



MORPHOLOGICAL, THERMAL AND WATER ABSORPTION PROPERTIES OF POLYVINYL ALCOHOL/ZNO NANOCOMPOSITES

M. Sumi¹ and G. R. Bella²

Abstract-Polyvinyl alcohol is a polymer that has good film forming, easy processability, optical transparency and semi-crystalline, widely applied as a polymer matrix for the synthesis of nanocomposites by cost efficient and environment friendly direct blending methods. Many nanomaterial have been used to prepare nanocomposites among these ZnO nanoparticles have a special place because of its good transparency, high electron mobility and direct wide band gap (3.37 eV at room temperature). In the present study we have synthesized ZnO nanoparticles by controlled precipitation method and filled in PVA at different weight percentage (0%, 1%, 3% and 5%) by using solution casting technique. The prepared samples were characterized with FTIR for structure and the nature of the functional groups, XRD to calculate the crystallinity and the crystallinity index, SEM for particle size, surface morphology and elemental composition. TGA-DTA analysis was used to determine the kinetics of thermal decomposition of the polymer composites. Water absorption test was done to study the water resistance and degradation properties of the composites. Present result revealed that the addition of ZnO with PVA in the presence of H₂O₂ increases the thermal stability and decreases the degradation ability of the polymer but in the presence of glycerol increases the crystallinity and crystallinity index but decreases the thermal stability and the degradation ability of the polymer.

Keywords: PVA, Nanoparticles, ZnO, Thermal properties, Crystallinity, Degradation.

INTRODUCTION

Nanoparticles and nanolayers have very high surface to volume and aspect ratios and this makes them ideal for use in polymeric materials. Such structures combine the best properties of each component to possess enhanced mechanical and super conducting properties for advanced applications¹. Various nanocomposites have been synthesized in a wide range of polymerization sol-gel, deposition, magnetron sputtering, supercritical fluid, sonochemistry, laser, etc. Recently, processing techniques have been developed to allow the size of inclusions to go down to nanoscale. Polymer nanocomposites have attracted tremendous attention due to their potential applications in biomedical, catalytic, separation, chemical sensing, fuel cell, capacitor, microfabrication, tribological etc². Polyvinyl alcohol a synthetic polar polymer is a good host material due to its good thermal stability, chemical resistance, film forming ability, non-toxic, bio-compatibility, bio-degradability and availability in different molecular weights³. The hydroxyl groups present in its main backbone of PVA are responsible for the strong intra- and intermolecular hydrogen bonds, endowing PVA with many good properties, such as high tensile strength, excellent adhesive properties, abrasion resistance, chemical resistance and gas barrier properties. Polyvinyl alcohol is the only known carbon-carbon backbone polymer that is biodegradable under both aerobic and anaerobic conditions. It has recently gained increasing attention both as a water-soluble biodegradable polymer and as a biodegradable segment in the polymer chain to be applied in a wide range of applications⁴. PVA is one of the few polymers which can be prepared via a non-petroleum route, i.e. by using natural gas as raw materials. For these reasons, PVA is widely applied in many industrial applications such as films, fibres, adhesives, textile sizing, emulsifiers, and paper coating etc⁵.

Zinc oxides of particle size in nanometre range have been paid more attention for their unique properties⁶. Zinc oxide with its unique physical and chemical properties such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photo stability is a multifunctional material. In materials science ZnO is classified as a semiconductor in group II-VI, whose covalence is on the boundary between ionic and covalent semiconductors. A broad energy band (3.37 eV), high bond energy (60 meV) and high thermal and mechanical stability at room temperature make it attractive for potential use in electronics, optoelectronics and laser technology. It is an important material in the ceramics industry while its low toxicity, biocompatibility and biodegradability make it a material of interest for biomedicine and in pro-ecological systems⁷.

¹ Department of Chemistry, Nesamony Memorial Christian College, Marthandam 629 165, Kanyakumari District, Tamil Nadu, India

² Department of Chemistry, Nesamony Memorial Christian College, Marthandam 629 165, Kanyakumari District, Tamil Nadu, India.

ZnO is a versatile material with unique properties which are suitable for a wide range of technological applications such as solar cells, transparent conducting electrodes, ultraviolet and blue light emitting diodes, laser diodes, thin film transistor, surface acoustic wave (SAW) devices, gas sensors, photo catalysts and so on. The uses of zinc oxide as a photo catalytic degradation material for environmental pollutants has also been extensively studied, because of its nontoxic nature, low cost and high photochemical reactivity^{8,9}. Glycerol is one of the most popular plasticizers used in the preparation of films and coatings due to its stability and compatibility with the hydrophilic nature of the biopolymers. It is a nontoxic, edible and biodegradable compound thus it will provide important environmental benefits to the new platform products. It is widely used in the manufacture of drugs, textile industry and lubricating, softening yarn and fabric etc¹⁰. The objective of this work is to prepare PVA-ZnO nanocomposite films with different compositions (0%, 1%, 3% and 5%) in the presence of H₂O₂ and glycerol. The obtained films were characterized by different spectroscopic methods such as FTIR, XRD, SEM and TGA-DTA analysis. The degradation percentage of the prepared composites was studied by water absorption studies.

EXPERIMENTAL PROCEDURE

SYNTHESIS OF ZINC OXIDE NANOPARTICLES

The ZnO nanoparticles were synthesized by controlled precipitation method. To the aqueous solution of Zinc Sulphate and Sodium hydroxide was added dropwise in a molar ratio of 1:2 under vigorous stirring for about 12 hours. The precipitate obtained was filtered, washed with deionised water and dried at 100 °C in an oven. The obtained powder was calcined in a muffle furnace, at 550 °C for two hours.

SYNTHESIS OF PVA-ZNO COMPOSITE FILMS

PVA 3g was dissolved in 100ml of deionised water by stirring and heating. The required quantity of the ZnO (0%, 1%, 3% and 5%) was dissolved in 20ml of deionised water and sonicated for about 5 minutes. The two solutions were mixed with the addition of 1% H₂O₂ and glycerol and the stirring was continued for about 10 minutes. Finally the solution was poured into the mould and kept at room temperature for one week. The polymer film was peeled off after the evaporation of the solvent. The lists of prepared polymer composites are given in table 1.

Table 1: Consolidated list of prepared composites

Serial no	Sample code	Composition
1	P/H	PVA + ZnO(0%) + H ₂ O ₂ (1%)
2	P/G	PVA + ZnO(0%) + Glycerol (1%)
3	P/1Z/H	PVA + ZnO(1%) + H ₂ O ₂ (1%)
4	P/3Z/H	PVA + ZnO(3%) + H ₂ O ₂ (1%)
5	P/5Z/H	PVA + ZnO(5%) + H ₂ O ₂ (1%)
6	P/1Z/G	PVA + ZnO(1%) + Glycerol (1%)
7	P/3Z/G	PVA + ZnO(3%) + Glycerol (1%)
8	P/5Z/G	PVA + ZnO(5%) + Glycerol (1%)

CHARACTERIZATION

FTIR spectra provide valuable information regarding the structure of the compound and the nature of the functional groups present in the PVA-ZnO composites. The FTIR spectra were recorded in the range of 4000-650 cm⁻¹ on a Shimadzu FTIR-470 infrared spectrometer by KBR disc technique. X-ray powder diffraction is a rapid analytical technique used for the identification of a crystallinity and crystallinity index and particle size of the PVA-ZnO composites. The XRD patterns were examined from panalytical XPERT-PRO Diffractometer using Cu α radiation in the 2 θ range of 0-90° diffraction angle. Scanning electron microscopy is a method for high resolution surface imaging. The SEM images of prepared polymer composites were studied from JEOL model JSM-6390LV and it records topography of the surface under observation with resolution on the order of (ACC V 20 KV, WD 10 mm, SEI). Thermal analysis is a group of technique in which a property of a sample monitor against time or temperature in a specified atmosphere. The thermal properties of polymer composites were studied from Perkin Elmer STA 6000 model.

WATER ABSORPTION TEST

Water absorption percentage was determined by placing weighed dry film in distilled water at room temperature for 24 hours. After 24 hours, moisture on the surface of the films was removed and the weight of the films was measured. The percentage of water absorption (Wa %) of the films was calculated by the following equation.

$$\% Wa = \frac{Ww - Wd}{Wd} \times 100$$

Where, Ww is the weight of wet film and Wd is the weight of dry film.

RESULTS AND DISCUSSION

FTIR ANALYSIS OF PVA-ZNO COMPOSITES

The FTIR spectrum of ZnO nanoparticles is shown in (fig.1). The absorption peak at 1662 cm⁻¹ could be attributed to the O-H bond of absorbed water on the surface, while another absorption peak at 1427 cm⁻¹ is related to C-H deformation mode¹¹. The peak at 1154 cm⁻¹ is assigned to OH deformation and the band at 998 cm⁻¹ is due to the presence of C-O stretching vibration. The absorption at 883 cm⁻¹ is due to the formation of tetrahedral coordination of Zn. The peak at 702 cm⁻¹ indicates the stretching vibration of ZnO nanoparticles¹².

The FTIR spectrum of P/5Z/H composite film is shown in (fig.2). In this spectrum, the broad band at 3280 cm⁻¹ is due to the stretching vibration of hydroxyl group. The strong band at 2918 cm⁻¹ is assigned to the CH₂ stretching and the shoulder peak at 2851 cm⁻¹ is due to the CH stretching vibration. The band at 1416 cm⁻¹ indicates the C-C bond. The band at 1093 cm⁻¹ is due to the C-O stretching vibration and the peak at 919 cm⁻¹ resulted from CH₂ rocking vibration. The band at 825 cm⁻¹ is assigned to the C-C stretching vibration and the peak at 691 cm⁻¹ arises from out of plane OH bending vibration.

The FTIR spectrum of P/5Z/G composite film is shown in (fig.3). The broad band at 3258 cm⁻¹ is assigned to hydroxyl group and the peak at 2946 cm⁻¹ is due to the CH₂ stretching. The peak at 1416 cm⁻¹ is due to the formation of C-C bond. The band at 1098 cm⁻¹ is assigned to the C-O stretching vibration and the band at 925 cm⁻¹ indicates the CH₂ rocking vibration^{13,14}.

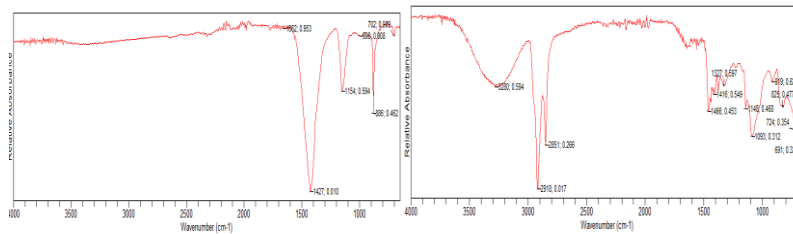


Fig.1 FTIR spectrum of ZnO

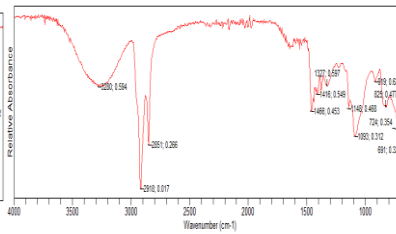


Fig.2 FTIR spectrum of P/5Z/H composite film

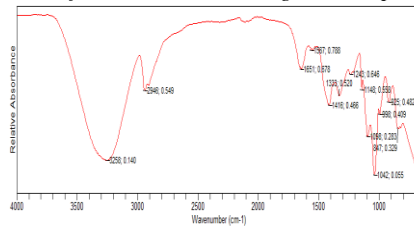


Fig.3 FTIR spectrum of P/5Z/G composite film

XRD ANALYSIS OF PVA-ZNO COMPOSITES

The XRD pattern of ZnO is shown in (fig.4), the observable peaks at scattering angles $2\theta = 31.77^\circ, 34.42^\circ, 36.27^\circ, 47.53^\circ, 56.67^\circ, 62.98^\circ, 66.39^\circ, 67.95^\circ, 69.14^\circ, 72.65^\circ,$ and 76.97° are correspond to reflections from 100, 002, 101, 102, 110, 103, 200, 112, 201, 004 and 202 crystal planes, confirmed the formation of the prepared ZnO in a pure single hexagonal phase and wurzite structure. The percentage of crystallinity of ZnO is 92.96% and the crystallinity index is 0.92. This XRD pattern of ZnO indicates ultra-fine nature of the crystallites. It is clear; the peaks are very sharp, indicating the complete formation of crystal structure.

The XRD pattern of P/5Z/H composite film is shown in (fig.6), when ZnO was added with PVA in the presence of H₂O₂, two major diffraction peaks are appeared at $2\theta = 19.73^\circ$ and $2\theta = 40.2^\circ$. The addition of ZnO decreases the intensity of the diffraction peaks of PVA. So the crystallinity and the crystallinity index is also decreased from 81.18% to 70.45% and 0.77 to 0.58 respectively.

The XRD pattern of P/5Z/G composite film is shown in (fig.8). When PVA was added with ZnO in the presence of glycerol the major diffraction peak is observed at $2\theta = 36.49^\circ$. The addition of ZnO increases the intensity of the diffraction peak of PVA and so the crystallinity and crystallinity index is also increased from 69.47% to 88.85% and 0.56 to 0.88 respectively. The average particle size of the prepared ZnO particles is calculated from XRD analysis by Scherrer's equation,

$$D_{XRD} = \frac{0.89\lambda}{\beta \cos \theta}$$

Where, λ is the wavelength of X-rays, θ is the diffraction angle and β is the width of half maximum of the peak. The average particle size of ZnO particles is 31.03 nm.

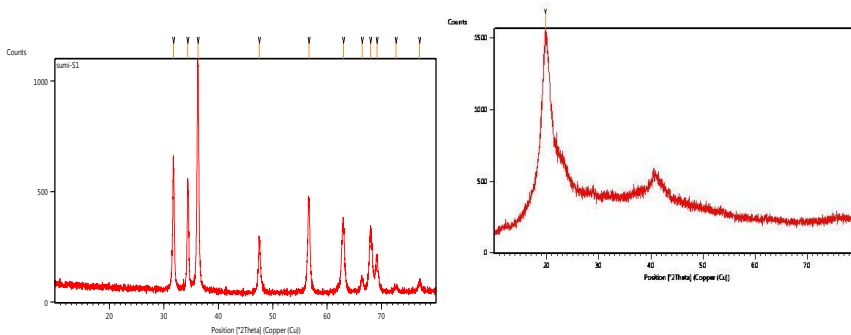


Fig.4 XRD pattern of ZnO

Fig.5 XRD pattern of P/H film

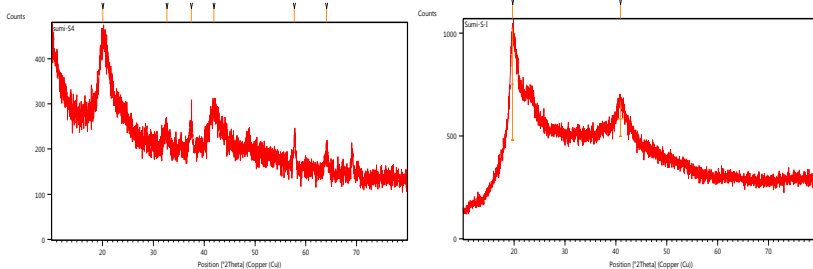


Fig.6 XRD pattern of P/5Z/H film

Fig.7 XRD pattern of P/G film

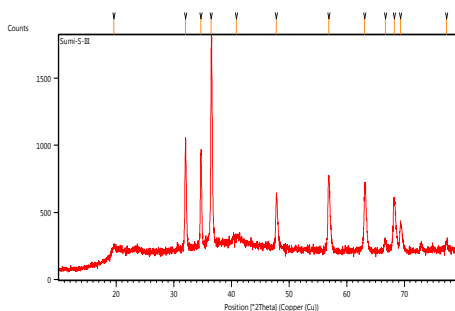


Fig.8 XRD pattern of P/5Z/G film

SEM ANALYSIS OF PVA-ZNO COMPOSITES

The surface morphological study of ZnO nanoparticles was done by using SEM analysis. The SEM image of ZnO (fig.9) shows the agglomeration of the tiny ZnO particles with size 161.25 nm, 184.39 nm, 203.96 nm etc. This result strongly consistent with the XRD result of average particle size of 31.03 nm described above in this chapter. These results confirm the nanoparticle nature of ZnO prepared by controlled precipitation method.

The SEM image of P/5Z/H composite (fig.10) shows the non-uniform distribution of needle shaped ZnO particles with breadth 250 nm, 300 nm and 340 nm etc on the surface of the PVA matrix. The SEM image of P/5Z/G composite film (fig.11) shows the non-uniform distribution and agglomeration of spherical shaped ZnO particles on the surface of the polymer matrix.

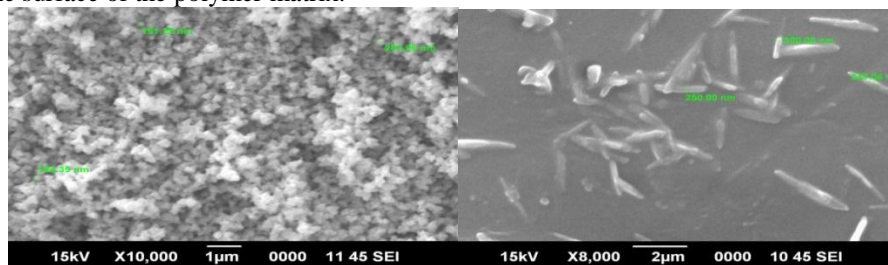


Fig.9 SEM image of ZnO nano particles Fig.10 SEM image of P/5Z/H composite film

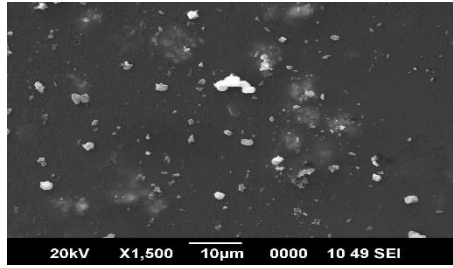


Fig.11 SEM image of P/5Z/G composite film

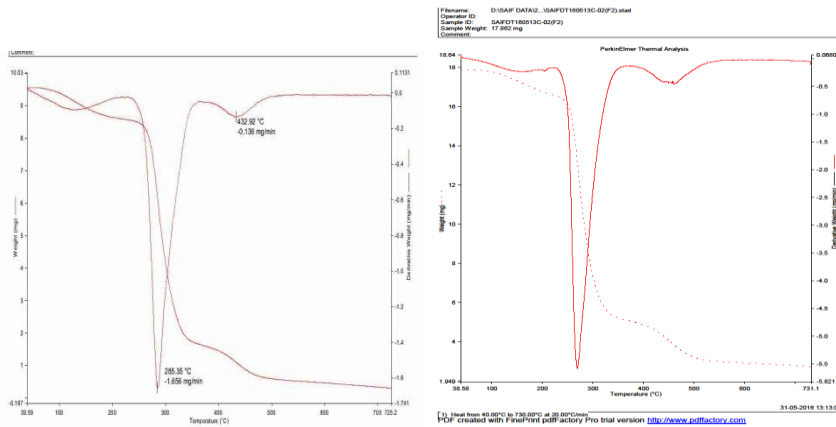
THERMAL PROPERTIES OF PVA-ZNO COMPOSITES

The thermal stability of PVA-ZnO nanocomposites can be analysed from TGA-DTA technique. The TGA-DTG thermogram of the prepared PVA-ZnO composite films is shown in Fig.13 and Fig.15. The first step of degradation around 100°C indicates the loss of water molecules and evaporation of trapped solvent. The second step of degradation appears in the temperature range between 100°C - 200°C indicates thermal phase transition at an early stage in nanocomposite films.

The third degradation step between 200°C - 300°C indicates the decomposition of composite films related to side chain scission reaction. The fourth step of degradation occurring above 400°C indicates increases in the beginning of complete degradation³. The percentage of weight loss of PVA/ZnO composites at various temperatures is given in table 2.

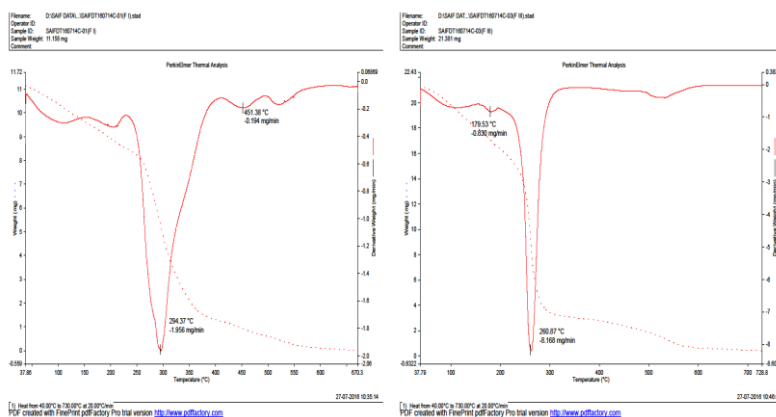
Table 2: Percentage of weight loss of PVA-ZnO composites at various temperatures

Sample code	Percentage of weight loss at various temperatures						
	100°C	200°C	300°C	400°C	500°C	600°C	Residue
P/H	1.06	8.61	54.99	82.06	92.55	94.02	5.98
P/5Z/H	0.179	6.058	50.17	72.96	81.97	83.43	16.57
P/G	7.15	19.34	56.44	87.36	93.91	99.19	0.81
P/5Z/G	7.25	22.46	82.84	88.76	94.02	96.87	3.13



(a) Fig.12 TGA-DTG thermogram of P/H film (b) Fig.13 TGA - DTG Thermogram of P/5Z/H composite film

The TGA-DTG thermograms of P/H (fig.12) and P/5Z/H (fig.13) show the addition of ZnO to PVA in the presence of H₂O₂ increases the thermal stability of the polymer. At 300°C the percentage of weight loss of P/H film is 54.99% and it decreases to 50.17% when it is added with 5% of ZnO. This also confirms the increase in thermal stability of P/H film after the addition of ZnO.



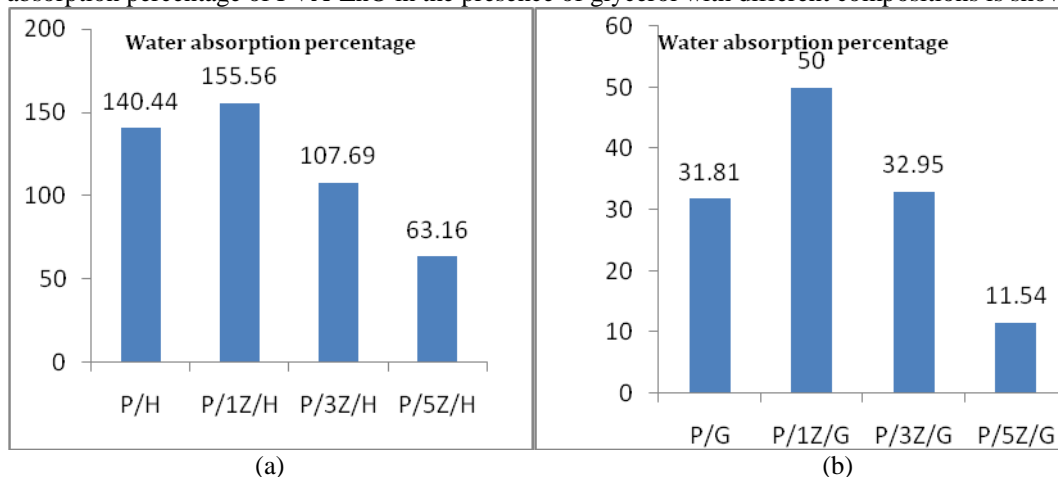
(c) Fig.14 TGA-DTG Thermogram of P/G film (d) Fig.15 TGA - DTG Thermogram of P/5Z/G composite film

The TGA-DTG thermograms of P/G (fig.14) and P/5Z/G (fig.15) suggest the addition of ZnO to PVA in the presence of glycerol decreases the thermal stability of the polymer. At 300°C the percentage of weight loss of P/G film is 56.44% and it increases to 82.84% when it is added with 5% of ZnO. This also confirms the decrease in thermal stability of PVA film after the addition of ZnO in the presence of glycerol.

WATER ABSORPTION TEST FOR PVA-ZNO COMPOSITES

Water absorption test is used to determine the amount of water absorbed under specified conditions. The amount of water absorbed depends on the nature of polymers, additives used, temperature etc. The percentage of water absorption of P/H film is 140.44% and it increases with the addition of 1% of ZnO (155.56%). On further addition of ZnO (3% and 5%) decreases the water absorption percentage in the presence of H₂O₂ (109.69% and 63.16%). This revealed that the addition of ZnO decreases the degradation ability of composite films in the presence of H₂O₂. The graphical representation of water absorption percentage of PVA-ZnO in the presence of H₂O₂ with different compositions is shown in fig.16.

The water absorption percentage of P/G film is 31.81%. The addition of 1% of ZnO to this PVA in the presence of glycerol increases the water absorption percentage. The loading of 3% and 5% of ZnO decreases the water absorption percentage of PVA film in the presence of glycerol. This indicates the increase in amount of ZnO reduce the degradation ability of PVA films in the presence of glycerol. The graphical representation of water absorption percentage of PVA-ZnO in the presence of glycerol with different compositions is shown in fig.17.



(a). Fig.16 Graphical representation of water absorption % of PVA-ZnO-H₂O₂ composite films
 (b). Fig.17 Graphical representation of water absorption % of PVA-ZnO-Glycerol composite films

CONCLUSION

In this study PVA-ZnO films were synthesized and characterized. When ZnO is added with PVA in the presence of H₂O₂ the crystallinity and crystallinity index of the polymer matrix decreases and the thermal stability of the polymer increases. Water absorption percentage was high in 1% addition of ZnO, increasing amount of ZnO decreases the water absorption capacity and it means that the degradation of the polymer was decreases with the addition of ZnO in the presence of H₂O₂. Addition of ZnO with PVA in the presence of glycerol was increases the crystallinity and crystallinity index and decreases the thermal stability of the polymer. 1% addition of ZnO

increases the water absorption percentage; further addition of ZnO decreases the water absorption percentage. So the degradation of the polymer matrix was decreases with the addition of ZnO in the presence of glycerol. The polymer composite films prepared in this study was environment friendly, biodegradable and it has high strength, light weight, good stiffness quality, good thermal stability, chemical reactivity etc. So these polymer composites promise new application in many fields such as biomedical, biosensing, drug delivery, food packaging, biocompatibility etc.

REFERENCES

- [1] Charles Chikwendu Okpala, "Nanocomposites an overview", International journal of Engineering research and development, e-ISSN : 2278-067X, Volume-8, Issue-11, 17-23, 2013.
- [2] Dr. Charles Chikwendu Okpala, "The benefits and applications of nanocomposites", International journal of advanced engineering technology, E-ISSN : 0976-3945, 2014.
- [3] Hemalatha K.S, Narsimha Parvatikar, Rukmani . K, "Influence of ZnO nanoparticles on thermal behaviour of polyvinyl alcohol films", International journal of advanced scientific and technical research, Vol - 5, ISSN 2249 – 9954, 106-113, 2015.
- [4] Andrea Dorigato, Alessandro Pegoretti, "Biodegradable single - polymer composites from polyvinyl alcohol", doi : 10.007/800396 - 011 - 2556 - Z, 359-370, 2012.
- [5] Marija B Radioicic, Zorav Saponjic, Milena T Marinovic inovic, Scott P Ahren Kel, Natasa M Bibic and Jovan M Nedal jkovic, "The influence of shaped TiO₂ nanofillers, on the thermal properties of polyvinyl alcohol", JSCS - 4301, 699-714, 2012.
- [6] Shi J.H, Huang S.M, Chu J.B, Zhu H.B, Wang Z.A, Lix D, Zhang D.W, Sunz, Chang W.J, and Huang FQ, "Effect of ZnO buffer layer on Azo film properties and photovoltaic application", J . Mater . sci : 21 - 1005, 2010.
- [7] Agnieszka Kolodziejczak-Radzimska and Teofil Jesionowski, "Zinc oxide - From synthesis to application : A review", doi : 10.3390/ma/7042833, 2833-2881, 2014.
- [8] Nazar Elamin, Ammar Elasanousi, "Synthesis of ZnO nanostructures and their photocatalytic activity", Journal of applied and industrial science, 32-35, 2013.
- [9] Matei A, Tucureans V, Dumitrescu L, "Aspects regarding synthesis and applications of ZnO nanomaterials", 45-52, 2014.
- [10] Ampaitepin, S; Tetsuo, T. A perspective on incorporation of glycerine purification process in biodiesel plants using waste cooking oil as feedstock. Energy 35: 504-2493, 2010.
- [11] Elham Gharoy Ahangar, Mohammad Hossein, Abbaspour-Fard, Nasser Shahtahmassebi, Mehdi Khojastehpour and Parisa Maddahi, "Preparation and characterization of PVA/ZnO nanocomposite", Journal of food processing and preservation, ISSN 1745-4549, doi:10.1111/jf pp.12363, 2014.
- [12] Ravichandrika K, Kiranmayi P and Ravikumar R.V.S.S.N, "Synthesis, characterization and anti-bacterial activity of ZnO nanoparticles", International journal of pharmacy and pharmaceutical sciences, Vol 4, Issue 4, ISSN: 0975-1491, 2012.
- [13] Ashis S Roy, Satyaj Gupta, Sindhu S, Amleena Parveen, Praveen C Raman urthy, composites: part B-47, 314-319, 2013.
- [14] Gunassekaran S, Sailatha E, Sesshadri S, Kumaresan S, Indian journal of pure and applied physics, 12-18, 2009.