Open Access Journal of Physics
Volume 2, Issue 2, 2018, PP 5-10

Thermal stability of polymer composite films based on polyvinyl alcohol doped with different fillers

Shko H.Salh, Dlzar A.Raswl

Department of Physics, College of Science, University of Sulaimani

***Corresponding Author:** Dlzar A.Raswl, Department of Physics, College of Science, University of Sulaimani*

ABSTRACT

Thermal stability of polymers and composites play an essential role for some specific applications and can be enhanced by using appropriate fillers. Thermal analysis as Thermogravimetric Analysis (TGA) has become the polymer characterization method the most frequently used. In the present study the influence of some transition metal salts and metal on the thermal decomposition behavior of the polyvinyl alcohol (PVA) as the matrix, have been carried out using thermogravimetric analysis. The films of pure PVA and doped with filers Copper sulfate (CuSO4), Silver sulfate (Ag2SO4), Copper chloride (CuCl2), and Copper powder, are prepared using casting technique. These fillers exhibit improvement in the thermal stability as realised by ashift in thermal decomposition of pure PVA. Similar observations were made by various researchers. A change in the thermal decomposition temperature of PVA was seen to depend upon the nature of the type of filers. The increase in the decomposition temperature for various composites, though not very significant, the decomposition patterns appear to be significantly different after 300 oC exhibiting slow degradation.

INTRODUCTION

Studies on the thermal degradation of plastics have been reported for many years, a considerable number of references on this topic being found in the literature [1-3]. Most of the early studies on polymer thermal degradation were aimed at determining the polymer thermal stability rather than at developing feasible alternatives for the conversion of polymeric wastes. It was in the 1970s that the thermal degradation of polymers began to be considered as an interesting alternative for the feedstock recycling of such wastes. Polymer decomposition by treatment at higher temperatures is also used as an analytical technique for polymer identification [4,5].

The polymer thermal decomposition is an endothermic process, at least the dissociation energy of the C-C bond in the chain must be supplied to break down the polymer. Moreover, this is the primary factor determining the polymer stability[6]. Thermal analysis methods have proved useful not only in defining suitable processing conditions for these polymers as well as drawing up useful service guidelines for their application but also in obtaining information on the relationships between thermal properties and polymer chain structure [7,8]. In recent years, several different configurations of instrumentation have been developed to accomplish degradation for both conventional qualitative and quantitative analysis. Thermal decomposition of polymers has been investigated by techniques like thermo gravimetry (TG), derivative thermo gravimetry (DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC)[9-11].

Thermo gravimetric analysis (TGA) is one of the members of the family of thermal analysis techniques used to describe a wide variety of organic and inorganic materials. TGA provides complimentary and supplementary characterization information to the most commonly used thermal technique [12].TGA measures the amount and rate of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. The measurements are utilized primarily to determine the thermal and oxidative stabilities of materials as well as their compositional properties. The technique can analyze materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture). It is particularly useful for the study of polymeric materials, including thermoplastics, thermo sets, elastomers, composites, films, fibers, coatings and paints[13,14].TGA measurements provide appreciated information that can be used to select materials for particular end-use applications, predict product performance and improve product quality[15,16].

The thermo-gravimetric analysis is a fast and accurate technique which is used for understanding thermal decomposition behavior of the material under test. In the thermo gravimetric analysis, the weight of a substance is monitored as a function of temperature or time in a controlled atmosphere [17].

Polyvinyl alcohol (PVA) has been extensively usedas a host of polymer composites because of its availability with different molecular weights, its good film-forming character, non-toxicity, biodegradability, and chemical resistance[18-20]. In addition to all these advantages associated with PVA, it contains a carbon backbone with a hydroxyl group attached to a methane carbon of each repeat unit which act as a source of hydrogen bonding and can possibly trap the metal ions or valent metals forming complexes [21]. Thermal stability of polymers and composites play an important role for some specific applications and can be enhanced by using appropriate fillers. In the present study the influence of some fillers (Copper sulfate (CuSO4), Silver sulfate (Ag2SO4), Copper chloride (CuCl2), and Copper powder) on the thermal decomposition behavior of the polyvinyl alcohol (PVA) as the matrix, have been carried out using thermogravimetric.

SAMPLE PREPARATION

The raw materials used in this study are Polyvinyl alcohol (PVA), 98-99% hydrolyzed, low molecular weight supplied from Alfa Aesar, and distilled water as a solvent for polymer material. The inorganic fillers used in this study are Copper sulfate (CuSO4), Silver sulfate (Ag2SO4), Copper chloride (CuCl2), and Copper powder.

The pure PVA film sample was prepared by dissolving 2 g of PVA in 30 mL distilled water at 90^{o}C for 1hr.The resulting solution was cast onto Petri dish and allowed to dry slowly at room temperature for films to form.

For the doped samples 2 gm of PVA, was fixed and dissolved in 30 mL distilled water at 90^{o}C for 1hr. The amount of 5% of dopant (CuSO4, Ag2SO4, CuCl2, and Cu powder), were dissolved in the 5 mL distilled water separately at ambient temperature. Then the solutions of fillers were added to the homogeneous solution of PVA at 40oC under stirring. For maximum dispersion, the mixture was further stirred continuously for (30 min) without heating until homogeneous solutions were obtained.

The resulting solution was cast onto Petri dish and allowed to dry slowly at room temperature for films to form. The dried films peeled off and transferred into the desiccator for continuous drying. Table 1 shows the concentration of the prepared samples.

Table1. *Composition of pure and doped PVA films.*

Samples	PVA (g)	distilled water (mL)	Type of fillers	Wight of fillers (g)
S1	2	30	-	0
S2	2	30	$CuSO_4$	0.105
S3	2	30	Ag_2SO_4	0.105
S4	2	30	$CuCl_2$	0.105
S5	2	30	Cu powder	0.105

EQUIPMENT AND TEST CONDITION

The thermal stability of the films was studied using thermal gravimetric analysis (TGA). The experiments are carried out on Perkin-Elmer Thermo gravimetric/ Differential analyzer TG/DTA; the micro-balance have least count of 0.001 mg. Samples weighing 4.35 to 8.86mg are heated in the temperature range of 30^{o}C to 500^{o}C at heating rate 10oC/min in anair atmosphere. The measured mass of samples (weight %) as a function of temperature was recorded.

RESULTS AND DISCUSSIONS

The thermo grams were recorded for pure PVA and for various composites prepared by embedding different transition metal salt and metals powder. Figure 1 shows the TGA curve of pure PVA. From TGA curve it is clear that PVA main decomposing starts at its melting temperature of 250 ^{o}C with continuous weight loss up to 360 °C exhibiting around 69.45% weight loss. From 400-520 °C, there is gradual decomposition with 12.01% weight loss. After 510 °C onwards, a plateau region exhibiting constant weight (around 15%) is seen in the TG curve. The initial weight (around 4.01%) loss may be due to degradation of large polymer chains into small fragments which subsequently undergo further decomposition. Similar observations were made by other workers [22-24]. Table1 includes temperature ranges for different decomposition stages along with percentage weight loss for pure PVA. The effect of various fillers of 5% concentration of copper sulphate, copper chloride, silver sulphate, copper metal on thermal stability of PVA are recorded, as shown in Figures 2, 3, 4, and 5 respectively.

The copper sulphate doped PVA composite exhibits four stage decomposition unlike PVA with different decomposition patterns as shown in Figure 2. Initial weight loss of around 1.17 % in the temperature range of 35-100 °C is observed. The second decomposition stage in the temperature range of 100-200°C showing around 5.48% weight loss. The third stage decomposition in the temperature range of 225-290°C showing around 28.47% weight loss may be due to pure PVA in the presence of partially dehydrated copper sulphate indicating the marginal increase in decomposition temperature of PVA present in the composites [25]. PVA undergoes further decomposition at 410°Cin the presence of anhydrous copper sulphate forming a copper oxide at around 540°C. After this temperature, it shows constant weight (around 2.5 %).

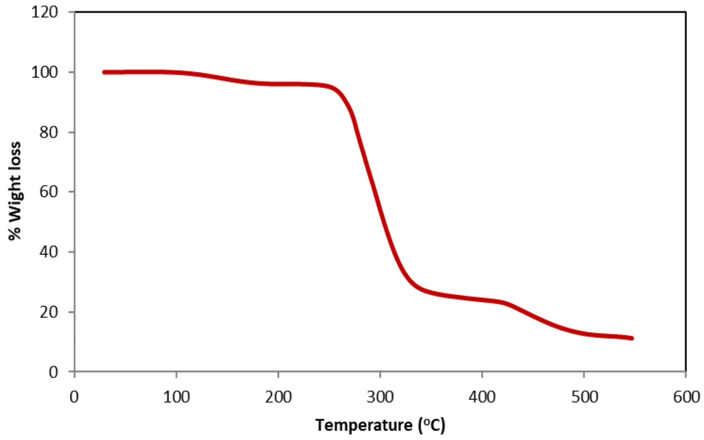

Figure1. *TG curves for pure PVA.*

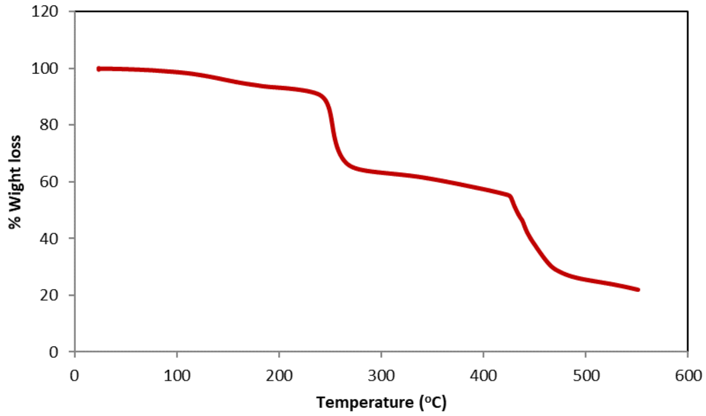

Figure2. *TG curves for PVA:CuSO4.*

Silver sulphate dopant in PVA matrix shows three-stage decomposition, as it was illustrated in Figure 3. Table 1 includes the decomposition temperature for various stages along with percentage weight loss. Initial weight loss at 100°C (around 5.50%) may be due to loss of water. Second stage decomposition starts around 210°C and shows continuous rapid degradation up to 300°C with around 43.67% weight loss. After 405°C, it shows a gradual weight loss up to 515°C with 17.81% weight loss. After 550°C onwards, a constant weight around 22% is realized.

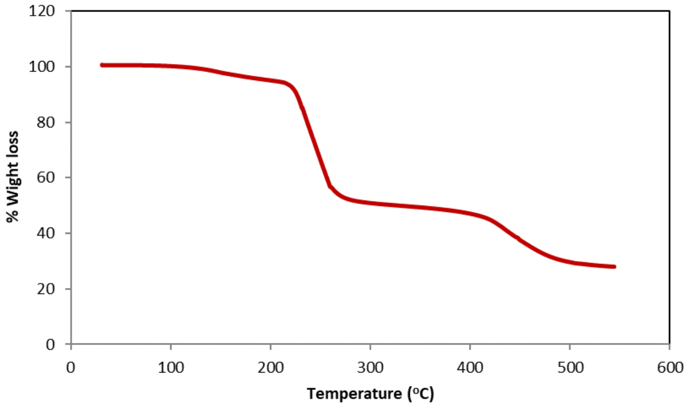

Figure3. *TG curves for PVA:Ag2SO4.*

The copper chloride PVA based composite shows two stage decomposition as seen in Figure 4. The copper chloride being anhydrous salt does not show weight loss up to 180^{o}C and start decomposing at that temperature with sharp weight loss up to 290^{o}C and later on slow but continuous weight loss up to 500^{o}C. It is clear from the TGA curve that the decomposition of PVA after 290^{o}C gets affected because of the presence of cupric chloride which may start decomposing after 300^{o}C along with PVA.

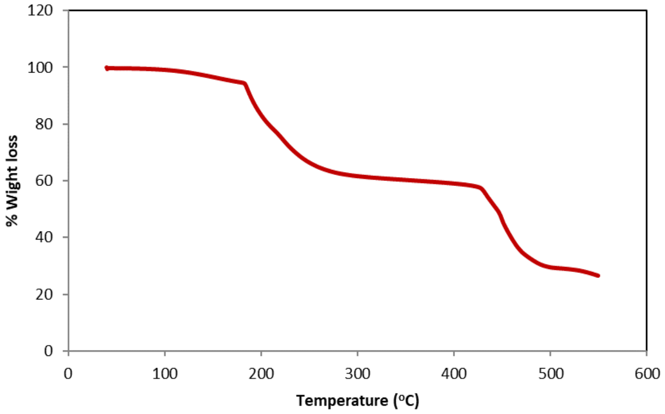

Figure4. *TG curves for PVA:CuCl2.*

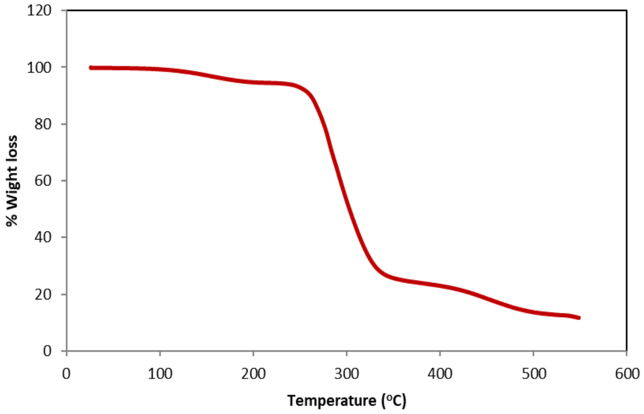

Figure5. *TG curves for PVA:Cu.*

The metallic copper powder in the PVA polymer matrix exhibited three-stage decomposition, as shown in Figure 5. The initial decomposition exhibits around 4.62 % weight loss in the temperature range of 110^{o}C to 225^{o}C may be due to adsorbed moisture. The decomposition temperature of PVA gets shifted to 225^{o}C and shows continuous degradation up to 370^{o}C with around 70.02 % weight loss. The slow degradation further continues from 400 ^{o}C up to 530°C with 10.35 % weight loss. After that, a constant weight around 15% is realized. From the above observation and data in Table 1, it is clear that the presence of copper sulfate or copper in PVA significantly affects the decomposition pattern of PVA and marginally increases the decomposition temperature of PVA.

Table 1. *TG data of PVA based composites.*

Samples	Fillers	Decomposition temp. range (°C)	%Weight loss
S1	-	90-200 250 – 360 400 – 520	4.01 69.45 12.01
S2	$CuSO_4$	35-100 100-200 225-290 410-540	1.17 5.48 28.47 33.72
S3	Ag_2SO_4	100-210 210- 300 405-515	5.50 43.67 17.81
S4	$CuCl_2$	180-290 420- 510	32.60 29.10
S5	Cu powder	110-225 230-370 400-530	4.62 70.02 10.35

CONCLUSION

Various polymer composites were synthesized by embedding different fillers in polyvinyl alcohol matrix using casting technique. The thermal decomposition behavior was studied by TG analysis. An increase in the decomposition temperature of PVA was noticed when metal salts were doped into it and depends upon the nature of the metal salt and water associated with it. The increase in the decomposition temperature for various composites, though not very significant, the decomposition patterns appear to be significantly different after 300 oC exhibiting slow degradation. In some stage the do pants exhibit improvement of thermal stability of the sample, this may be due to the entrapment of metal salts/metals forming coordination complex through weak Vander-Waals forces requiring more heat for decomposition.

REFERENCES

[1] Joel R. Fried, "Introduction to Polymer Science", 2nd Edition, Prentice Hall, (2013).

[2] D.I. Bower, "An Introduction to Polymer Physics", Cambridge University Press, D.I. Bower (2002).

[3] O.G. Abdullah, "Synthesis and optical band gap investigation of PVA/CdS nanocomposite films", Journal of Zankoy Sulaimani 17A(1): 185-192 (2015).

[4] M.P. Groover, "Fundamentals of Modern Manufacturing",2nd Edition, John Wiley & Sons, Inc,New York (2002).

[5] N.K. Verma, S.K. Khanna, B. Kapila, "Comprehensive Chemistry XII", Laxmi Publications, LTD, New Delhi, (2011).

[6] O.G. Abdullah, D.R. Saber, L.O. Hamasalih, "Complexion Formation in PVA/PEO/$CuCl_2$ Solid Polymer Electrolyte", Universal Journal of Materials Science 3(1): 1-5 (2015).

[7] S.F. Bdewi, O.G. Abdullah, B.K. Aziz, A.A.R. Mutar, "Synthesis, Structural and Optical Characterization of MgO Nanocrystalline Embedded in PVA Matrix", Journal of Inorganic and Organometallic Polymers and Materials 26(2): 326-334 (2016).

[8] Robert J. Young, Peter A. Lovell, "Introduction to Polymers", 3rd Edition, CRC Press, (2011).

[9] O.G. Abdullah, Y.A.K. Salman, S.A. Saleem, "In-situ synthesis of PVA/HgS nanocomposite films and tuning optical properties", Physics and Materials Chemistry 3(2): 18-24 (2015).

[10] O.G. Abdullah, D.R. Saber, S.A. Taha, "The optical characterization of polyvinyl alcohol: cobalt nitrate solid polymer electrolyte films", Advanced Materials Letters 6(2): 153-157 (2015).

[11] J. Aguado, D.P. Serrano, "Feedstock Recycling of Plastic Wastes", series editor James H. Clark, The Royal Society of Chemistry (1999).

[12] Charles E. Carraher, Jr., "Introduction to Polymer Chemistry", Third Edition, Taylor & Francis Group, LLC, (2013).

[13] K. Pielichowski, J. Njuguna, "Thermal Degradation of Polymeric Materials", Rapra Technology Limited, UK, (2005).

[14] R. Chen, Y. Kirsh, "The Analysis of Thermally Stimulated Processes", R. Chen and Y. Kirsh, (1981).

[15] O.G. Abdullah, D.A. Tahir, K. Kadir, "Optical and structural investigation of synthesized PVA/PbS nanocomposites", Journal of Materials Science: Materials in Electronics 26(9): 6939-6944 (2015).

[16] O.G. Abdullah, "Synthesis of single-phase zinc chromite nano-spinel embedded in polyvinyl alcohol films and its effects on energy band gap", Journal of Materials Science: Materials in Electronics 27(11): 12106-12111 (2016).

[17] C.L. Beyler, M.M. Hirschler, "Thermal Decomposition of Polymers", Chapter 7, pp. 111-131.

[18] O.G. Abdullah, D.R. Saber, "Optical absorption of polyvinyl alcohol films doped with nickel chloride", Applied Mechanics and Materials 110-116, 177-182 (2012).

[19] O.G. Abdullah, S.R. Saeed, "Effect of NaI doping on some physical characteristic of $(PVA)_{0.9}$-$(KHSO_4)_{0.1}$ composite films", Chemistry and Materials Research 3(11): 19-24 (2013).

[20] O.G. Abdullah, D.A. Tahir, D.R. Saber, "Optical properties of the synthesized Cr_2S_3 nanoparticles embedded in polyvinyl alcohol", ARO: The Scientific Journal of Koya University 3(1): 45-49 (2015).

[21] ASTM E 176, Standard Terminology of Fire Standards, Vol. 4.07, American Society for Testing and Materials, West Conshohocken, PA.

[22] C.M. Hassan, N.A. Peppas, Advances in Polymer Science 153, 37-65, (2000).

[23] O.G. Abdullah, S.A. Saleem, "Effect of copper sulfide nanoparticles on the optical and electrical behavior of Poly (vinyl alcohol) films", Journal of Electronic Materials 45(11): 5910-5920 (2016).

[24] O.G. Abdullah, "Influence of barium salt on optical behavior of PVA based solid polymer electrolytes", European Scientific Journal 10(33): 406-417 (2014).

[25] R. Singh, S.G. Kulkarni, N.H. Naik, "Effect of nano sized transition metal salts and metals on thermal decomposition behavior of polyvinyl alcohol", Adv. Mat. Lett. 4(1): 82-88 (2013).