JCBPS; Section C; February 2018 – April 2018, Vol. 8, No. 2; 001-011, E- ISSN: 2249 –1929
[DOI: 10.24214/jcbps.C.8.2.00111]

Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

*Available online at*www.jcbsc.org

Section C: Physical Sciences

CODEN (USA): JCBPAT

Research Article

DSC and TGA Properties of PVA Films Filled with $Na_2S_2O_3.5H_2O$ Salt

Sabah A. Salman, Nabeel A. Bakr*, Hudaa T. Homad

Department of Physics, College of Science, University of Diyala, Diyala, Iraq.

Received: 02 February 2018; **Revised:** 25 February 2018; **Accepted:** 04 March 2018

Abstract: Pure and sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$) salt filled polyvinyl alcohol (PVA) films with different concentrations of (2, 4, 6, 8, 10, 12, 14, and16) wt % were prepared by solution casting method to study the effect of this salt on thermal properties of (PVA) films by using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). The DSC test showed that most of the samples filled with ($Na_2S_2O_3.5H_2O$) salt exhibit an increase in the glass transition temperature compared with pure PVA film, while melting point had unsystematic dependence on the ($Na_2S_2O_3.5H_2O$) salt concentration compared with pure PVA film. Moreover, TGA curves indicated that the pure PVA film underwent two stages of thermal decomposition of the weight loss while ($Na_2S_2O_3.5H_2O$) salt filled PVA films had two and three stages of thermal decomposition of the weight loss process where the values of total weight loss of the films are lower compared with pure PVA film.

Keywords: Thermal Properties, DSC, TGA, PVA, Sodium Thiosulphate Pentahydrate.

INTRODUCTION

Polyvinyl alcohol (PVA) has many interesting physical properties, and because of that, it is very useful in material science and technical applications. This polymer (Polyvinyl alcohol) is a linear polymer having the formula $[CH_2CH(OH)]_n$ as shown[1] in **figure (1)**. PVA has many applications as a binder in fibers, ceramics, pigments, catalyst pellets, plastics, cement, and cork compositions etc. Moreover, PVA has increasing attention in the biomedical applications[2]. Furthermore, PVA is unstable against heat treatment especially near melting point which is attributed to the hydroxyl groups and that makes its melting point close enough to the glass transition temperature [3,4].

Thermal properties of polymers can be improved by many techniques including blending and copolymerization [4,5]. In this study, thermal decomposition features of ($PVA\text{-}Na_2S_2O_3.5H_2O$) composite films has been systematically studied by thermogravimetric (TGA) analysis and differential scanning Calorimetry (DSC).

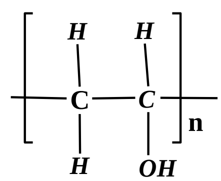

Figure (1): Chemical structure of polyvinyl alcohol (PVA) [1].

2. EXPERIMENTAL PART

2.1 Preparation: PVA powder with molecular weight of (14000 g/mol) and $Na_2S_2O_3.5H_2O$ powder with molecular weight of (248.17 g/mol) from (Central Drug House (P) Ltd., INDIA) were used to prepare films of PVA filled with different salt concentrations of (2, 4, 6, 8, 10, 12, 14, and 16) wt %. The composites were prepared by dissolving PVA and ($Na_2S_2O_3.5H_2O$) salt in distilled water and then mixed them using magnetic stirrer for one hour at (80 ºC), until homogenous polymer solution was formed. These homogenous solutions were casted in glass dish of 5 cm diameter.

2.2 Thermal Characterization: Thermal stability of Pure and ($Na_2S_2O_3.5H_2O$) salt filled polyvinyl alcohol (PVA) films were investigated by employing (Linseis STA PT1000) system. The temperature range was from ambient temperature to (600 $^{\circ}$C) at heating rate of (10 $^{\circ}$C/min) under argon stream flow.

3. RESULTS AND DISCUSSION

3.1 DSC Analysis: Glass transition temperature (T_g) and melting temperature (T_m) of pure PVA films and PVA films filled with $Na_2S_2O_3.5H_2O$ salt with different weight ratios were estimated from the DSC curves. **Figures from (2) to (10)** show the DSC curves (red color) of pure PVA and PVA filled with $Na_2S_2O_3.5H_2O$ salt composite films, and the results of the curves analysis are shown in **Table (1).** It can be noticed that the glass transition temperature value of pure PVA film is (53.2 ^{o}C) which agrees well with other reports[6], while the melting temperature value is (130.6 ^oC). After filling the pure PVA films with $Na_2S_2O_3.5H_2O$ salt, the glass transition temperature value increased unsystematically for the samples having weight ratios of (4, 6, 8, 12, 14, and 16) wt %, while it decreases for the samples with weight ratios of (2 and 10) wt % compared with the glass transition temperature of pure PVA. The increase in the glass transition temperature value at some weight ratios of $Na_2S_2O_3.5H_2O$ salt indicates the miscibility between $Na_2S_2O_3.5H_2O$ salt and the polymer (PVA), as the hydroxyl groups (-OH) of PVA are closely related to the hydrogen bonds, which lead to a high degree of glass transition, where the increase in the weight ratio of $Na_2S_2O_3.5H_2O$ salt means introducing other functional groups that may support this transition and increases the value of the glass transition degree to the maximum value and this is what happened at the weight ratio of (16 wt %) with the highest glass transition[7] temperature value (118.9 ^oC).

Table (1): The glass transition temperature and melting temperature values of (PVA-$Na_2S_2O_3.5H_2O$) composite films.

Concentration (wt %)	**(PVA-$Na_2S_2O_3.5H_2O$) T_g (^oC)**	**(PVA-$Na_2S_2O_3.5H_2O$) T_m (^oC)**
Pure (PVA)	53.2	130.6
2	46.6	213.6
4	54.7	111.9
6	57.1	115.4
8	62.4	107.1
10	52.5	200.7
12	95.7	215.6
14	55.5	215.8
16	118.9	217.2

In general, the unsystematic change of the glass transition temperature as the weight ratio of $Na_2S_2O_3.5H_2O$ salt increases is due to the fact that dissolving $Na_2S_2O_3.5H_2O$ salt reduces the chains elasticity of the polymer (PVA)[8]. Moreover, an unsystematic behaviour and differences in the shape and the area of the melting temperature were noticed which may be attributed to the differences in crystallization degree which is found in (PVA-$Na_2S_2O_3.5H_2O$) composite films with different weight ratios of filling. This increase and decrease in the melting temperature value compared with pure PVA film shows that the crystallization and improvement of the crystal structure decrease with increasing of entanglement degree, where the change in crystalline structure may result from the interaction between the polymer (PVA) and the $Na_2S_2O_3.5H_2O$ salt in the random phase which is due a disturbance in the crystals[7]. We also notice several inverted peaks (endothermic) which represent the temperature of decomposition symbolized by (T_d) located after the melting temperature within the temperature range (218.3 - 275.6) ^oC for pure PVA) film. Similar peaks can be noticed in the DSC curves of the salt filled

PVA samples, followed immediately by the appearance of one or several (exothermic) peaks located within the temperature[6,9] range (427.3 - 590.4) °C .

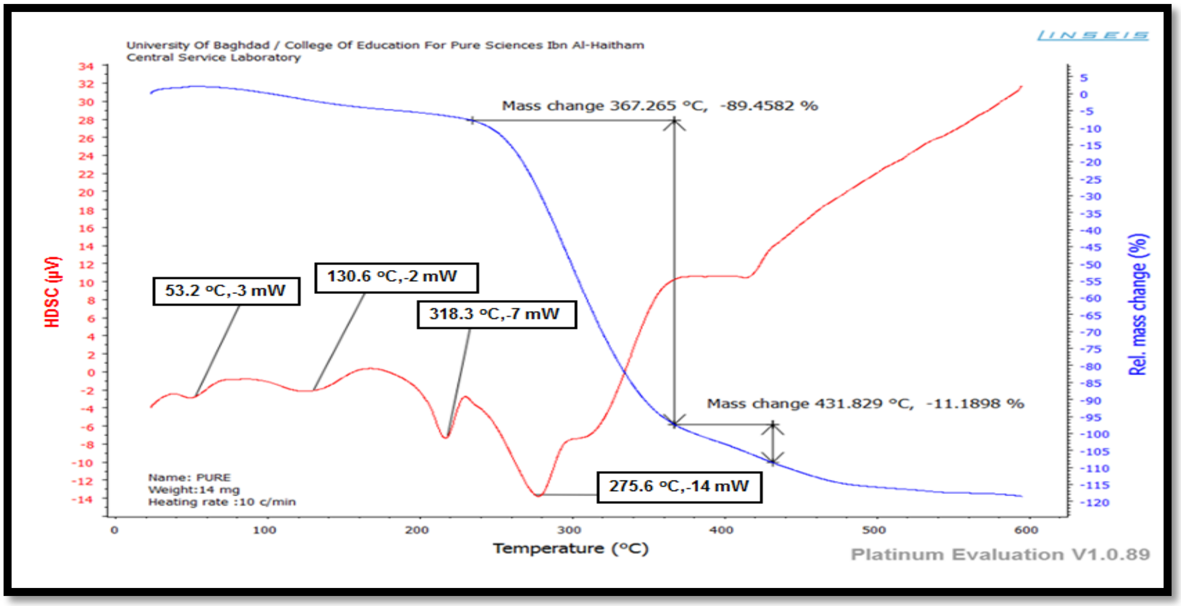

Figure (2): Diagram of (DSC) thermal weight of pure PVA film.

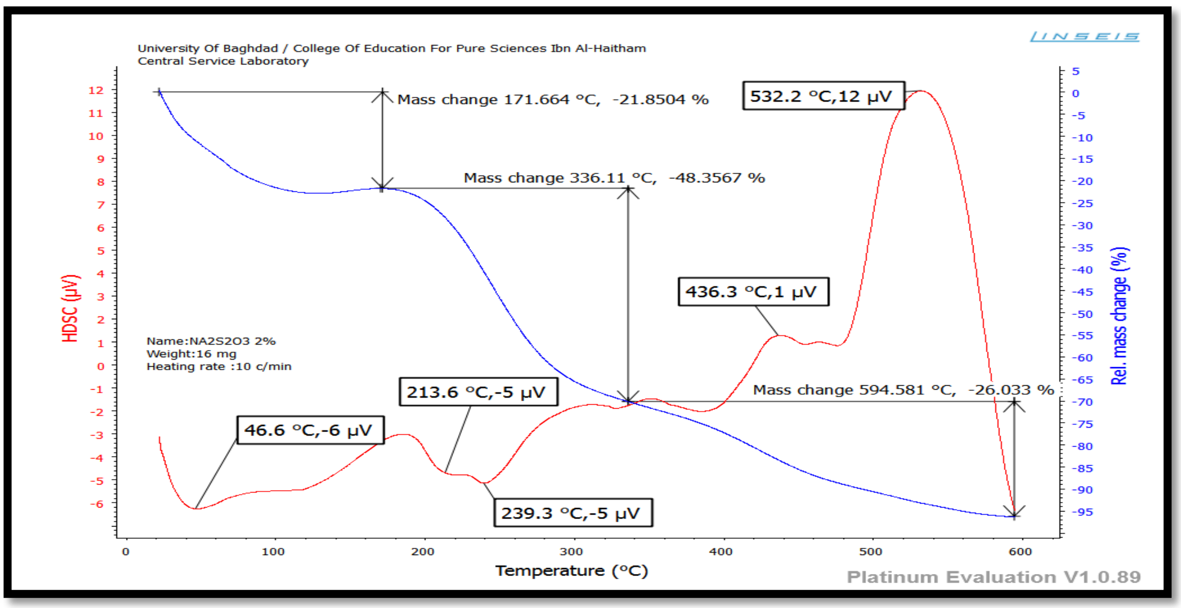

Figure (3): Diagram of (DSC) thermal weight of PVA film filled with (2 wt %) of $Na_2S_2O_3.5H_2O$ salt.

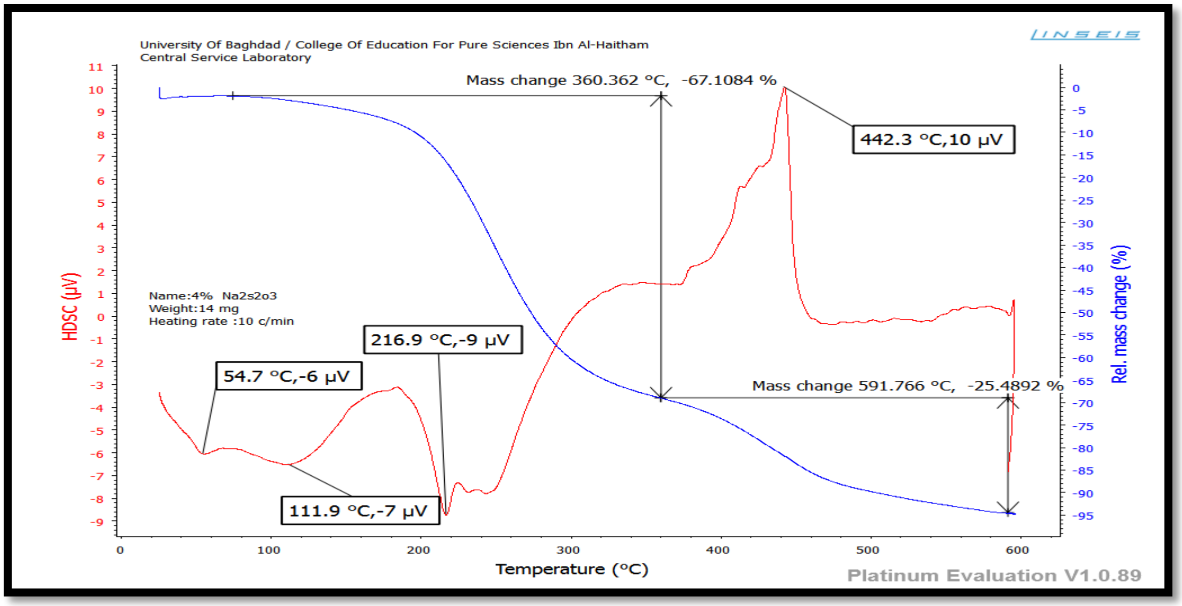

Figure (4): Diagram of (DSC) thermal weight of PVA film filled with (4 wt %) of $Na_2S_2O_3.5H_2O$ salt.

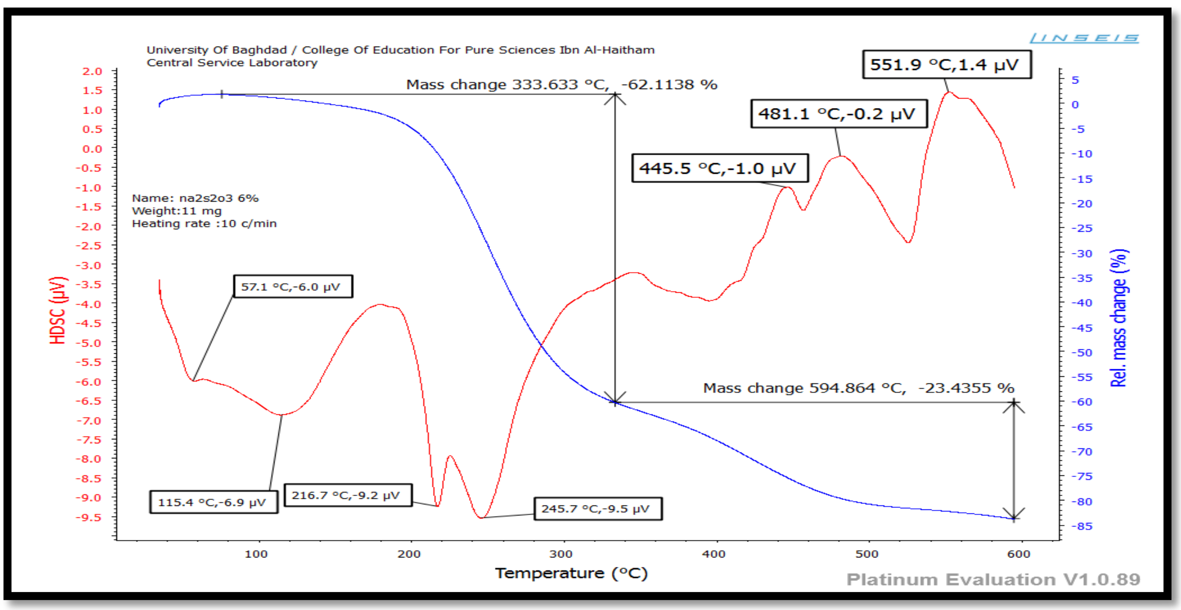

Figure (5): Diagram of (DSC) thermal weight of PVA film filled with (6 wt %) of $Na_2S_2O_3.5H_2O$ salt.

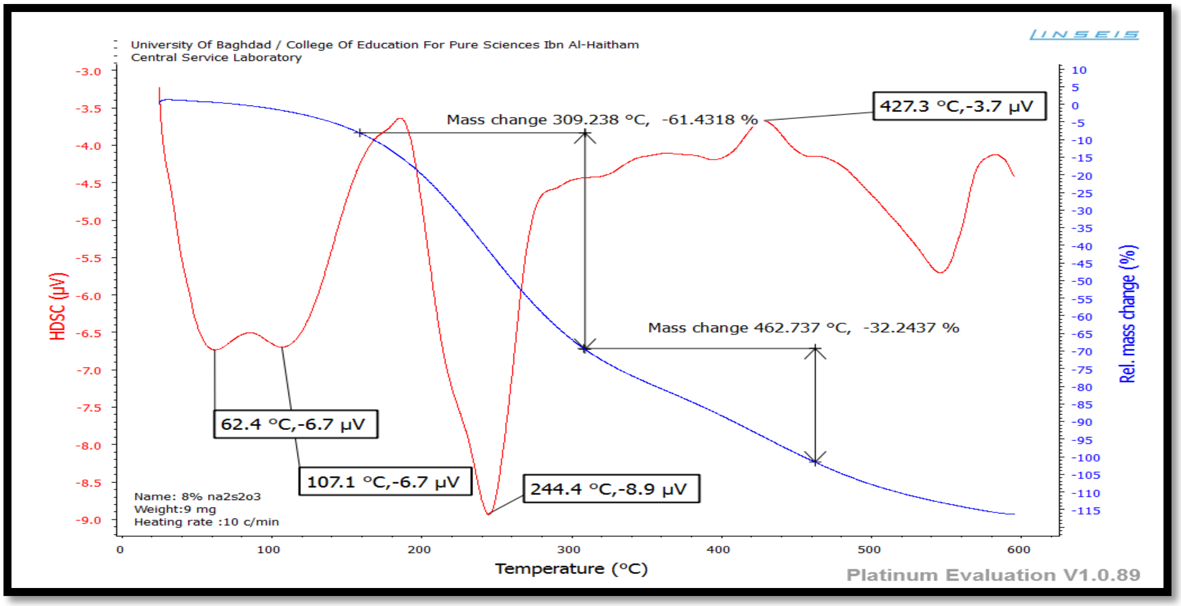

Figure (6): Diagram of (DSC) thermal weight of PVA film filled with (8 wt %) of $Na_2S_2O_3.5H_2O$ salt.

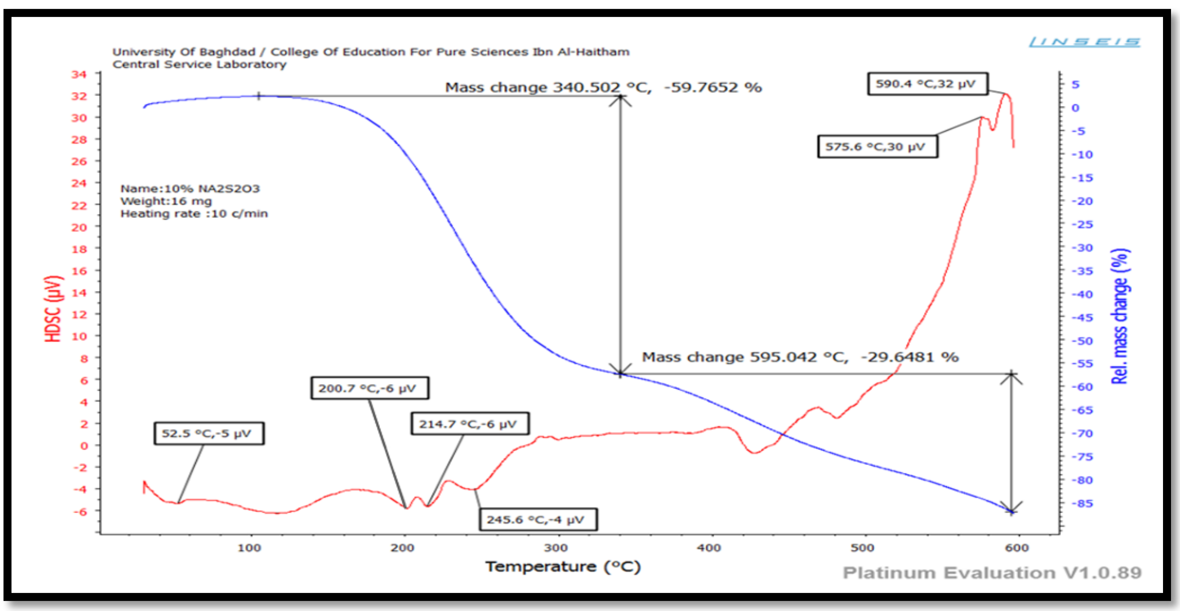

Figure (7): Diagram of (DSC) thermal weight of PVA film filled with (10 wt %) of $Na_2S_2O_3.5H_2O$ salt.

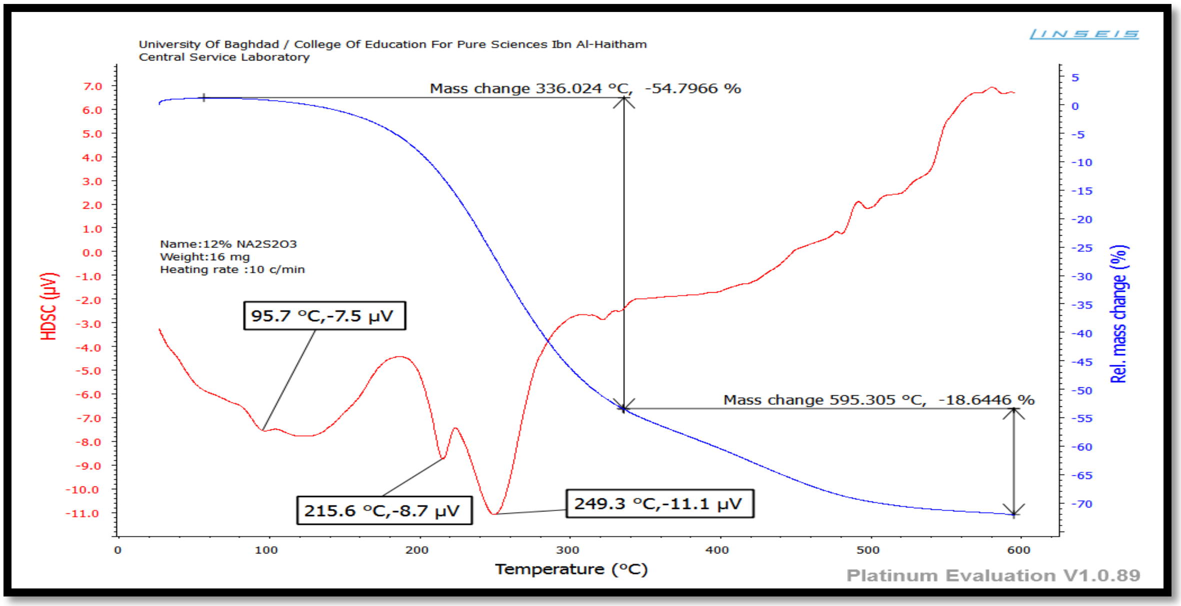

Figure (8): Diagram of (DSC) thermal weight of PVA film filled with (12 wt %) of $Na_2S_2O_3.5H_2O$ salt.

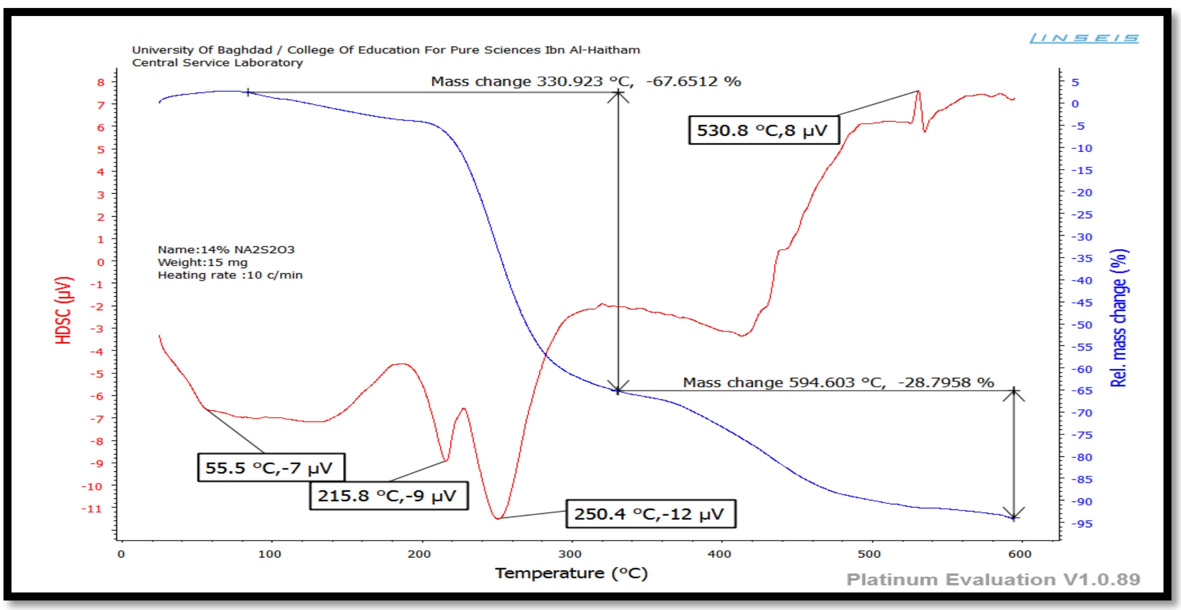

Figure (9): Diagram of (DSC) thermal weight of PVA film filled with (14 wt %) of $Na_2S_2O_3.5H_2O$ salt.

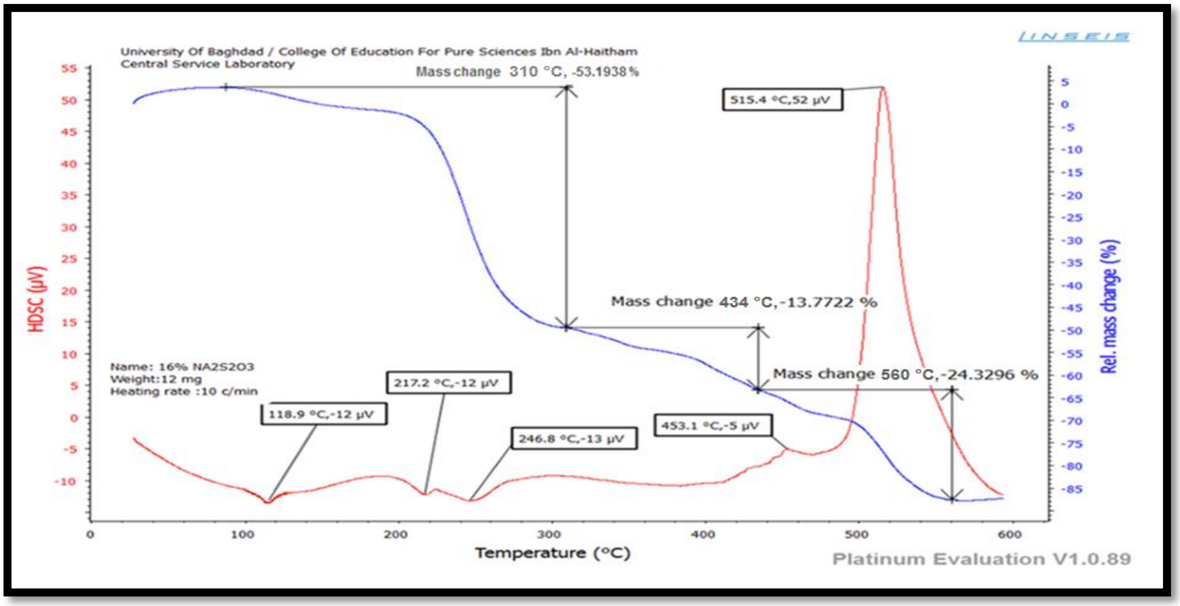

Figure (10): Diagram of (DSC) thermal weight of PVA film filled with (16 wt %) of $Na_2S_2O_3.5H_2O$ salt.

3.2 TGA Test

Polymers undergo with several changes when they are heated and they release gases and liquids with a change in their shape, color and molecular weight. The polymer's ability to resist these changes at high temperature is called thermal stability[10]. To test the mobility of reactions and products at the stages of thermal dissolution of a certain material, the technique of measuring the weight loss of that material as a function of temperature, which is called TGA, is often used by means of DSC system [11]. Figures from (2) to (10) show the TGA curves (blue color) of pure PVA films and PVA films filled with $Na_2S_2O_3.5H_2O$ salt with different weight ratios. **Figure (2)** shows the TGA curve of the pure PVA film, where two stages of thermal decomposition of the weight loss process can be observed. The temperature range of the first stage of thermal decomposition process is (242 - 367) ^oC with a partial loss of weight of (89 %), which may be attributed to the decomposition of the PVA long chains to short ones. The second stage of the of thermal decomposition process is at the temperature range of (367 - 431) °C with a partial loss of weight of (11 %). This partial loss of weight may be attributed to that the chains of PVA are exposed to more decomposition and a cleavage of (C-C) bonds occurs to form carbonate[12]. The total loss of weight of pure PVA film is (100%), and after filling it with $Na_2S_2O_3.5H_2O$ salt, we notice that the total loss of weight for all composite samples decreases compared with pure PVA film. The sample with weight ratio of (12 wt %) showed the lowest total loss of weight of (73.43 %).

Table (2) shows the stages of the thermal decomposition process and the partial and total loss of weight values of the (PVA-$Na_2S_2O_3.5H_2O$) composite films. From the table, it can be noticed that the first stage partial loss of weight values of the thermal decomposition process for all composite samples are less than that of pure PVA film. It can be observed also that the composite samples with (4, 6, 8, 10, 12, and

14) wt % of $Na_2S_2O_3.5H_2O$ salt have two stages of thermal decomposition of the weight loss process with different temperatures range. The greater value of the partial loss of weight occurs at the first stage of the decomposition process for all composite samples, which may be due to the splitting or volatilization of small molecules or the evaporation of the remaining absorbed water. The second stage of the decomposition process has a low value of partial loss of weight; this indicates a chemical decomposition process resulting from the separation of the carbonate bond (C-C) in the polymer (PVA) structure [13].

Table (2): TGA curve values of (PVA- $Na_2S_2O_3.5H_2O$) composite films.

Concentration (wt %)	Region of Decomposition	Temperature Range (^OC)		Weight Loss (%)	
		Start	End	Partial	Total
Pure	1st 2nd	240 367	367 431	89% 11%	100 %
2	1st 2nd 3d	38 171 336	171 336 594	21.85% 48.35% 26.03%	96.23 %
4	1st 2nd	73 360	360 591	67.10% 25.48%	92.58 %
6	1st 2nd	68 333	333 594	62.11% 23.43%	85.54 %
8	1st 2nd	156 309	309 462	61.43% 32.24%	93.67 %
10	1st 2nd	105 340	340 595	59.76% 29.64%	89.4 %
12	1st 2nd	55 336	336 595	54.79% 18.64%	73.43 %
14	1st 2nd	80 330	330 594	67.65% 28.79%	96.44 %
16	1st 2nd 3d	85 310 434	310 434 560	53.19% 13.77% 24.32%	91.28 %

The composite samples with weight ratios (2 and 16) wt % of $Na_2S_2O_3.5H_2O$ salt undergo three stages of thermal decomposition of the weight loss process at different temperatures range. The greatest value of the partial loss of weight is in the first stage of the thermal decomposition process at the weight ratio of (16 wt %), while the sample with weight ratio of (2 wt %) showed the lowest value of partial loss of weight in this stage of thermal decomposition process which represents the loss of solvent. The second stage of the thermal decomposition process of the partial loss of weight showed that the sample with weight ratio of (2 wt %) has the greatest value for partial loss of weight, while the sample with weight ratio of (16 wt %) has the lowest value of the partial loss of weight at this stage of the thermal decomposition process; this stage of the thermal decomposition process represents decomposition of the side hydroxyl group (OH-) to produce carbonyl group (C=O). Moreover, the third stage of the thermal decomposition process of the partial loss of weight showed that the samples with weight ratios of (2 and 16) wt % have the mean value of partial loss of weight at this stage of the thermal decomposition process; where this stage of the thermal decomposition process represents the separation of carbonate bond (C-C) in the main chain of polymer (PVA)[14].

4. CONCLUSIONS

The analysis of DSC diagrams for pure PVA films and PVA films filled with $Na_2S_2O_3.5H_2O$ salt with different weight ratios showed that:

- The added $Na_2S_2O_3.5H_2O$ salt to PVA has a significance effect on the thermal properties of the prepared films.
- Some of the prepared films, such as the sample prepared with (16 wt %) of added salt, can be improved further to make them good candidates in moderate temperature applications.
- The glass transition temperature of the PVA films filled with $Na_2S_2O_3.5H_2O$ salt with different weight ratios increased unsystematically for the samples having weight ratios of (4, 6, 8, 12, 14, and 16) wt %, while it decreases for the samples with weight ratios of (2 and 10) wt % compared with the glass transition temperature of pure PVA.
- The melting temperature of PVA films filled with $Na_2S_2O_3.5H_2O$ salt with different weight ratios showed unsystematic change with the increase in salt weight ratio, where it is lower than that of pure PVA for some samples and higher for other samples.
- TGA curves showed that pure PVA film passes through two stages of thermal decomposition process with (100 %) total loss of weight, and when filling by $Na_2S_2O_3.5H_2O$ salt, the total loss of weight decreases compared with pure PVA film; and the samples having salt weight ratios of (4, 6, 8, 10, 12, and 14) wt % showed a two stages of thermal decomposition of the weight loss process, while the samples with weight ratios of (2 and 16) wt % showed three stages of thermal decomposition of the weight loss process.

REFERENCES

1. E. J. Mark, "Polymer Data Handbook", Oxford University press, U.K., 1998.
2. G. Attia and M. F. H. Abd El-kader, "Structural, Optical and Thermal Characterization of PVA/2HEC Polyblend Films", Int. J. Electrochem. Sci., 2013, 8, 5672-5687.
3. P. J. Liu, W. H. Chen, Y. Liu, S. B. Bai and Q. Wang, "Thermal Melt Processing to Prepare Halogen-Free Flame Retardant Polyvinyl Alcohol", Polymer Degradation and Stability,2014, 109, 261-269.
4. T. Nishino, S. Kani, K. Gotoh and K. Nakamae, "Melt Processing of Polyvinyl Alcohol Through Blending with Sugar Pendant Polymer", Polymer, 2002, 43, 2869-2873.

5. H. Nishimura, N. Donkai, T. Miyamoto, "Preparation and Thermal Properties of Thermoplastic Polyvinyl Alcohol Complexes with boronic acids", Polymer Chemistry, 1998, 36, 3045-3050.
6. K. Chrissafis, K. M. Paraskevopoulos, G. Z. Papageorgiou, and D. N. Bikiaris, "Thermal and dynamic mechanical behavior of bionanocomposites: Fumed silica nanoparticles dispersed in poly (vinyl pyrrolidone), chitosan, and poly (vinyl alcohol)", Journal of Applied Polymer Science, 2008,110, 3, 1739-1749.
7. O. W. Guirguis and T. H. Moselhey, "Thermal and Structural Studies of Polyvinyl Alcohol and Hydroxypropyl Cellulose Blends", Natural Science, 2012, 4, 1, 57-67.
8. L. C. Shen, "Studies on the Effect of Nanosized Ceramic Filler Polyvinyl Alcohol/Lithium Perchlorate Based Polymer Electrolytes", M.Sc. Thesis, University of Malaya, Faculty of Science, Department of Physics, 2012.
9. A. Al-khodary, "Vibrational, Thermal, Optical, and Magnetic investigations of PVA Films Filled with $FeCl_3$ and $CoCl_2$", Physica B, 2009, 404, 1287-1294.
10. A. A. Mohammed, "Plastics Chemistry", Library Printing and Publishing, University of Mosul, Iraq, 1993.
11. M. P. Stevens, "Polymer Chemistry: An Introduction", Addison-Wesley Publishing Company, London, 1975.
12. R. Singh, S. G. Kulkarni and N. H. Naik, "Effect of Nano Sized transition Metals on Thermal Decomposition Behavior of Polyvinyl Alcohol", Advanced Materials Letters", 2013, 4, 1, 82-88.
13. A. M. Shehap, "Thermal and Spectroscopic Studies of Polyvinyl Alcohol/Sodium Carboxy Methyl Cellulose Blends", Egypt J. Solids, 2008, 31, 1, 75-91.
14. N. A. Betti, "The Effect of Cesium Chloride on Thermal Properties of Polyvinyl Alcohol", Eng. &Tech. Journal, 2016, 34, 12, 2193-2206.

*** Corresponding Author: Nabeel A. Bakr**

Department of Physics, College of Science, University of Diyala, Diyala, Iraq.

Online Publication Date: 04.03.2018