



GSJ: Volume 9, Issue 1, January 2021, Online: ISSN 2320-9186

www.globalscientificjournal.com

EFFECT OF ADDITIVE AND GAMMA IRRADIATION ON THE THERMAL PROPERTIES OF POLYVINYL ALCOHOL DOPED WITH SILVER NITRATE

Ibrahim M. Osman¹, Prof. Mubarak Dirar Abdalla¹, Prof. Ahmed H. Elfaki¹, Khalid Y. A. Yagoub², Abdalla M. Eldoma³

1- *Physics Department, College of Science, Sudan University of Science and Technology, Khartoum, Sudan. Email: ibrahim_physics@yahoo.com*

2- *Medical Physicist at National Cancer Institute, University of Gazira, Wad-madani, Sudan.*

3- *Calibration Laboratories, Administration of Measurement and Calibration, Sudanese Standards and Metrology Organization, Khartoum, Sudan.*

KeyWords

Composed materials, DTGA, DSC, Gamma irradiation, inorganic additives, polymers pyrolysis, polyvinyl alcohol (PVA), thermal stability, thermogravimetric analysis (TGA), UV spectroscopy.

ABSTRACT

Thermal properties of polyvinyl alcohol (PVA) doped with silver nitrate (AgNO_3) composite Films synthesized by casting method has been investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The effect of the addition of AgNO_3 to PVA was studied. The results indicated that the addition of AgNO_3 led to a more compact structure compared to the pure PVA which resulted in an improvement in its thermal stability with an increase in the isotropic character of the polymer samples. The results also clearly demonstrate that the composite films of AgNO_3 and PVA are more stable at higher temperature than pure PVA. Samples were irradiated with gamma rays in the dose range 0-10 Gy. The variation of onset temperature of decomposition, glass transition temperature and residual mass has been investigated. Thus, this work suggests the possibility of using the gamma irradiated PVA/ AgNO_3 films in different electronic and semiconductors applications.

1- Introduction:

Polymeric materials are of great interest in scientific and technological research. Solid polymer blends have been intensively studied due to its potential applications for novel systems and devices [1-3]. By addition of dopants, blends, or copolymers to the main polymer matrix, the optical, electrical, thermal, mechanical and electrochemical properties of these materials could be selectively modified obtaining particular characteristics for various applications in different fields of science [3, 4]. This field of polymer additives has attracted strong interest in today's materials research, as it is possible to achieve impressive enhancements of material properties as compared with the pure polymers [5, 6]. Furthermore, irradiation of polymers has established itself as one of the most acceptable, easy and non-toxic approach to alter polymer properties significantly [1-3]. Irradiation of polymers destroys the initial structure by introducing defects inside the material which leads to changes in the properties of these polymers. Ionizing radiation effects on polymers include cross-linking of the molecular chains, degradation of macromolecules (chains scission) and changes in the number and nature of the double bonds [2, 3]. This entire process can occur either in one or all together, depending on the chemical nature of the polymer, radiation dose applied and other external factors. Polyvinyl alcohol (PVA) is the most studied polymer throughout the last decades in scientific research and continues to attract considerable attention due to its fascinating and desirable characteristics specifically for various pharmaceutical and biomedical applications and also due to its relatively simple chemical structure with a pendant hydroxyl group [4, 7]. PVA is highly hydrophilic, non-toxic and biocompatible polymer with excellent film formation by casting [8-11]. PVA has been of particular interest also due to its abundance, high absorption coefficients in the visible light, chemical stability, easy polymerization, and low cost of monomer [12-15].

Inorganic additives, such as transition metal salts, have considerable effects on the optical, thermal and electrical properties of PVA [5, 8]. PVA doped with inorganic metal such as silver (Ag) [16], gold (Au) [17], Copper (Cu) [18], TiO₂ [19] and CeO₂ to form PVA/metal composite films and hydrogels have been used to improve physical, mechanical, and electrical properties of these composite materials. Since silver has a very good electrical conductivity among all the metals; the combination of PVA/Ag with uniform dispersion can yield functional composite material with enhanced electrical properties. The obtained composites have characteristic advantages compared to their single component counterparts and can have potential applications in new devices [20-22]. In particular, transition metal particles dispersed/encapsulated within a polymer matrix can offer attractive and practicable routes for combining properties arising from metal particles and from that of polymers [9, 10]. This could greatly improve the optical and dielectric properties of the PVA composites. These particles could act as conductive junctions between the PVA chains that resulted in an increase of the electrical conductivity of the composites [2, 11]. Several methods have been employed to prepare polymer-metal composites such as blending of both components and irradiation [1-3]. All these metallic particles (Gold, Silver, Platinum...etc) exhibit unusual electrical, magnetic, optical and electrochemical properties due the near-free conduction electrons, which are dependent on their size, surface Plasmon, surface free energy and surface area, as well as on the surrounding dielectrics [23]. Among these important metal particles used, silver (Ag) particles are of great interest in today's materials world due to its special electronic, optical, and magnetic properties [15, 24] and its wide variety of applications in catalysis [18], conducting inks, microelectronics, thick-film electrode material, and solar cells [1, 3]. These mentioned properties are dependent on the particle size, shapes and the method of composites synthesis. Varieties of synthesis method have been developed, including reduction from metallic salts, ultrasonic irradiation technique, ion implantation, and thermal process and microwave technique [5, 13 and 25]. However, fabrication of PVA/Ag composite films without using of toxic chemical agents still remains highly challenging. This challenge may be surpassed by using irradiation technique which has a capability to produce polymer and metal particle components without using any chemical agents. The synthesis of silver composites by using γ - irradiation has been mentioned by Ali et al., (2007) and M.M. Abutalib [26]. The combination of PVA as polymer with silver as a noble metal may produce hybrid composed material that possesses very interesting behaviors [25].

The practical applicability of polymer/metallic composites and Conducting Polymers (CPs) depends on their electrochemical properties, environmental and thermal stabilities [27]. Although their methods of preparation, morphology and electrochemical characterizations have been extensively studied, research on the evaluation of their thermal properties has received less attention. Only a small amount of work has been devoted to this subject [28]. The thermal behavior of materials can be explored extensively using various techniques such as differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetry (TGA). Kinetic analysis of the data obtained by these techniques provides important insights into the fundamental issues of the reactivity and stability of materials. Stability is of great importance to relate the chemical structure to the physical properties of polymers. Thermo Gravimetric Analysis (TGA) is the main and the most important technique for measuring the weight loss and its rate of change with respect to temperature/time in a controlled atmosphere. TGA studies are generally used for finding the material composition and its thermal stability up to very high temperatures. In this study, weight loss stages are investigated for the

amount/percent (%) weight loss, the amount/percent (%) of the non-combusted residue with a change in temperature as well as the temperature of different degradation steps. The data obtained from TGA is applicable for calculating kinetic parameters of degradation of the polymer. Thermal stability of composite and (CPs) is useful for their applicability to various technologies [29].

Various modifications in PVA have been observed due to additive or irradiation [9-13]. Nouh S A and R A Bahareth [30], studied the effect of electron beam irradiation on the structural, thermal and optical properties of polyvinyl alcohol thin film, they concluded that the electron beam irradiation in the dose range 95–210 kGy enhances the scope of the polymer in high temperatures. In the present study, AgNO₃ is used as additive stabilizer to PVA. The aim is to investigate the feasibility of modifying its thermal and optical properties to study the possibility of further enhancement of these properties using gamma irradiation

Experimental

2.1 Samples

The PVA stock was supplied by TECHNO PHARMCHEM (Mol. wt = 85000 to 124000 g/mol Degree of hydrolysis 86-89 %). The PVA/AgNO₃ Films were made using solvent casting technique with a concentration of AgNO₃ /PVA that is, [C = 10% AgNO₃], by dissolving each concentration of PVA powder in 100 ml distilled water at room temperature on a beaker. The solutions were magnetically stirred at room temperature for 3 hours then poured in a Petri-dish to form films by casting method in a dark room. Films were left to dry at ambient temperature at least 2 days, the ambient condition was measured using data logger [Temperature = 24.1 0 C, Humidity = 28.5%, atmospheric pressure = 961 mBar]. Films were peeled off the Petri-dish, cut into small films 2x2 cm (suitable for measurements), loaded in sealed dark dental film envelopes. The thickness of the films was measured using a micrometer.

2.2 Irradiation facility

TERABALT Cobalt-60 unit was used for samples irradiation. Different radiation doses which were specify with treatment planning system (TPS) PlanW2000 (0 Gy, 5 Gy and 10 Gy) at Surface Source Distance (SSD) 95cm, field Size (FS) 10x10 cm², Gantry angle 0°, Collimator angle 0°. The films were placed at the center of the field size. ⁶⁰Co γ-rays irradiation facility (TERABALT - radiotherapy cobalt unit type 80–model SCS, UJP PRAHA, CZECH REPUBLIC) from National Cancer Institute, University of Gazira, Wad-Madani, Sudan, was used in this study.

2.3 Analysis of the samples

Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) was performed on irradiated and non-irradiated PVA/AgNO₃ films using the TGA/DSC apparatus model NETZSCH STA 449F3. Thermal experiments were carried out on all samples at a heating rate of 10 K/min with nitrogen as a carrier gas at a flow rate of 20 ml/min.

Results and Discussion

3.1 Thermogravimetric (TGA) Analysis

TGA was performed to confirm the existence of initial scission that occurs and the possible chemical crosslinking in the samples. The Thermogravimetric curves obtained from room temperature up to 1000 °C, heating rate 10 °C/min in nitrogen flow of 20 ml/min for the non-irradiated and irradiated PVA/AgNO₃ samples are given in figures below for comparisons as well as their DTG. The DTG shows that the thermal degradation runs in two or three main stages based on the rate of thermal decomposition peaks which indicates a different degradation pathway according to the blends composition and irradiation dose. The TGA behavior of the non-irradiated PVA/AgNO₃, **Fig. 1**, when heated in nitrogen is divided into two main stages based on the rate of thermal decomposition peaks. At the first stage, the temperature is below 180 °C due to the moisture evaporation, vaporization of physically absorbed solvent, to a maximum loss of 63.18% of its weight at a maximum rate of -4.6%/min with DTG peak of 185 °C. In the second stage, more rapid weight loss is observed with a maximum 88.14% of its original weight at a maximum rate of -9.45%/min with DTG peak of 313.7 °C. The marked loss of weight in the second stage is attributed to the degradation reaction by either of the side chain decomposition or the random chain scission in the backbone, this second weight loss at higher temperature indicates a structural decomposition of the polymer in nitrogen atmosphere and was confirmed by the DSC observations.

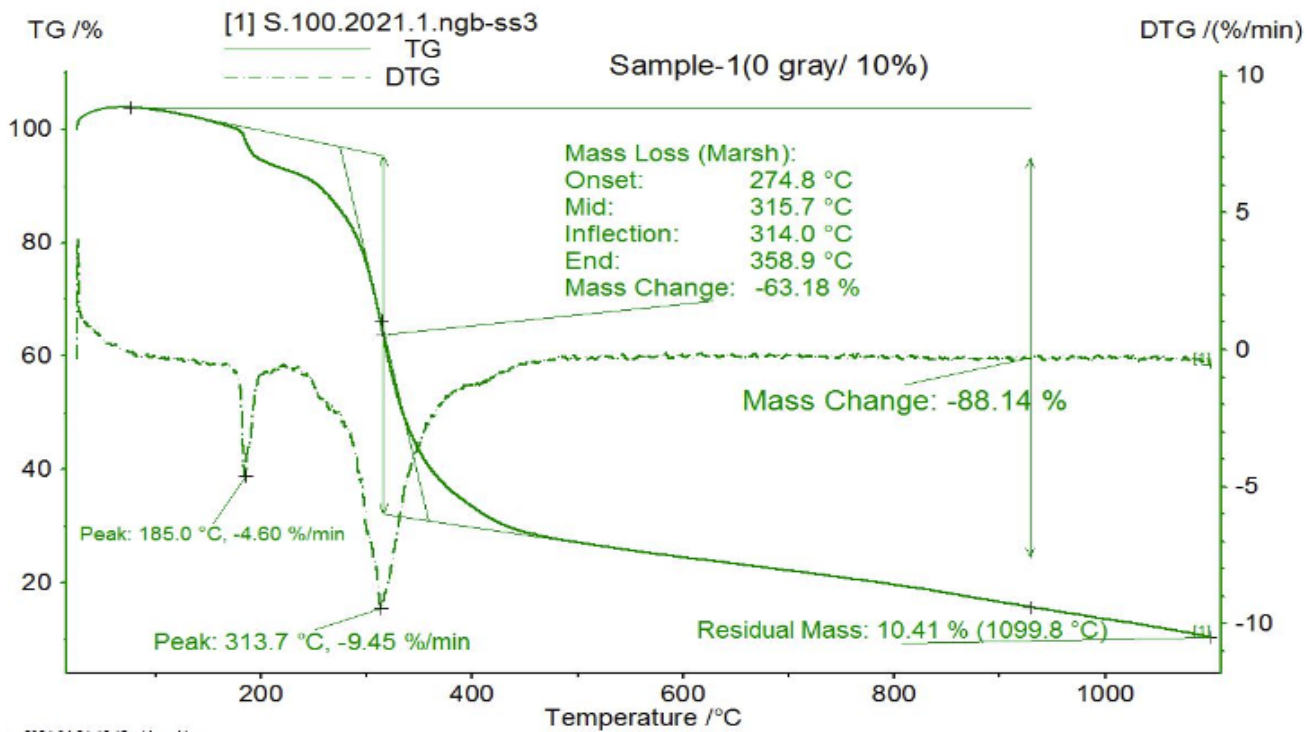


Fig 1: TGA Thermogram measured in the temperature range from room temperature up to 1000 °C at a heating rate of 10 °C min⁻¹ of the non-irradiated PVA/AgNO₃ composite.

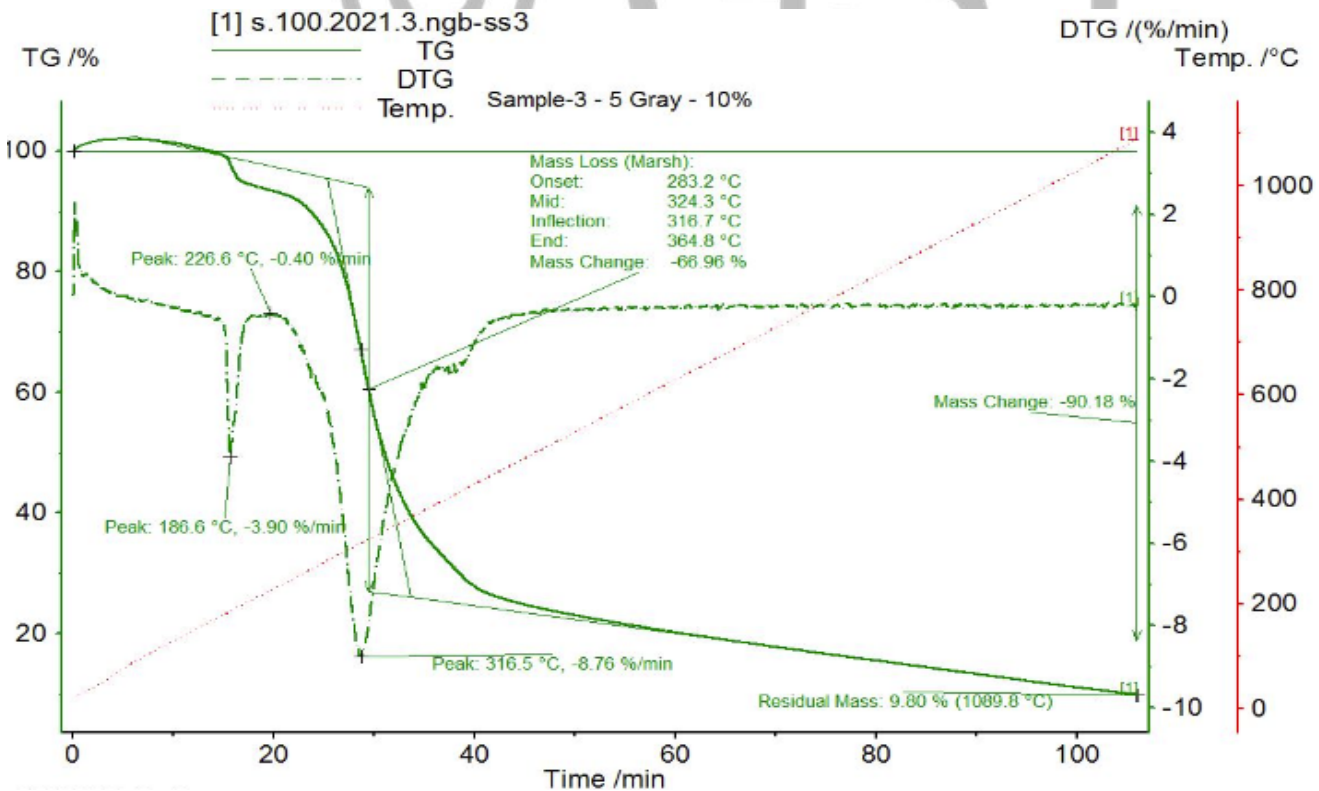


Fig 2: TGA Thermogram measured in the temperature range from room temperature up to 1000 °C at a heating rate of 10 °C min⁻¹ of the 5 Gy irradiated PVA/AgNO₃ composite.

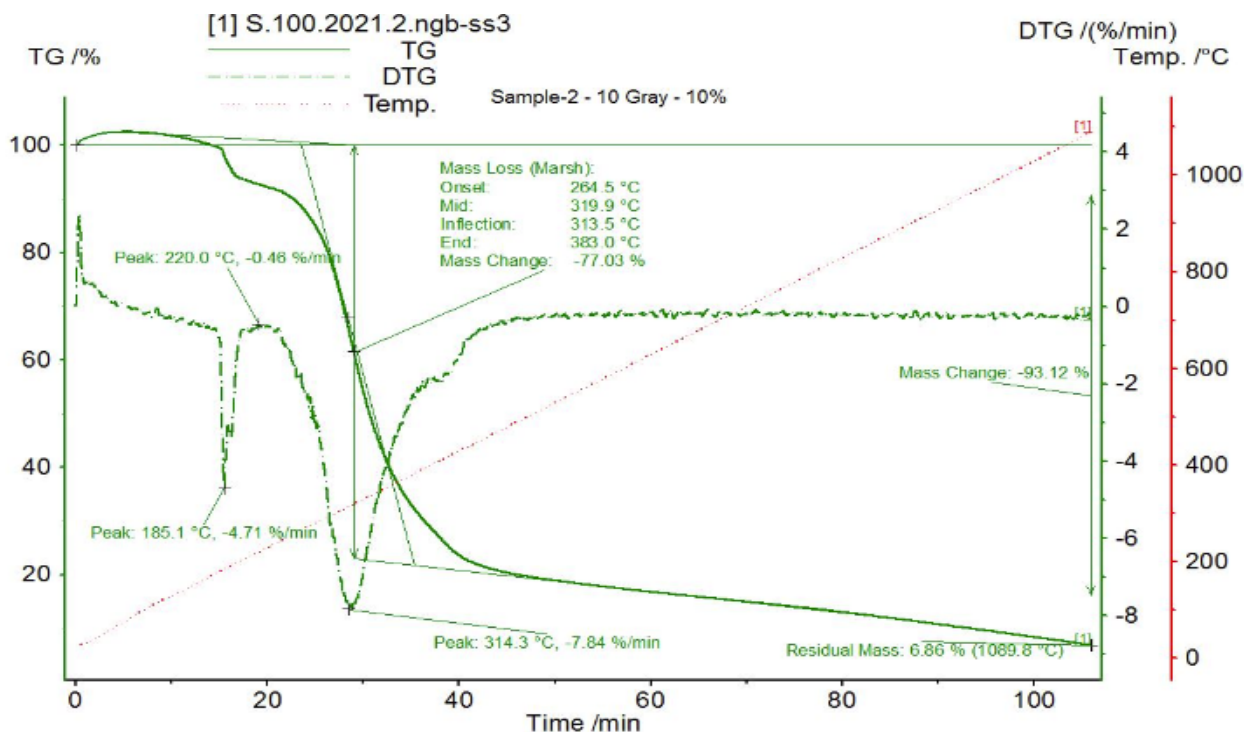


Fig 3: TGA Thermogram measured in the temperature range from room temperature up to 1000 °C at a heating rate of 10 °C min⁻¹ of the 10 Gy irradiated PVA/AgNO₃ composite.

From **Fig. 1**, we observe that non-irradiated PVA/AgNO₃ is thermally stable up to 274.8 °C, while the irradiation enhances the thermal stability in the low doses around 5 Gy it falls beyond the non-irradiated value at 10 Gy. A clear distinction between the different stages of the degradation process is evidenced in the DTG curves. A summary of the important thermogravimetric characteristics obtained from the thermograms is listed in **Table 1**. In the second stage of the irradiated of 5 and 10 Gy samples, **Fig. 2 and Fig. 3**, the weight loss is observed to be 90.18 and 93.12% of its initial weight at rate loss of -8.76 and -7.84%/min with a DTG peak of 316.5 and 314.3 °C respectively. This is confirmed again by the DSC measurements. Increasing the radiation dose leads to a random breaking of bonds, thus degradation predominates.

Table1. Thermogravimetric characteristics of the composition as functions of irradiation dose.

| M residue % | T _{Peak} (°C) | T _{Onset} (°C) | Stages | Samples |
|-------------|------------------------|-------------------------|--------|-------------------------------|
| 10.41 | 185.0 | 165.7 | I | PVA/AgNO ₃ (0 Gy) |
| | 313.7 | 274.8 | II | |
| 9.80 | 186.6 | 171.6 | I | PVA/AgNO ₃ (5 Gy) |
| | 316.5 | 283.2 | II | |
| 6.86 | 185.1 | 169.5 | I | PVA/AgNO ₃ (10 Gy) |
| | 314.3 | 264.5 | II | |

The thermal stability values observed and residue mass left behind at 1000 °C for the non-irradiated PVA/AgNO₃, irradiated samples of 5 and 10 Gy were 10.41, 9.8 and 6.86 % respectively. In the dose range around 5 Gy, the free radicals formed due to scission are chemically active and can be used in some chemical reactions that lead to the crosslinking mechanism. As the dose increases, chain scission started to dominate over crosslinking lowering thermal stability [30]. The onset temperature of thermal decomposition (the temperature where the decomposition process starts) values observed for the non-irradiated PVA/AgNO₃ and irradiated samples of 5 and 10 Gy were 274.8, 283.2 and 264.5 °C respectively. The largest weight loss (greatest rate of change on the weight loss curve), also known as the inflection point values observed for the non-irradiated PVA/AgNO₃ and irradiated samples of 5 and 10 Gy were 314.0, 316.7 and 313.5 °C respectively. This leads to a rapid decomposition of the polymer composed and auto self combustion process accompanied by evolution of volatile by-product as confirmed by the DSC.

3.2 Differential scanning calorimetry (DSC) Analysis

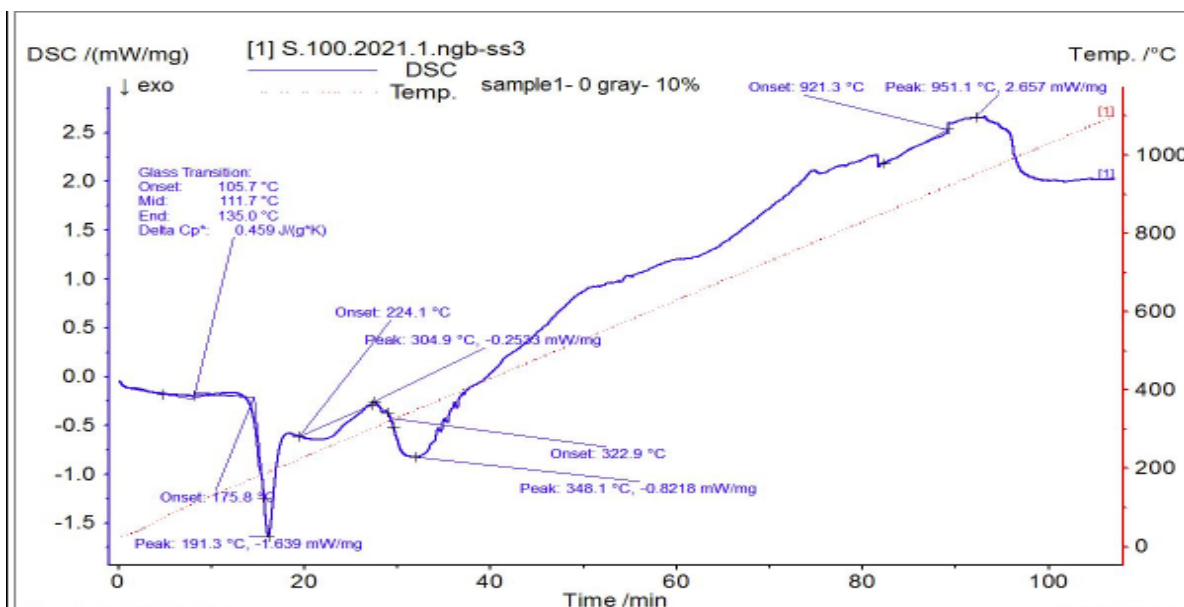


Fig 4: DSC Thermogram of the non-irradiated PVA/AgNO₃ composite.

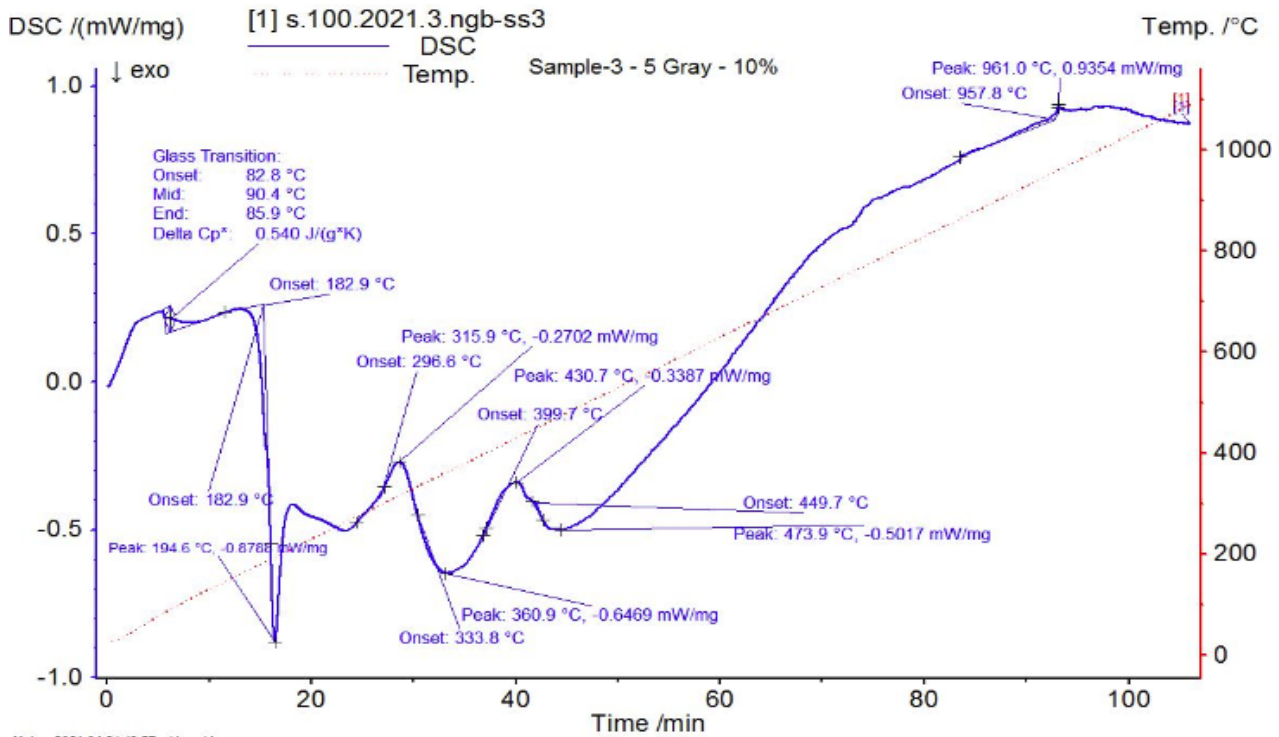


Fig 5: DSC Thermogram of the irradiated 5 Gy PVA/AgNO₃ composite.

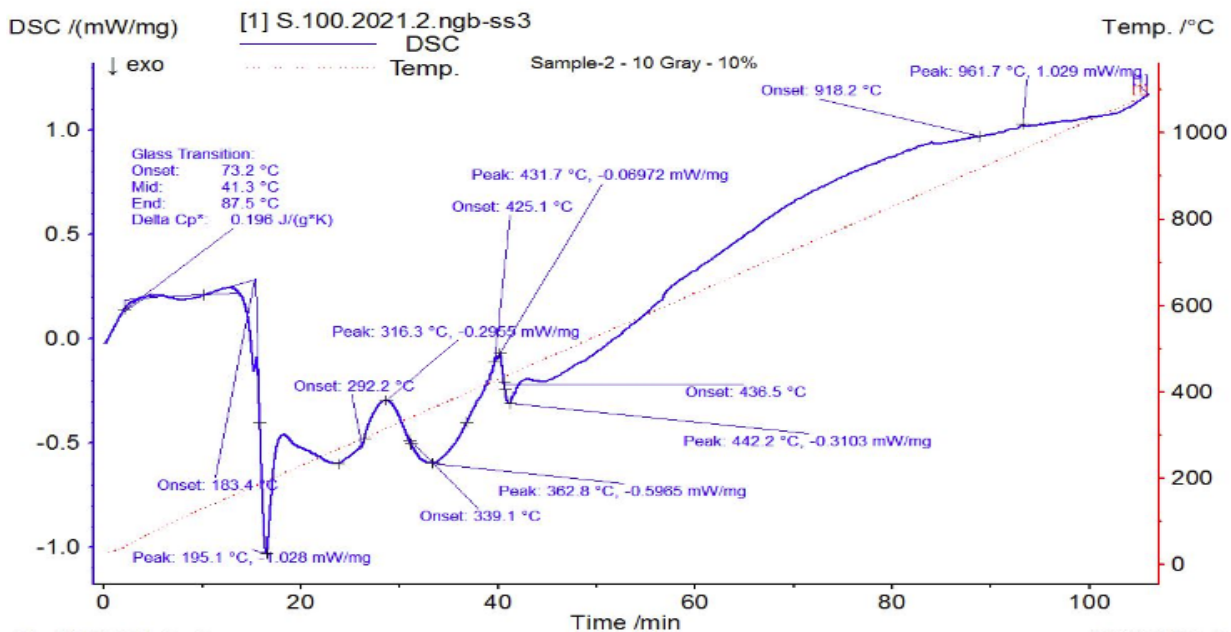


Fig 6: DSC Thermogram of the irradiated 10 Gy PVA/AgNO₃ composite.

DSC can be used to determine the thermal transition temperatures, glass transition, melting, crosslinking and decomposition as well

as the specific heat. However, it measures only the total heat flow and the sum of all thermal transitions in the sample. **Fig. 4, Fig. 5 & Fig. 6** show the DSC curves, endothermic peaks lesser than 200 °C which can be attributed to make out moisture in the polymer [5] which is consistent with the TGA result. The chemical process associated with the exothermic peaks may be related to crystallization or crosslinking reactions. TGA information is further supported by the DSC analysis.

The glass transition values of composite films of PVA/AgNO₃ shift to lower temperatures with the increase of dose. From **Fig. 4, Fig. 5 & Fig. 6**, the glass transition of the non-irradiated and the irradiated of 5 and 10 Gy samples, are observed to be 105.7, 82.8 and 73.2 °C respectively. Therefore, it reflects there are some interactions between the components. We observe that increasing the radiation dose leads to a random breaking of bonds, thus degradation predominates, in other terms, chain scission started to dominate over crosslinking lowering thermal stability. PVA melting point is 230 °C for the fully hydrolyzed grades and glass transition temperature is 85 °C [2, 30].

Conclusion

The effect of gamma irradiation on PVA/AgNO₃ composed films has been investigated. The gamma irradiation, up to 10 Gy, led to crosslinking reaction domination over chain scission and removal of –OH groups and formation of carbonyl and double bond groups causing an increase in the thermal stability of the films. At higher dose above 10 Gy, chain scission started to dominate over crosslinking causing lower thermal stability. The TGA and DSC thermograms show a degradation of the composed polymer under gamma irradiation at doses up to 10 Gy causing the polymer to decompose earlier than the non-irradiated sample. These results indicate that the non-irradiated copolymer films or those irradiated with low dose up to 10 Gy may be suitable for applications as a semiconductor polymeric material in the electrical and electronic industries.

Acknowledgment

The authors wish to thank MRC chemistry laboratories for providing TGA and DSC characterization facility.

References

- [1] Long, N.V.; Thi, C.H.; Nogami, M.; Ohtaki, M. *Novel issues of morphology, size, and structure of Pt nanoparticles in chemical engineering: surface attachment, aggregation or agglomeration, assembly, and structural changes.* *New J. Chem.* 2012, 36, 1320–1334.
- [2] Alan, J.H. (2002). *Semi-conducting and metallic polymers: the fourth generation of polymeric materials.* *Synth. Met.* 125, 23-42.
- [3] Chiang, C. K., Fincher, Jr., C. R., Park, Y. W., Heeger, A. J., Shirakawa, H. & Louis, E. J. (1977). *Electrical conductivity in doped polyacetylene.* *Physics Review Lett.* 39, 1098-1101.
- [4] Chuang, F.-Y.; Yang, S.-M. *Cerium dioxide/polyaniline core-shell nanocomposites.* *J. Colloid Interface Sci.* 2008, 320, 194–201.
- [5] Reda, S.M.; Al-Ghannam, S.M. *Synthesis and electrical properties of polyaniline composite with silver nanoparticles.* *Adv. Mater. Phys. Chem.* 2012, 2, 75–81.
- [6] Kros, A., Van Hovel, S. W., Nolte, R.J.M., Sommerdijk, N.A. (2001). *A printable glucose sensor based on a poly(pyrrole)-latex hybrid material.* *Sensors and Actuators.* 80, 229-233.
- [7] Yamauchi, T., Tansuriyavong, S., Doi, K., Oshima, K., Shimomura, M., Tsubokawa, N., Miyauchi, S. & Vincent, J.F.V. (2005). *Preparation of composite materials of polypyrrole and electroactive polymer gel using for actuating system.* *Synthetic Metals.* 152, 45-48.
- [8] Kaeami, H., Mousavi, M.F. & Shamsipur, M. (2003). *A new design for dry polyaniline rechargeable batteries.* *Power Sources.* 117, 255-259.
- [9] Lin, C.W., Hwang, B.J. & Lee, C.R. (1998). *Methanol sensors based on the conductive polymer composites from polypyrrole and poly(vinyl alcohol).* *Materials Chem. Phys.* 55, 139-144.
- [10] Lee, C.Y., Kim, H.M., Park, J.W., Gal, Y.S., Jin, J.I., Joo, J. (2001). *AC electrical properties of conjugated polymers and theoretical high-frequency behavior of multilayer films.* *Synthetic Metals.* 117, 109-113.
- [11] Marija, G.N., Jadranka, T.S., Bowmaker, G.A., Cooney, R.P., Thompson, C. & Kilmartin, P.A. (2004). *The antioxidant activity of conducting polymers in biomedical applications* *Current Appl. Phys.* (4), 347-350

- [12] Goto, H. A possibility for construction of an iodine cleaning system based on doping for π -conjugated polymers. *Polymers* 2011, 3, 875–885.
- [13] Stejskal, J.; Gilbert, R.G. Polyaniline: Preparation of a conducting polymer (IUPAC technical report). *Pure Appl. Chem.* 2002, 74, 857–867.
- [14] Bhadra, S.; Singha, N.K.; Khastgir, D. Electrochemical synthesis of polyaniline and its comparison with chemically synthesized polyaniline. *J. Appl. Polym. Sci.* 2007, 104, 1900–1904.
- [15] Khanna, P.K.; Singh, N.; Charan, S.; Viswanath, A.K. Synthesis of Ag/polyaniline nanocomposite via an in situ photo-redox mechanism. *Mater. Chem. Phys.* 2005, 92, 214–219.
- [16] Wankhede, Y.B.; Kondawar, S.B.; Thakare, S.R.; More, P.S. Synthesis and characterization of silver nanoparticles embedded in polyaniline nanocomposite. *Adv. Mater. Lett.* 2013, 4, doi:10.5185/amlett.2012.icnano.108.
- [17] Sridevi, V.; Malathi, S.; Devi, C. Synthesis and characterization of polyaniline/gold nanocomposites. *Chem. Sci. J.* 2011, 2011, 1–26.
- [18] Athawale, A.A.; Bhagwat, S. Synthesis and characterization of novel copper/polyaniline nanocomposite and application as a catalyst in the Wacker oxidation reaction. *J. Appl. Polym. Sci.* 2003, 89, 2412–2417.
- [19] Nabid, M.R.; Golbabaee, M.; Moghaddam, A.B.; Dinarvand, R.; Sedghi, R. Polyaniline/TiO₂ nanocomposite: Enzymatic synthesis and electrochemical properties. *Int. J. Electrochem. Sci.* 2008, 3, 1117–1126.
- [20] S. Bhadra, D. Khastgir, N.K. Singha, J.H. Lee, Progress in preparation, processing and applications of polyaniline, *Prog. Polym. Sci.* 34 (2009) 783-810.
- [21] G.A. Snook, P. Kao, A.S. Best, Conducting-polymer-based supercapacitor devices and electrodes, *J. Power Sources* 196 (2011) 1-12.
- [22] J. Liu, L. Zhang, H.B. Wu, J. Lin, Z. Shen, X.W.D. Lou, High-performance flexible asymmetric supercapacitors based on a new graphene foam/carbon nanotube hybrid film, *Energy Environ. Sci.* 7 (2014) 3709-3719.
- [23] Stakheev A.Y., Kustov L.M. (1999). Effects of the support on the morphology and electronic properties of supported metal clusters; modern concepts and progress in 1990s. *Applied Catalysts*, A188: 3-7.
- [24] Gao C., Li S., Song H., Xie L.: Radiation induced crosslinking of ultra high molecular weight polyethylene fibers by means of electron beams. *Journal of Applied Polymer Science*, 98, 1761–1764 (2005).
- [25] Riyadh Ch, Ghufuran AH, Shabeeb M, Hammouti B (2011). Characterization of table sugar dosimeter for gamma-radiation dosimetry, *Der Pharma Chemica*, 3(6): 182-188.
- [26] M.M. Abutalib. Effect of additive concentration and X-ray irradiation on the thermal and color properties of Polyvinyl alcohol. *Life Sci J* 2014;11(9):512-517. (ISSN:1097-8135). <http://www.lifesciencesite.com>. 85
- [27] Abthagir P., Syed K., Dhanalakshmi., Saraswathi R., Thermal Studies on Polyindole and Polycarbazole, *synth. Met.*, 93 (1): 1-7 (1998).
- [28] Mallakpour S., Taghavi M., The Accuracy of Approximation Equations in the Study of Thermal Decomposition Behavior of Some Synthesized Optically Active Polyamides, *Iran. Polym. J.*, 18(11): 857-872 (2009).
- [29] Abthagir P.S., Saraswathi R., Sivakolunthu S., Aging and Thermal Degradation of Poly (N-methylaniline), *Thermochim. Acta .*, 411 (2): 109-123 (2004).
- [30] Nouh S A and R A Bahareth, Effect of electron beam irradiation on the structural, thermal and optical properties of PVA thin film. *Radiation Effects Defects in Solids* 168 274 (2013).