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# Thermogravimetric Analysis on PVA / PVP Blend Under Air Atmosphere

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## ABSTRACT

Films of poly vinyl alcohol (PVA) /poly vinyl pyrrolidone (PVP) blends have been prepared by solution casting method with different ratios of each other (100/0 , 80/20 , 60/40 , 50/50 , 40/60 , 20/80 , 0/100) to investigate their thermal stability comparing to correspondent pure polymers by using thermogravimetric analysis (TGA) under air atmosphere. It was found that PVA and PVP films show two decomposition steps while PVA/PVP blend films show three decomposition steps except the film of the ratio (20/80) that shows four decomposition steps .It was also found that blending decreases the temperature ranges at which the first and the second decomposition steps of PVA and PVP occur. It was found that blending PVA with PVP has significant effect on weight loss at first decomposition step of PVA by increasing it as the ratio of PVP increases. It was also found that blending PVA with PVP has significant effect on weight loss at second decomposition step of PVA by decreasing it as the ratio of PVP increases. It was found that the weight loss at third decomposition step of PVA/PVP blend films increases as the ratio of PVP increases . According to TGA thermograms under air atmosphere, PVA , PVP and PVA/PVP blend films show almost the same total weight loss which means of same thermal stability.

**Keywords** : Poly vinyl alcohol , Poly vinyl pyrrolidone, TGA, Polymer blends, Thermal stability

## INTRODUCTION

Polymer blending is an important technique to design materials with improved properties[1].

Three kinds of polymer blends can be distinguished :miscible , partially miscible and immiscible .The enhancement of polymer blends properties depends greatly on the degree of compatibility or miscibility (at molecular level) of polymers being blended with each other.
Through recent research it has been clear that a large class of polymers may form miscible blends with another class of polymers through formation of inter associated hydrogen bond[2].

Poly vinyl alcohol (PVA) as well as poly vinyl pyrrolidone (PVP) are synthetic polymers that used in medicine. PVP known to have good complexing ability whereas PVA represents a potential materials for many applications due to hydrophilicity , biocompatibility ,texture industry and well processibility on film formation[3],[4]. PVA has melting and decomposes rapidly above this temperature [5] .The major setback of PVA is suffering suspension under physiological conditions but blending with PVP can reduce this through interconnection by hydrogen bond that increased stability of the blend under physiological conditions.
PVA has the following structure:

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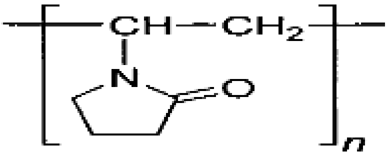
[redacted]

**Scheme (1) chemical structure of PVA**

The hydroxyl groups of PVA are interconnected by hydrogen bonding leading to high melting and glass transition temperatures.

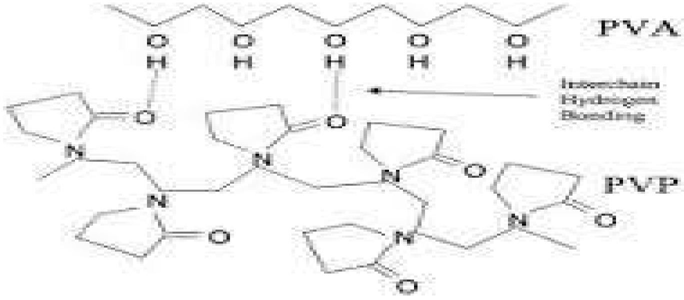
Poly (*N*-Vinyl-2-Pyrrolidone) or poly vinyl pyrrolidone (PVP) for short has the following chemical structure :



**Scheme (2) chemical structure of PVP**

PVA and PVP could form miscible blend through interconnecting by hydrogen bond between hydroxyl group (-OH) of PVA and carbonyl group (-C=O) of PVP [6], [7].

Blending PVA with PVP represents a new tool for preparation of biomaterials and multifunctional utilities.



**Scheme(3) illustration of interconnection between PVA and PVP through hydrogen bonding**

All polymers including their blends would experience some type of degradation by applying heat where the long chain backbone of polymers begin to separate (molecular scission) thus undergo changing in its properties. Thermal degradation has many types of mechanisms depending on existence or absence of some parameters such as oxygen , light or moisture .

the general mechanism for thermal degradation under oxygen atmosphere include three major steps [8]:

**1) initiation :**

$RH \xrightarrow{\text{heat and /or light}} R^{\cdot} + H^{\cdot}$ .....................(1)

RH = polymer $R^{\cdot}$ , $H^{\cdot}$ =free radicals

**2) propagation**

$R^{\cdot} + O_2 \longrightarrow R\text{-}O\text{-}O^{\cdot}$ .....................(2)

$R\text{-}O\text{-}O^{\cdot} + RH \longrightarrow R\text{-}O\text{-}OH + R^{\cdot}$ .......................(3)

$R\text{-}O\text{-}OH \longrightarrow R\text{-}O\text{-}O^{\cdot} + OH^{\cdot}$ ......................(4)

$R\text{-}O\text{-}O^{\cdot}$ =peroxide radical R-O-OH = hydroperoxide

**3) termination**

$R^{\cdot} + R^{\cdot} \longrightarrow R\text{-}R$ ....................(5)

$R^{\cdot} + R\text{-}O\text{-}O^{\cdot} \longrightarrow R\text{-}O\text{-}O\text{-}R$ ...................(6)

R. V. Kulkarni et al have studied hydrogel based interpenetrating network (IPN) of poly(vinyl alcohol) and poly(vinyl pyrrolidone) loaded with an anti-diabetic drug by TGA under nitrogene atmosphere and found that the thermal stability of IPN hydrogel is high in comparition with pure PVA and pure PVP[9].E.M. Abdelrazek et al have studied many properties including thermal properties of PVA / PVP blend filled with lithium bromide by TGA under nitrogen atmosphere and found that the thermal stability of PVA / PVP blend improved after filling with lithium bromide [10]. C. Ravindra et al have studied Thermal Properties of Poly (vinyl pyrrolidone)/Vanillin by TGA/DTA and found that all the components in the blend films are miscible showing single glass transition temperature and are stable up to $185^0$C suggesting that, a considerable amount of interactions may exist between components in each blend films ,but according to TGA The incorporation of PVP and Vanillin did not influences thermal stability of these films, as predicted only small variation in the blend film[11].

This work focuses on thermal stability of PVA blend with PVP under air atmosphere and hence under effect of oxygen.

## Experimental work

### 1)Place of experiment:

The experiment was carried out at materials engineering department / university of technology

### 2)Preparation:

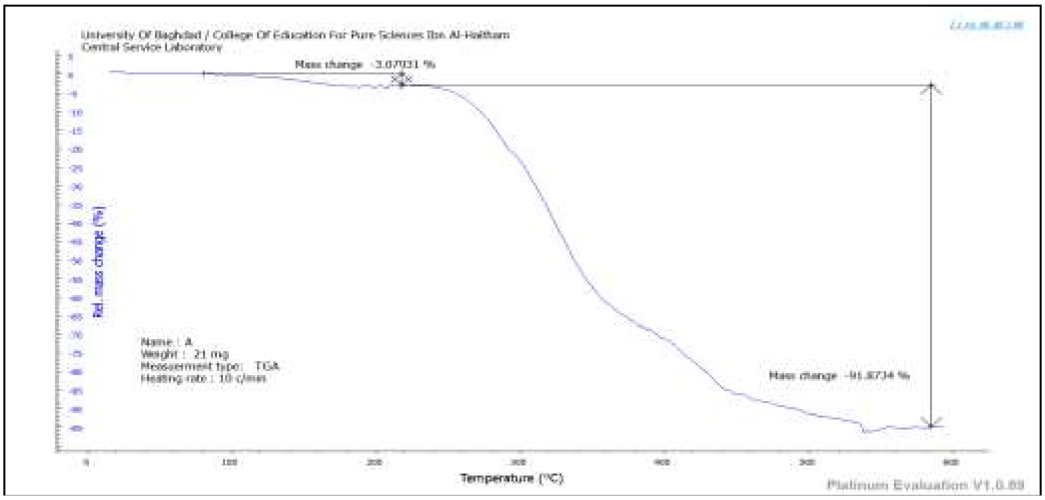
PVA from( barcelona assay 99.9%) and PVP from( Qurchem ) with M.W. of 30000 were used to prepare thin films of PVA, PVP and PVA/PVP blend by solution casting method with different ratios of each (100/0 ,80/20 , 60/40 , 50/50 , 40/60, 20/80 and 0/100) denoted as (A, $AB_1$ , $AB_2$ , $AB_3$ , $AB_4$ , $AB_5$ and B) respectively. PVA and PVP films were prepared by dissolving separately a certain amount of each polymer powder in distilled water and stirred vigorously at 85 $^0$C in case of PVA preparation and at $70^0$C in case of PVP preparation while films of the blend were prepared by dissolving separately a certain amount of each polymer in distilled water and then mix these solutions at $85^0$C with vigorous stirring to form the wanted concentration of the blend . After well mixing the solutions were poured in petri dishes and left for two weeks to dry and then peeled off to conduct thermogravimetric analysis (TGA).

### 3)Equipments:

Thermogravimetric analysis was carried out at university of Baghdad / college of education for pure science Ibn Al - Haitham 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 air stream

## Results and Discussion

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 [12].TGA thermograms for prepared films are shown in figures(1-7) bellow:



**Figure(1) TGA thermogram of film A**

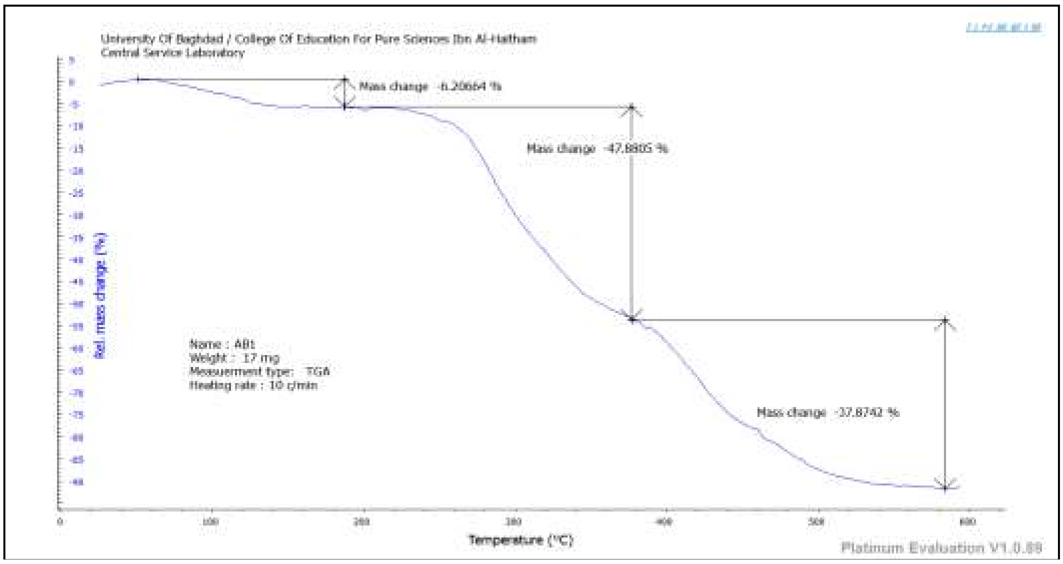


**Figure (2) TGA thermogram of film AB$_1$**

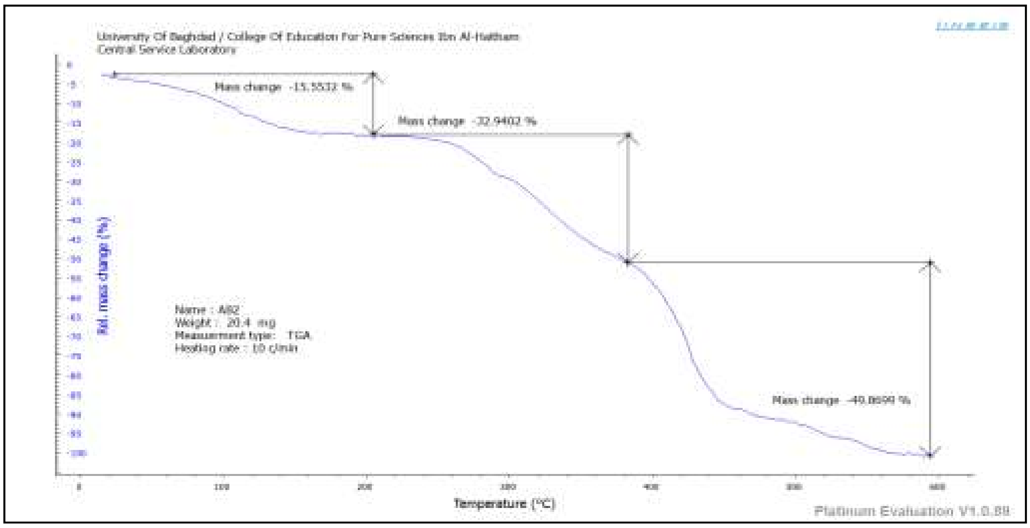


**Figure (3) TGA thermogram of film AB$_2$**

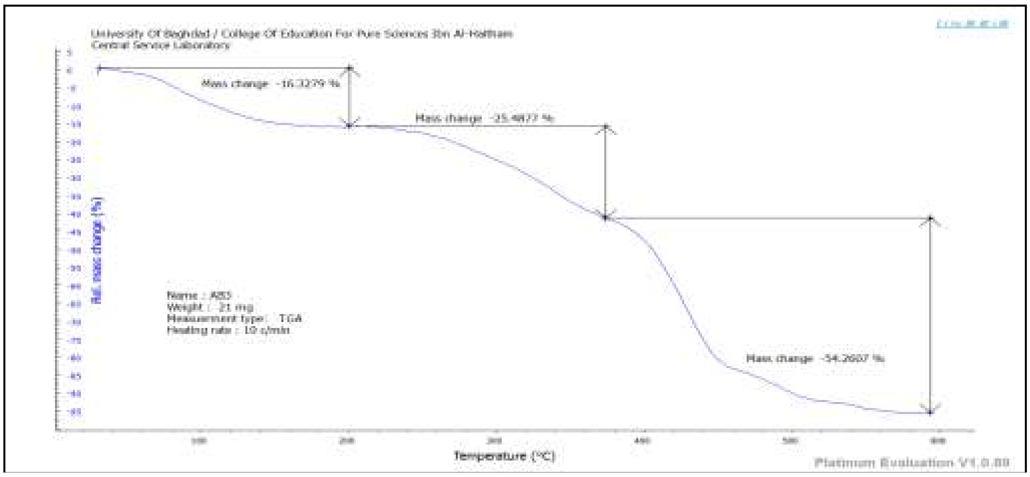


Figure (4) TGA thermogram of film $AB_3$

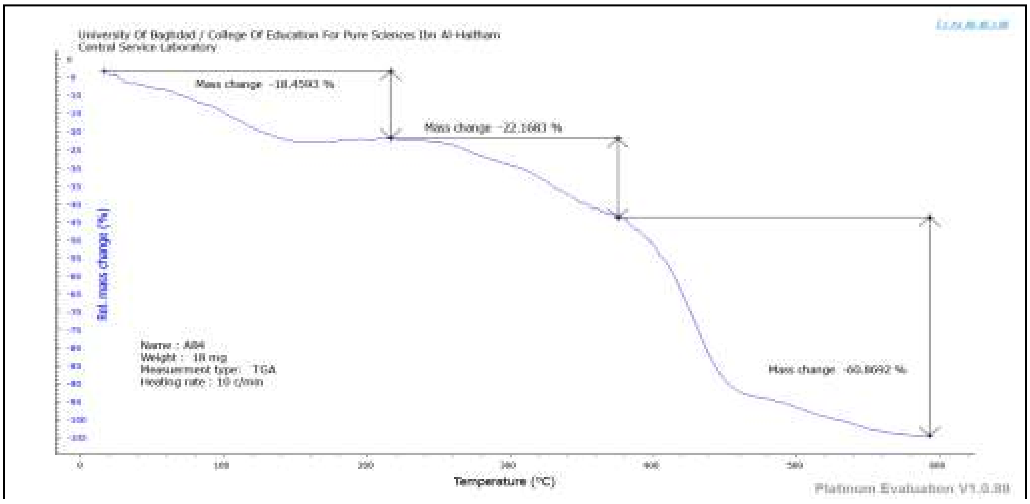


Figure (5): TGA thermogram of film $AB_4$

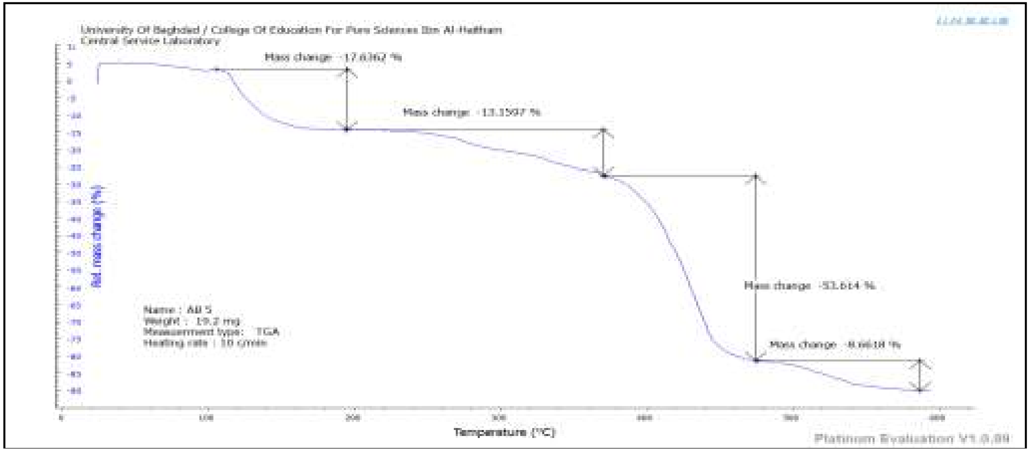


Figure (6) TGA thermogram of film $AB_5$

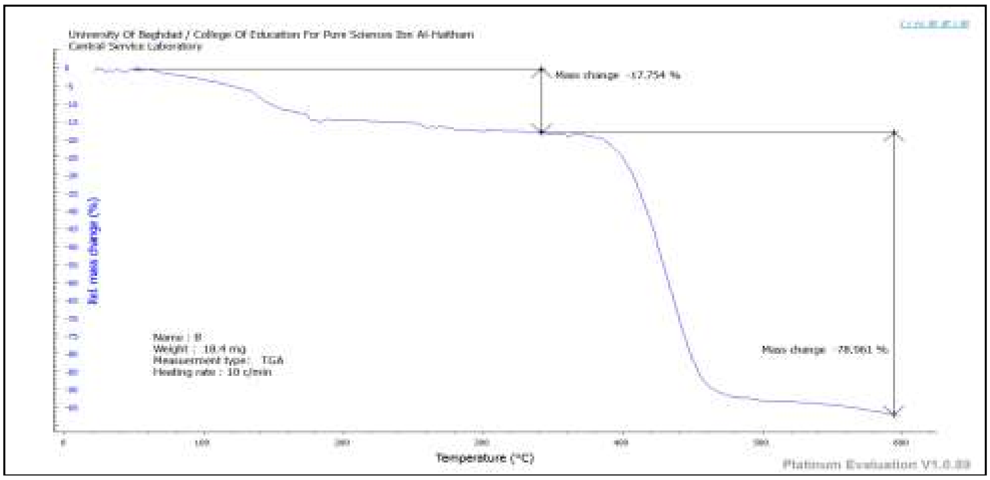


**Figure (7) TGA thermogram of film B**

According to TGA thermogram , PVA undergoes two decomposition steps. The first occurs at temperature range of (90 - $170^{0}$C) with a weight loss of 3.07% which can be attributed to removal of residual solvent [13] while the temperature range at which the second decomposition step occurs is (260 - $420^{0}$C ) with weight loss of 91.87% which represents the more significant weight loss due to degradation of side group (-OH) to give polyene [14] and also due to the cleavage of (C-C) in the main chain of PVA which called carbocation[15] .

According to TGA thermogram, PVP undergoes two decomposition steps ,the first occurs at temperature range of (80 - $190^{0}$C) with weight loss of 17.75% that represents the loss of residual solvent and low molecular weight oligomers [16] whereas the second decomposition step occurs at temperature range of (400 - $460^{0}$C) with weight loss of 78.96% that represents the decomposition of PVP [17],[18].

If we compare PVA with PVP we find that the latter loses more weight at first decomposition step since this step represents losing residual water besides low molecular weight oligomers in case of PVP [16] while in PVA represents losing only residual water [13] and also find that PVP loses less weight than PVA at second decomposition step .

According to TGA thermograms under air atmosphere all PVA/PVP blend films , PVA and PVP show almost the same total weight loss which means have same thermal stability but if we focus at the decomposition steps of all PVA/PVP blend films and comparing to PVA we can find that blending with PVP split the second decomposition step of PVA into two decomposition steps and elevate the temperature that represents the completion of decomposition of PVA to range from ($450^{0}$C) to ($480^{0}$C) rather than ($420^{0}$C) in case of PVA and hence all PVA/PVP blend films show three decomposition steps(except film $AB_5$ that show four decomposition steps ).

The first decomposition step of all PVA/PVP films represents the loss of solvent [10]and oligomers while the second and the third represent the degradation of side group (- OH )[14] and structural decomposition of the blend respectively. The fourth decomposition step of film $AB_5$ represent the continuation of blend decomposition.

Table (1) summarizes data deduce from TGA thermograms for all prepared films:

**Table(1) TGA data for prepared films**

| Film | PVA/PVP ratio | Decomposition step | Temperature range $^0$C | | Weight loss % | |
|---|---|---|---|---|---|---|
| | | | Start | End | Partial | Total |
| A | 100 / 0 | 1ST<br>2nd | 90<br>260 | 170<br>420 | 3.07<br>91.87 | 94.94 |
| AB$_1$ | 80 / 20 | 1st<br>2nd<br>3d | 40<br>250<br>390 | 140<br>340<br>480 | 6.20<br>47.88<br>37.87 | 91.95 |
| AB$_2$ | 60 / 40 | 1st<br>2nd<br>3d | 60<br>260<br>400 | 150<br>370<br>460 | 15.55<br>32.94<br>49.86 | 98.35 |
| AB$_3$ | 50 / 50 | 1st<br>2nd<br>3d | 50<br>250<br>400 | 140<br>400<br>470 | 16.32<br>25.48<br>54.26 | 96.06 |
| AB$_4$ | 40 / 60 | 1st<br>2nd<br>3d | 30<br>260<br>400 | 140<br>400<br>470 | 18<br>22<br>60 | 100 |
| AB5 | 20 / 80 | 1st<br>2nd<br>3d<br>4th | 110<br>240<br>400<br>490 | 140<br>400<br>450<br>560 | 17.63<br>13.15<br>53.61<br>8.66 | 93.05 |
| B | 0 / 100 | 1st<br>2nd | 80<br>400 | 190<br>460 | 17.75<br>78.96 | 96.71 |

All PVA/PVP blend films start and end their first decomposition step at temperature less than that of both PVA and PVP (except film AB$_5$ that starts at temperature higher than all ) so we can say that blending decrease the temperature range at which this step occur for both PVA and PVP and this may due to the formation of interconnected hydrogen bond between PVA and PVP in the blend making the solvent more free to evaporate at lower temperature [19].

There is no organized pattern in decreasing the temperatures at which all PVA/PVP films start and end their first and second decomposition steps comparing to PVA and PVP.

Since PVP is more hydrophilic than PVA and reduces the crystallinity of PVA , the amount of absorbed water will increases as the ratio of PVP increases in the PVA/PVP blend films [20] and as we mentioned earlier that the weight loss at first decomposition step of PVA/PVP blend films represents the removal of solvent and oligomers we find, comparing to PVA ,that the weight loss at first decomposition step of all PVA/PVP blend films increases as the ratio of PVP increases .

The weight loss at second decomposition step of all PVA/PVP blend films is less than that of both PVA and PVP but comparing to PVA the weight loss decreases as the ratio of PVP increases which means that PVP reduces the degradation of side group (- OH) of PVA at this step because the carbonyl group of PVP could make ,as we mentioned earlier , an interconnected hydrogen bond (that serve as physical crosslinks) with hydroxyl group of PVA and as a fact such crosslinks could change thermoplastic into thermoset [21]and hence making side group (- OH) of PVA more difficult to be degradated unless high temperature is applied which means blending with PVP increases thermal stability of PVA at this step , so the blending has a significant effect on weight loss at second decomposition step comparing to both PVA and PVP.

We find that the weight loss at third decomposition step, that occur at high temperature range, of the PVA/PVP blend films increases as the ratio of PVP increases and this is due to the continuation of degradation of side group ( - OH ) of PVA that restricted to some extant at the second decomposition step , carbocation of PVA and also decomposition of PVP as mentioned earlier which means that blending with PVP has significant effect on the weight loss at this step.

## CONCLUSION

We can conclude the followings:

**1.**blending decrease the temperature range at which the first and second decomposition step of PVA and PVP occur

**2.**blending with PVP has significant effect on weight loss at first decomposition step of PVA by increasing this weight loss as the ratio of PVP increases

**3.**blending with PVP split the second decomposition step of PVA into two stepsblending has significant effect on weight loss at second decomposition step of PVA by decreasing this weight loss as the ratio of PVP increases

4.PVP reduces the degradation of side group (- OH) and the carbocation of PVA at second decomposition step and then complete this degradation and carbocation at the third decomposition step of higher temperature range .

**5.**the weight loss at third decomposition step of PVA/PVP blend films increases as the ratio of PVP increases

**6.**PVA/PVP blend films , PVA and PVP show almost the same total weight loss under air atmosphere which means of same thermal stability

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