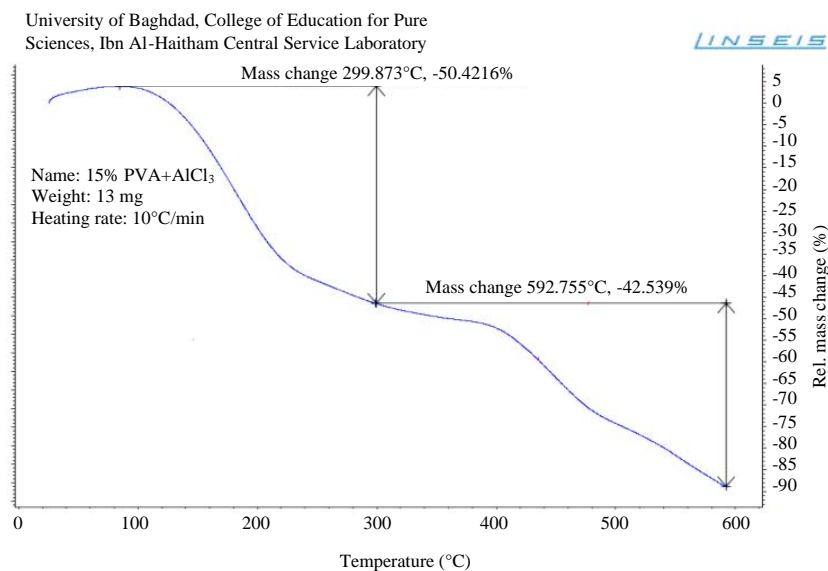


Fig. 9: Diagram of DSC thermal weight of PVA film filled with (15 wt.%) (AlCl<sub>3</sub>.6H<sub>2</sub>O) salt (platinum evaluation V1.0.89)

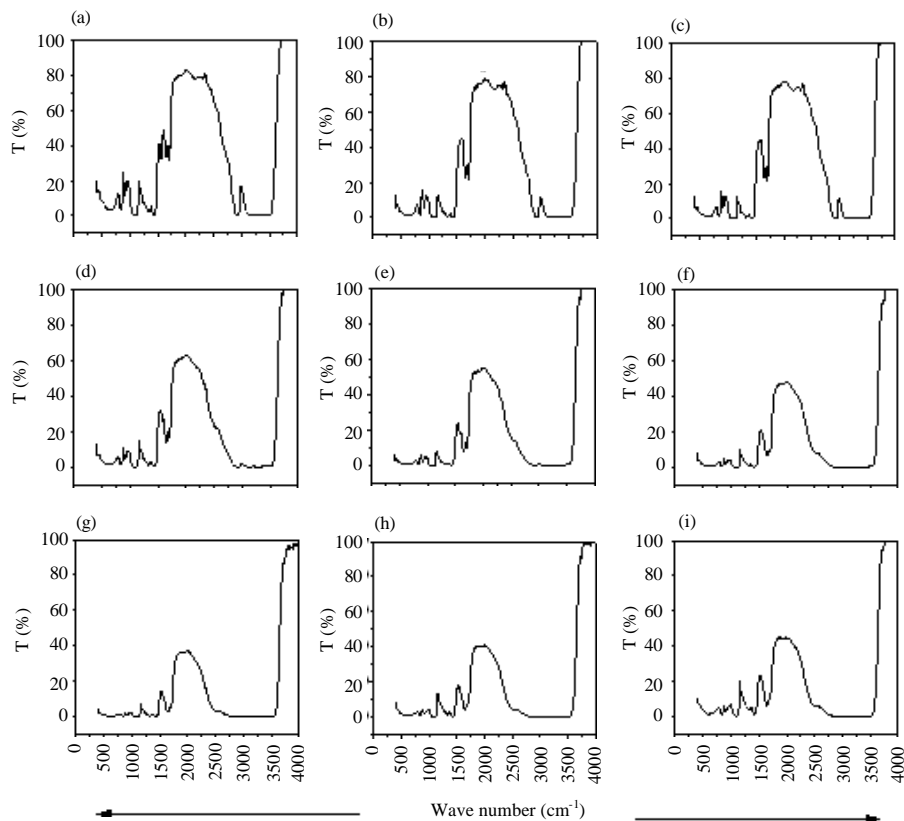


Fig. 10: FTIR spectra of PVA-AlCl<sub>3</sub> composite films at different weight ratios of AlCl<sub>3</sub>.6H<sub>2</sub>O salt: a) Pure PVA; b) PVA+1% AlCl<sub>3</sub>; c) PVA+3% AlCl<sub>3</sub>; d) PVA+5% AlCl<sub>3</sub>; e) PVA+7% AlCl<sub>3</sub>; f) PVA+9% AlCl<sub>3</sub>; g) PVA+11% AlCl<sub>3</sub>; h) PVA+13% AlCl<sub>3</sub> and i) PVA+15% AlCl<sub>3</sub>

the wavenumber of 1568 cm<sup>-1</sup> which is due to the bending vibrational band of -CH<sub>2</sub> bond of pure (PVA) and a band

at the wavenumber of 1332 cm<sup>-1</sup> related to the wagging vibrational band of -CH<sub>2</sub> bond of pure (PVA). These

bands were also affected (change their wavenumber) by  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  salt filling. Based on the above discussion, the interaction between ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) salt and (PVA) has broken the hydrogen bond of PVA (Pu-You *et al.*, 2014; Luo *et al.*, 2015).

### CONCLUSION

TGA shows that ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) salt affects thermal stability of PVA depending on its weight ratios. According to the total weight loss, all the weight ratios of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  salt showed more thermal stability compared to the pure (PVA) film, except the (PVA) sample filled with (7 wt.%) where it showed a thermal stability equal to that of the pure (PVA) film. Moreover,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  salt could form interactions with the polymer (PVA) chains via hydrogen bonding between the ions and the hydroxyl group.  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  salt could effectively destroy the crystals of PVA and thus decreases the degree of crystallinity of PVA.

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