EFFECT OF ZINC OXIDE NANOPARTICLES CONCENTRATION ON OPTICAL PROPERTIES OF PMMA/ZNONANOCOMPOSITES THIN FILM

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Abstract- Linear optical properties of polymer/ZnOnanocomposites have received a great interest due to a wide range of applications in optical devices. In the current work, the nanocomposites as thin films have been prepared by using spin coating technique. Nanocomposites were prepared by mixing ZnO nanoparticles with Polymethyl methacrylate (PMMA) as polymer matrix. Different contents of ZnO nanoparticles were used as filler in the nanocomposites. Photoluminescence and UV-Vis spectra including transmittance and absorbance were evaluated.Energy gap of samples was calculated. Thin film's samples showed peak absorption at 375 nm . Decreasing the transmittance and theenergy band gap with increasing the concentration of ZnOnanoparticles in nanocomposites were observed. The high absorbance of samples in UV region indicated a promising candidate to be used as protecting for that region of spectrum.

Keywords- Nanocomposites, PMMA/ZnO, Optical properties, ZnO nanoparticles.

I. INTRODUCTION

Nowadays, significant scientific and technological interest have been focused on polymer inorganic nanocomposites. A combination of organic polymer and inorganic nanoparticles offeres materials with improved mechanical, electrical, optical, magnetic and thermal properties, to name a few . So their effect on composite properties is either enhanced or the same impact is achieved at lower concentrations of the filler. By successfully combining materials of different characteristics to prepare nanocomposites a single material with novel properties can be obtained. The optical properties of nanocomposite have received much attention because they are different from the individual polymers. In addition, they offer unexpected properties which greatly differ from that of conventional materials.

Due to a unique combination of electrical and optical properties, Zinc oxide isconsidered as one of the most attractive semiconductors. ZnO has a wide band gap (3.37 eV) which makes it an efficient UV absorber, where the absorption edge of ZnO is about 368 nm. Due to its large exiton binding energy(60meV) which is much larger than the room temperature, and thermal energy(26meV), ZnO has become a promising material[7] for optoelectronic devices of short wavelength, especially for UV laser diode and light-emitting diodes. ThusZnO nanoparticles and its nanocompositeshave been the focus of attention.

PMMA has got the unlimited care and significant attributes because of its unique properties such asbeing rigid, hard andhighly transparent in the visible region with low optical absorption, thermal capability, electrical performance, excellent mechanical properties, low cost,simple synthesis and low refractive index. PMMA is a favorite matrix containing the suitable components with good outdoor weather resistance and resistance to hydrolysis characteristics. It is a thermoplastic ,soit can be designed for different purposes.

Many studies have described the preparation of nanocomposite containingpolymer(PMMA) and inorganic nanoparticles (ZnO). Firstly, the nano-fillers of ZnO were synthesized or purchased(as ready nanoparticles), then, added to dissolve polymer directly or dispersed into the monomer followed by polymerization. It is important to notice that while preparing nanocomposite includes nanoparticles of ZnO, their dispersion is corroborated homogeneously. In addition to the poor bonding between the polymer and nanoparticles,there may be some defects and voids that have a harmful effect on their optical and mechanical properties. In the current work, Chloroform was used as a solvent for PMMA, whichis seldom used for that purpose, in spite of its important parameters. This paper described the preparation and characterization of Nanocomposites of PMMA/ZnO thin films by spin coating. The transmittance and absorbance spectra of samples were evaluated. Theenergy gap was calculated. Besides, the PL of samples was checked.

II. MATERIALS AND METHOD

Nanocomposites PMMA/ZnO of different concentration of ZnO have been prepared by two

steps: firstly, the PMMA solution was prepared by adding chloroform ($CHCl_3$) as a solvent to Poly (methyl methacrylate**)** (PMMA) which was supplied by (Sigma-Aldrich).Chloroform is considered as the greatest soluble limit for PMMA, and it has the greatest evaporation rates, less viscosity and least chemical hazard than other solvents. To prepare 5wt % of the PMMA / chloroform solution, 0.064 ml of chloroform should be used for every 5mg of PMMA. Thus 100 mg of PMMA was dissolved in 1.28 ml of chloroform, by using a sonicator for 15 minutes .After that, magnetic stirrer (angular velocity 400 rpm and time of one hour at room temperature) was used to help dissolve and prevent agglomerates.

Secondly, Zinc Oxide (ZnO) purchased from (Sigma-Aldrich), nanoparticles (50<size<100nm), with concentrations of (1-15 wt.%) were added to a mixture of PMMA/chloroform. Then, sonicator was used for 15min to disperse nanoparticles in the solution. Next, the solution was stirred at room temperature for one hour by a magnetic stirrer (angular velocity 400 rpm) to get homogeneous solution. By using the spin coating method (0.2 ml of mixture, angular velocity 800 rpm and time 30 sec), thin film has been prepared on Quartz substrate (2 cm x2 cm) which was washed with detergent, then cleaned in methanol.After that,it was washed in acetone by sonicator for 10 minutes for each one. Afterwards, substrates were rinsed with distilled water, and then dried in hot air. The solvent was then allowed to evaporate inside the lab at room temperature, until a dried thin film of pure PMMA and PMMA/ZnOnanocoposites of different concentration have been obtained.

The transmittance and absorbance spectra values of the present samples were measured using UV-Vis spectrophotometer (PerkinElmer instruments-Lambda 900 UV/VIS Spectrometer). Photoluminescence (PL) spectra of samples were recorded using a Perkin-Elmer LS-55 (Perkin-Elmer Co., USA) luminescence spectrometer with a xenon lamp.

III. RESULTS AND DISCUSSION

A. Uv-Vis Spectroscopy

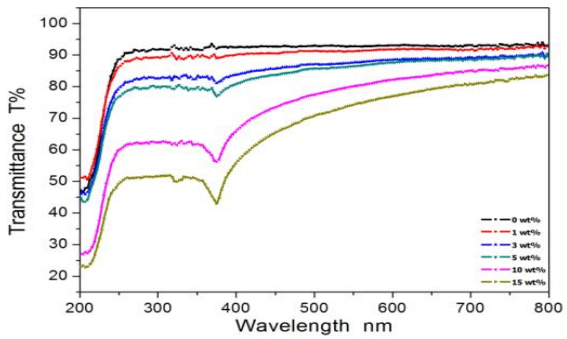


Fig.1 UV-Vis transmittance spectra of PMMA/ ZnONanocomposites .

Fig.1 shows the UV- Visible transmittance spectra of PMMA and PMMA/Zn Onanocomposites prepared as thin film. The transmittance of the pure PMMA thin film (0 wt%) was high in both UV and visible range, but the transmittance of PMMA/ Zn Onanocompositesof different concentrations of ZnO nanoparticles decreases with increase of concentration of ZnO.

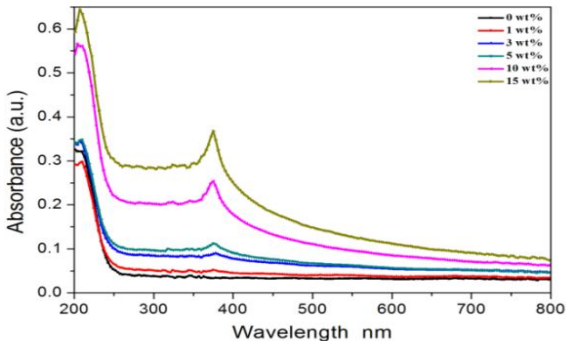


Fig.2 UV-Vis absorbance spectra of PMMA/ZnONanocomposites .

Fig.2shows the UV-Visible absorption spectra of PMMA pure(0 wt %) and PMMA/Zn On a no composites prepared as thin film. The PMMA (Pure) has low absorbance in both UV as well as visible region, but the PMMA/ZnOnanocomposites have high absorbance in UV region, and indicated absorption peak at 375 nm that belongs to behaviour of nanoparticles of ZnO, which means it is able to absorb in the UVA range (320-400 nm).The peak of absorbance increased when the concentration of ZnO nanoparticles increased due to the nano –size of ZnO that increases the surface area, hence, the strong absorption was found.

B. Calculation of Energy Gap (Eg):

The value and nature of energy gap (Eg) depend on the linear absorption coefficient (α). To determine (Eg) ,the following relation can be used:

$$(\alpha h\nu)m = A\,(h\nu - Eg) \qquad (1)$$

Where α is the absorption coefficientfor thin film samples calculated by :

$$\alpha = 1/d \ \ln 1/T \qquad (2)$$

Where d thickness of the thin film samples is determined by the FESEM image cross section; it was around 800 nm, and T the transmittance was obtained from data of UV-Vis spectroscopy.ν is the frequency, h is Planck's constant and Eg is the optical energy band gap between the valence band and the conduction band. A is a constant which depends on the transition probability; m is an index that describes the optical absorption process. Theoretically, it is equal to 2 for direct allowed, 2/3 for direct forbidden, 1/2 for indirect allowed and1/3 for indirect forbidden transition. The value of m decides the nature of energy gap or transition involved.By using Tauc's plot, the value of the band gap (Eg) was calculated from the graph of $(\alpha h\upsilon)^2$ versus (hυ) . The value of

Egis given by extrapolating the linear portion of the curve to the hυ - axis.

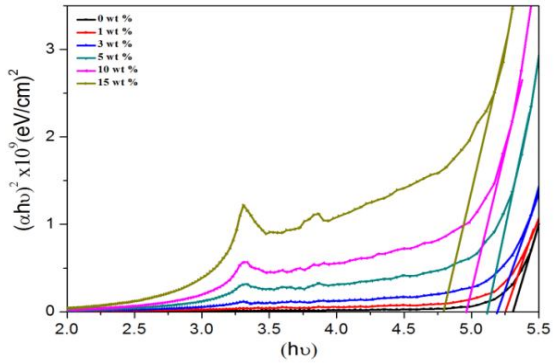


Fig.3 $(\alpha h\upsilon)^2$ and photon energy (hυ) of PMMA/ZnONanocomposites.

Fig.3demonstratesthe relationship between $(\alpha h\upsilon)^2$ and photon energy (hυ) of PMMA/ZnONanocomposites as Thin films. The results show that the values of energy gap decrease with increase of the weight percentage of ZnO, nanoparticles as illustrated in Fig.4. The proportional of energy gap with a weight percentage of ZnO nanoparticles is inverse, so the increasein nanoparticles generates a new energy level between the valence band and the conduction band. The larger amount of weight percentage of ZnO (15wt%) satisfied value of energy gap equals (4.8 eV) ,whereas the energy gap of pure PMMA (0 wt%) equals (5.32 eV) .

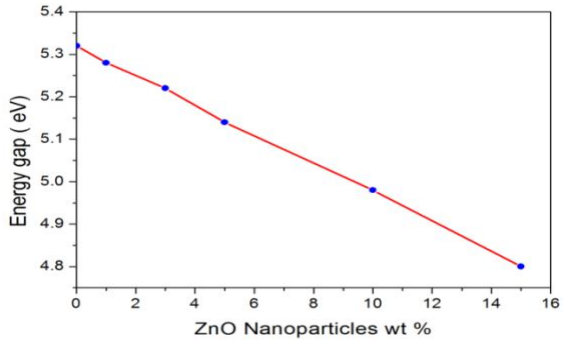


Fig.4 Energy gap as a function of concentration of ZnO% in PMMA/ZnONanocomposites .

C. Photoluminescence (PL) Spectra

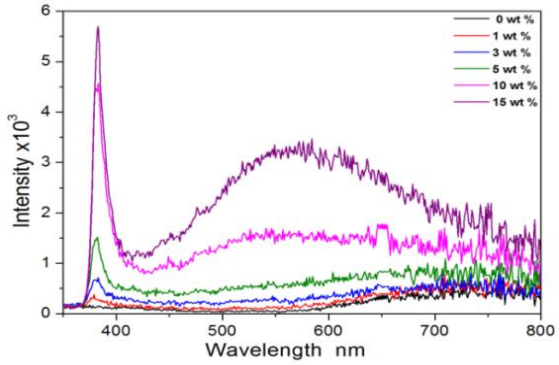


Fig.5Photoluminescence spectra of PMMA/ ZnONanocomposites.

PL spectra results of Nanocomposites PMMA/ZnO, as Thin Films in the wavelength range from 350 to 800 nm are shown in Fig.5. Excitation Xenon lamp at 325 nm was used. There is no peak in curve of PMMA Pure (0wt%). But the narrow and strong peaks, especially, at high concentration of ZnO nanoparticles are observed in UV region at around 380 nm in the ZnO/PMMA nanocomposites as thin film. The UV emissions are attributed to the exciton recombination of the ZnO nanoparticles. Beside that, there is a broad peak in the visible region its centering at around 580 nm ,that is clear in high concentration of ZnO nanoparticles (10wt% & 15wt%). The visible emissions are due to the defects such as the oxygen vacancies.

The (15 wt%) ofZnOnanocomposite satisfied maximum emission, due to the transferring of high energy from the nanoparticles to the polymer . The intensity at the UV peak is higher than that found at visible peak in all samples. All of the emission bands for PMMA/ZnOnanocompositesare placed above the pure PMMA bands. Those results corresponding to PL spectrum of ZnOgenerally Show narrow UV emissions from the exciton states and one or more broad visible emissions from the defects.

CONCLUSION

Thin films of pure PMMA and nanocomposites of PMMA/ZnO with different concentrations of ZnO nanoparticles have been prepared. The thin film thickness was checked by FESEM image, which is equal to 800 nm.UV-Visible tests showed low transmittance and high absorbance for UV radiation by PMMA/ZnO depending on the concentration of ZnO.All nanocomposites have an absorption peak at a wavelength of 375 nm which belonging to ZnO nanoparticles, which is increased with increase of ZnO's concentration.

The values of energy gap decreases with the increase of the weight percentage of ZnO nanoparticles in nanocomposites.

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