



PREPARATION, CHARACTERIZATION AND THERMAL ANALYSIS OF POLYMERIC BLEND NANOCOMPOSITES BASED ON PVA-PVP-PEGDOPED WITH ZINC OXIDE NANOPARTICLES

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ABSTRACT

A polymeric blend contain three polymers; Poly vinyl pyrrolidone (PVP), Polyvinyl alcohol (PVA), and Polyethylene glycol (PEG) have been prepared as a composite with different weight ratio of Zinc Oxide (ZnO) nanoparticles (0,1,2,3 and 4%). The composites were casted into films and then they characterized by (FTIR), (XRD) X-ray diffraction, and (AFM) Atomic force microscope. The thermal behavior of the films was investigated by using thermoanalytical methods (DSC) differential scanning calorimetry and (TG) thermogravimetric analysis. It was found that the thermal stability of polymeric blend nanocomposites had decreased with increasing of weight ratio of (ZnO) nanoparticles.

Keywords: polymeric blend, nanocomposites, ZnO, thermal analysis, XRD, AFM.

1. INTRODUCTION

Polymeric blend give efficient tendency to construct modern properties in polymeric materials, it's imaginable to create a new materials have unique properties that are better than individual parts [1]. Fundamental priorities of the blending are ease prepared and controlling for properties, also it normally requires small addition compared to fabricate new polymer [2]. Anyway, the constituent's miscibility for the polymeric blend on the molecular scale is accountable for super properties of material [3]. ZnO nanoparticle is a semiconductor material with great potential in optoelectronic, and their stability under conditions of ambient toward air, water and sunlight [4]. These features make ZnO nanoparticles a promising efficient material. In this study we prepared new composites containing zinc oxide nanoparticles with mixture of polymers consist of PVA, PVP and PEG.

2. EXPERIMENTAL

2.1 Preparation of ZnO nanoparticles

ZnO nanoparticles have prepared as the method in the paper [5]. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaOH, which used in this work from Sigma Aldrich.

2.2 Polymeric blend nanocomposite film fabrication

Polyvinyl alcohol (PVA -72000 obtained from Dalton), polyethylene glycol (PEG-1000 obtained from Merck) and Polyvinylpyrrolidone (PVP- 40000 obtained from Merck).

A weight ratio of PVA, PVP and PEG respectively was 8:1:1, those materials were dissolved in distilled water with stirring for one hour at room temperature until the homogenous solution was formed. That solution divided into five parts each one containing 20ml, then each part was mixed ultrasonically for 25 minutes with different weight ratio (0, 1, 2, 3 and 4%) of

ZnO nanoparticles to form the composites, the samples named 0,1,2,3 and 4 respectively. By solution casting, the films were prepared and each sample had size equal (5cm x15cm x15 cm), then the films let to dry at room temperature for 150hr. After that, the films became ready to peel off the casting glass plate. The morphology of the samples was assessed by FTIR (FT-IR Shimadzu Spectrophotometer), Atomic Force Microscopy (AFM) analysis (SPMAA 3000 Angstrom Advanced Inc; USA 2008 AFM Contact Mode) and XRD (Shimadzu XRD-6000) with Cu K_α , 1.5406 Å as incident radiation, and with. The thermal properties of polymeric blend nanocomposites were studied using Linseis model STA PT-1000, Germany. The thermal behavior of the films was investigated by using thermoanalytical methods (differential scanning calorimetry DSC and thermogravimetric analysis TG).

3. RESULTS AND DISCUSSIONS

3.1 FT-IR Characterization

Figure 1 shows FT-IR Characterization of the synthesized nanomaterials, it shows Zn-O absorption band at 486.08 cm^{-1} [6]. Figure-2 shows FT-IR Characterization of polymeric blend nanocomposite samples 0 and 1 for weight ratio of ZnO nanoparticles (0 and 1%), respectively, in 2b the overlap broad peak returned to O-H and N-H groups stretching vibration was shifted to 3506 cm^{-1} . The vibrational band observed at 2924.09 and 2901.09 cm^{-1} were the result of the C-H stretch from alkyl groups and the peaks were returned to C=O were appeared stronger, sharper and shifted to 1674.21 cm^{-1} . The bending at 1416 cm^{-1} returned to CH₂ group. The bands due to C-O stretching mode were merged in the very broad envelope centred on 1260.72 cm^{-1} arising from C-O, and C-O-C stretches. The peak was returned to C-O alcoholic group stretching vibration was appeared in same



frequency at 1114 cm^{-1} . The new peak was appeared at 486.9 cm^{-1} which are characteristic of the Zn-O group.

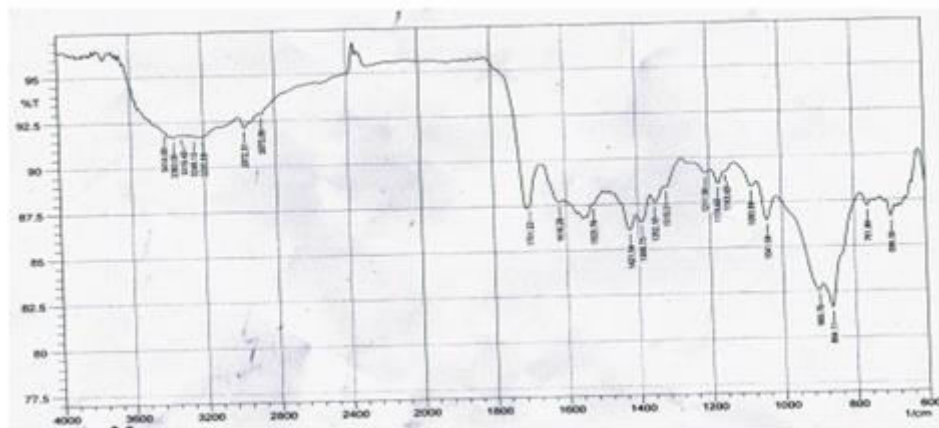
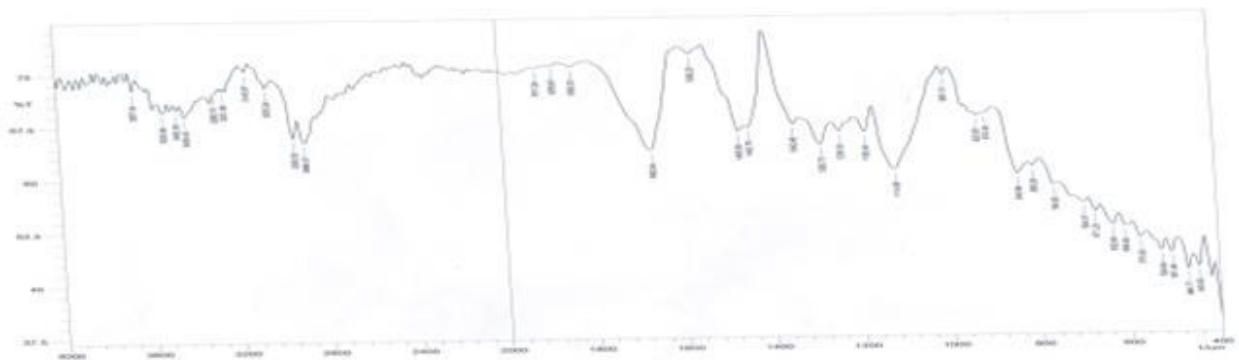
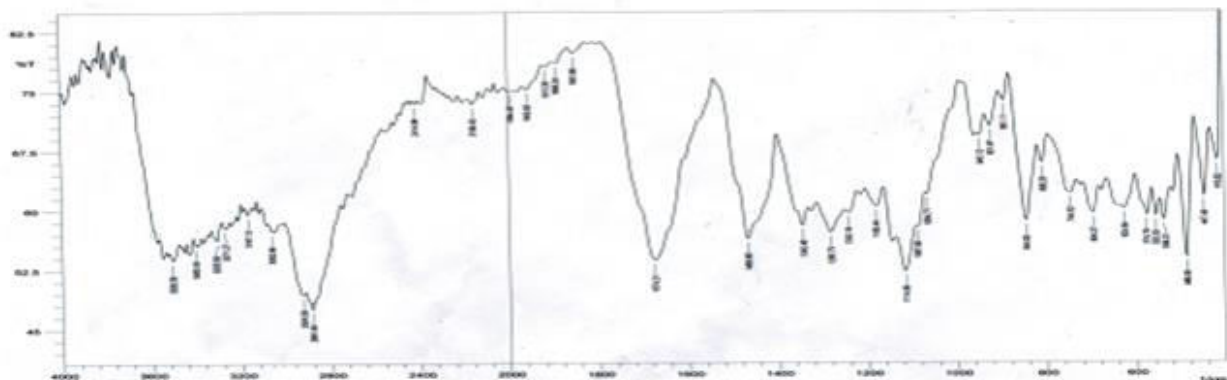


Figure-1.The FTIR spectra of ZnO nanoparticles powder.



(a)



(b)

Figure-2.The FTIR spectra of polymeric blend nanocomposite(a): sample 0 and (b): sample 1.

3.2 X- Ray diffraction

The XRD studies of Pure and Doped ZnO samples in the range of 2θ ($10^\circ - 80^\circ$) reveal that (0,1,2%) samples show non-crystalline structure and (3,4%) samples show polycrystalline structure. There is a broad intense peak appearing at scattering angle between ($10-30^\circ$), refers to the polymeric blend. The crystalline peaks

observed at $2(31.78^\circ, 34.46^\circ, 36.28^\circ)$ associated with planes (100), (002), (101) correspond to the hexagonal (wurtzite) structure of zinc oxide (PDF 36-1451) [7]. The diffraction pattern confirms the presence of ZnO in the films. The change in intensity of sharp peaks for different values can be attributed to the change in the content of the mixed dopants when added to the polymeric blend matrix.

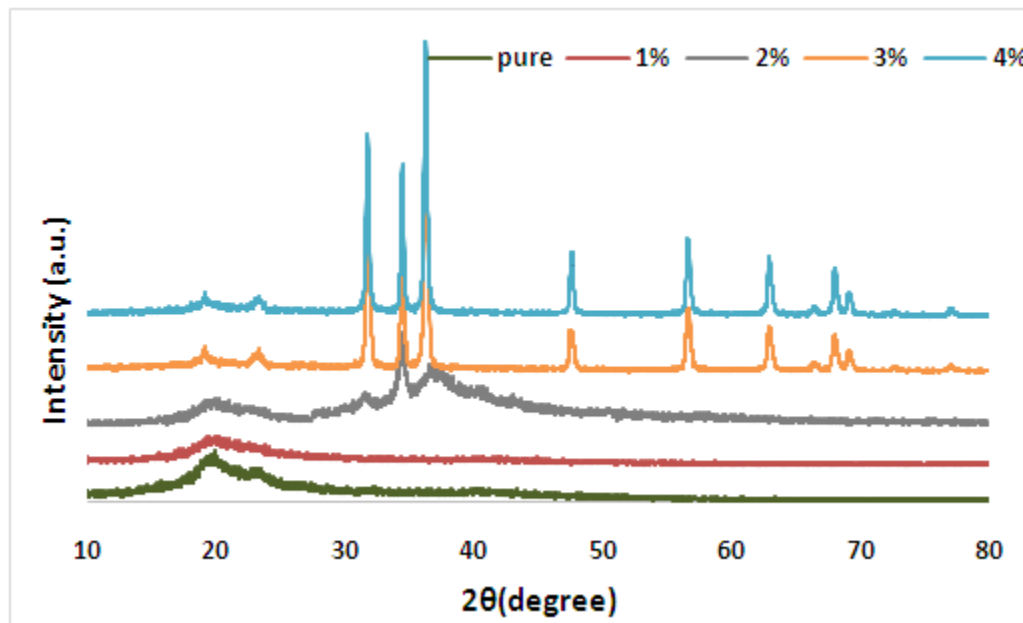


Figure-3. The XRD patterns of composite samples.

3.3 Atomic force microscopy analysis

Figures 4, 5 and 6 represent the Atomic Force Microscopy (AFM) pictures of topography of ZnO nanoparticles powder and polymeric blend nanocomposite samples 0 and 1 for weight ratio of ZnO nanoparticles (0 and 1%), respectively. From Figure-4, the particle size histogram of ZnO nanoparticles is about (77.92 nm).

Pictures of sample 0 is shown in Figure-5 with nanoparticles size about (78.81 nm). From Figure-6 which represents AFM pictures of sample 1 is shown the accumulation of ZnO nanoparticles coating with polymeric blend and with nanoparticles size about (93.28 nm).

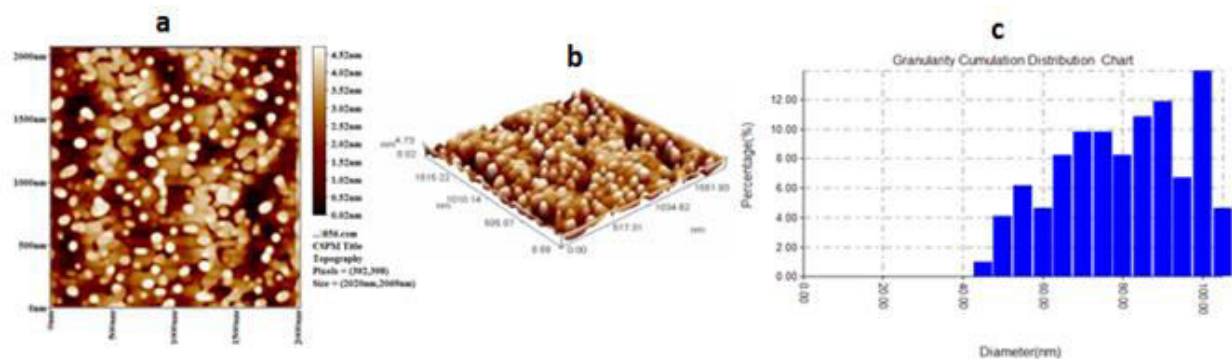


Figure-4. AFM pictures of the synthesized ZnO nanoparticles (a): 2-D topographic (b): 3-D topographic and (c): line graph topographic.

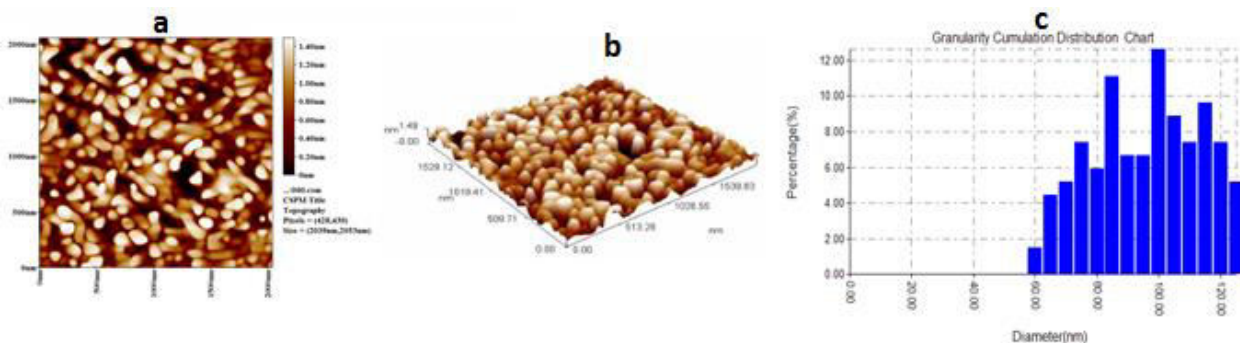


Figure-5. AFM pictures of sample 0 (a): 2-D topographic (b): 3-D topographic and (c): line graph topographic.

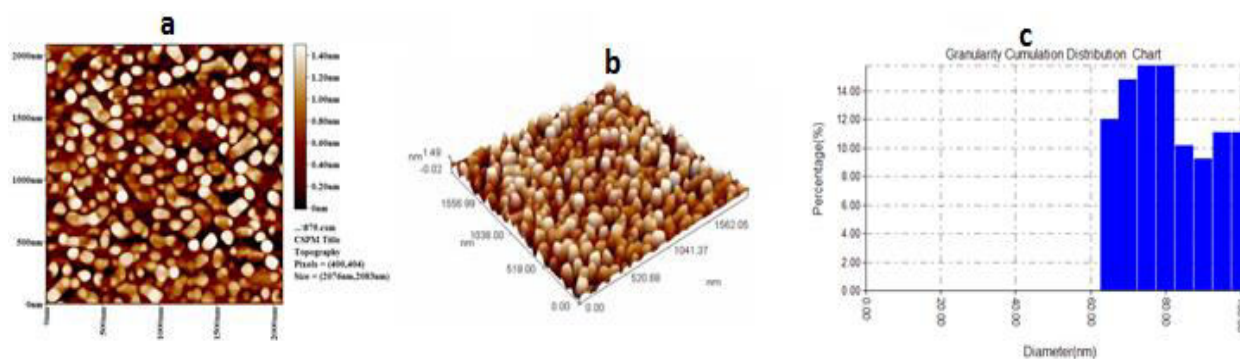


Figure-6. AFM pictures of sample 1 (a):2-D topographic (b):3-D topographic and (c): line graph topographic.

3.4 Thermal analysis

DSC measurements of polymeric blend nanocomposites samples (0,1,2,3 and 4)% were carried out. The typical DSC traces can be seen in Figure-7. As we see there are four separated glass transition temperatures (T_g) for every one of above composites, the first at (55.5, 56.2, 56.5, 57.1 and 58.00 $^{\circ}\text{C}$) for the above composites, respectively, were ascribed to the water evolving [8]. The second ones at (180, 170.4, 208.8, 200 and 181 $^{\circ}\text{C}$), and the third ones at (250, 349, 356.4, 360.1 and 360 $^{\circ}\text{C}$) for the above composites, respectively, the breakdown of the organic skeleton of polymeric blend has happened. Also the figure gave separated melting temperatures (T_m) at (440, 448.2, 404.4, 458.3 and 400 $^{\circ}\text{C}$) for the above composites, respectively. As can be seen from DSC curves that separated glass transition temperatures (T_g) and separated melting temperatures (T_m) is shifted to higher temperatures at increasing amount of ZnO nanoparticles.

Figure-8 shows the thermal gravimetric curves of polymeric blend nanocomposites samples (0,1,2,3 and 4) for weight ratio of ZnO nanoparticles (0,1,2,3 and 4%), respectively, it can be observe two decomposition stages

of thermal degradation, the first one at (200-360, 120-400, 180-402, 100-405 and 60-350), ranges. The corresponding mass loss of polymeric blend nanocomposites samples (0,1,2,3 and 4) are (14.8, 46, 48, 49 and 34.3%) respectively. This is stage can be referred to polymer main chain scission and decomposition of more stable degradation products. As be seen in the first stage, temperature at maximum process rate (T_{max}) is shifted to higher temperatures at increasing amount of ZnO nanoparticles.

The second stage at (380-600, 400-600, 400-600, 500-600 and 360-580) ranges, with the corresponding mass loss of (41, 16, 38, 18 and 28%) for polymeric blend nanocomposites samples (0,1,2,3 and 4) respectively. Also it can be imputed to polymer main chain scission and decomposition of more stable degradation. The thermal stability of polymeric blend nanocomposites are decreasing with increasing of nanoparticles, which can be attributed to presence ZnO nanoparticles can be decomposed of macromolecules strongly bonded to nanoparticles surface. As can be seen from TG curves that the energy is consistently released through thermal degradation of polymeric blend nanocomposites. This results correspond with previous paper [9].

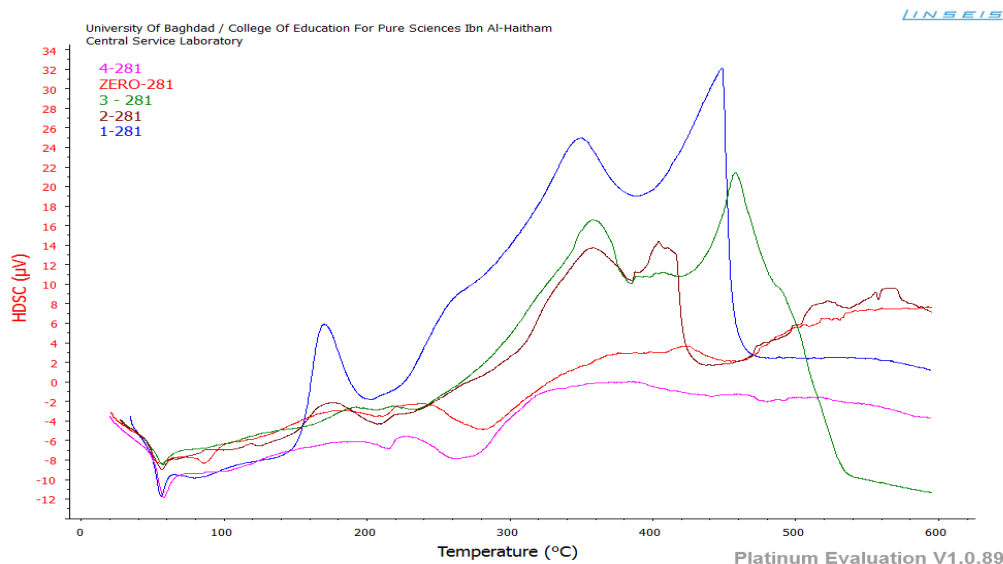


Figure-7. DSC curves of the prepared samples.

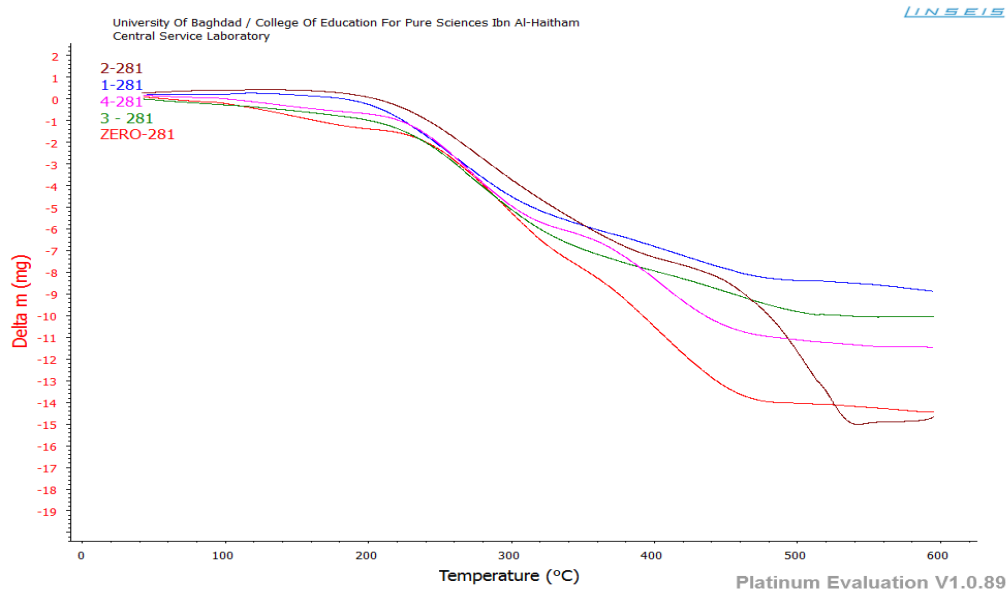


Figure-8. TG curves of prepared samples.

4. CONCLUSIONS

Nanocomposites films consists of PVA, PVP and PEG blend doped with 0,1,2,3 and 4% of Zinc Oxide nanoparticles (ZnO), they named 0, 1, 2, 3 and 4 respectively. The changing in the structural properties before and after adding ZnO nanoparticles to the blend was studied by FTIR, XRD and with Atomic Force Microscopy (AFM) techniques. The thermal behaviour of the films was investigated by using thermoanalytical methods. The thermal stability of polymeric blend nanocomposites is decreasing with increasing of nanoparticles, which can be attributed to presence ZnO nano particles can be decomposed of macromolecules strongly bonded to nanoparticles surface. As can be seen from TG curves that the energy is consistently released through thermal degradation of polymeric blend nanocomposites.

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