Optical Properties of PMMA/ZnONanocomposites as Foils Prepared by Casting Method

1Haider Mohammed Shanshool, 2Muhammad Yahaya, 3Wan Mahmood Mat Yunus and 4IbtisamYahya Abdullah

1School of Applied Physics, Faculty of Science and Technology, UniversitiKebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
2Department of Physics, Faculty of Science, University Putra Malaysia, 43400 UPM,Serdang, Malaysia
3Ministry of Science and Technology, Baghdad, Iraq
4Department of Physics, College of Science, University of Mosul, Iraq

ABSTRACT

Background: Linear optical properties of polymer/ZnOnanocomposites have been getting a great interest due to a wide range of applications in the optical devices. Objective: in the current work, the PMMA/ZnOnanocomposites as foils have been prepared by using the casting method. Nanocomposites are prepared by mixing the ZnO nanoparticles with Polymethyl methacrylate (PMMA) as polymer matrix. Different contents of ZnO nanoparticles were used as fillers in the nanocomposites. Results: UV-Vis spectra: transmittance, absorbance and reflectance, beside Photoluminescence were evaluated. Absorption coefficient, extinction coefficient, energy gap and refractive index were calculated. The FTIR spectra were analysed. The foil samples showed peak absorption at 375nm, decreased the transmittance with the increase of the peak absorption of ZnO nanoparticles concentration but the reflectance increased with the increase of them. The decreasing of the band gap with the increasing of the ZnO concentration in nanocomposites was observed. PL spectra of the samples showed narrow UV emissions and broad visible emissions. Conclusion: the high absorbance of samples in the UV region indicated a promising candidate to be used as shielding for this region of spectrum.

INTRODUCTION

During the last two decades, significant scientific and technological interest was focused on the polymer inorganic nanocomposites. Nanocomposites are one kind of composite materials comprising of relatively small content inorganic nanoparticles at nanometer-sized, which are dispersed into a polymer matrix uniformly. The addition of inorganic nanoparticles into a polymer matrix will change both properties from inorganic nanoparticles and polymer to be enhanced and hence advanced new functions can be generated to the nanocomposite (Shanghuaet al., 2010). The combination of organic polymer and inorganic nanoparticles will be offerred materials with improved mechanical, electrical, optical, magnetic, thermal and many other specific properties. Thus their effect on composite properties is either enhanced or the same impact is achieved at the lower concentrations of the filler (Azlovavet al., 2011). By successfully joining materials of different characteristics to prepare nanocomposites as a single material, 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 (Indolia and Guaar, 2013). The optical properties of nanocomposites are certainly influenced by many factors such as the size of the filler, size of distribution, degree of dispersion, and filler contents (Rajagopalan and Khanna, 2013). The important factor which affects many optical properties of nanocomposites is the size of the inorganic nanoparticles as nano-fillers. According to the latest advancement, the efforts of getting the size of nanoparticles (100-50 nm) have led to the reduction of the scattering light because they are significantly smaller than the wavelength of light. Therefore nanocomposites contain nanoparticles acted as optically homogeneous materials that modified optical properties, have attracted much interest. For example, the refractive index of polymers, usually 1.3-1.5, when added with
nanoparticles with high refractive index, can increase to 2.5 (Chen et al., 2003).

Zinc oxide is one of the most attractive semiconductors due to the unique combination of electrical and optical properties, and important features like biocompatibility, long-term environmental stability, non-toxicity and low cost (Jeejuet et al., 2012). For more than 75 years, ZnO has been considered as a familiar field in the scientific studies, and it has been highlighted as the subject of thousands of researches, since the first study of ZnO as a semiconductor material which began in 1935.C. W. Bunn, "The lattice-dimensions of zinc oxide" Proc. Phys. Soc. London 47: 835,1935). ZnO has a wide band gap (3.37 eV) which makes it an efficient UV absorber, and the absorption edge of ZnO is about 368 nm. Due to its large exiton binding energy (60 meV) which is much larger than the room temperature thermal energy (26 meV), ZnO has become a promising material for optoelectronic devices of short wavelength, especially for UV laser diode and light-emitting diodes. Hence, it refers to the stability (Hassan and Hashim, 2013) of the electron-hole pairs that are constant even at room temperature. Besides that, ZnO can be synthesized in a wide range of particle sizes and shapes at the low cost preparation method (Azlovare et al., 2008; Seowet al., 2009; Saleem et al., 2012; Shahidet al., 2012; Noet al., 2013; Nagarani and Vasu, 2013; Son, 2009).

ZnO has been added as fillers into many polymers, such as PMMA, PS, PVDF, PVA, PV and PC(Indolia and Guar, 2013; Chen et al., 2003; Jeejuet al., 2012; Sangawar and Golchha, 2013; Abd El-kader et al., 2013; Al-Taa’yet al., 2014; Al Jaaferi and Ayesh, 2011).

Nowadays, PMMA has got the unlimited care and significant attributes because of its unique properties such as rigid, hard, high transparency in the visible region, low optical absorption, thermal capability, electrical performance, excellent mechanical properties, low cost and simple synthesis, and low refractive index. PMMA becomes the favorite as matrix to contain the components due to its good outdoor weather resistance and resistance to hydrolysis. It is a thermoplastic, so users can use it to design anything they want (Chiaid et al., 2010; Azlovare et al., 2011). Chloroform, which is used as a solvent for PMMA, is considered (Qian et al., 2010; Wagner, 1987; Baker et al., 2010) as the greatest soluble limit for PMMA; it has the greatest evaporation rates, less viscosity and the least chemical hazard than other solvents.

Recently, many studies have described the preparation of nanocomposite containing the polymer (PMMA) and inorganic nanoparticles (ZnO) (Chen et al., 2003; Sharma et al., 2011; Kulyket et al., 2011; Wong et al., 2012). Firstly the nano-fillers of ZnO were synthesized or purchased (as ready nanoparticles) then added to dissolve polymer directly or disperse into the monomer followed by polymerization (Shanghua et al., 2010). The very important things to be aware of, when preparing nanocomposite including the nanoparticles of ZnO, is to confirm the dispersion of them is done homogeneously. In addition the poor bonding between the polymer and nanoparticles may present defects and voids that have a harmful effect on the optical and mechanical properties. The study of the optical characteristics of ZnO nanoparticles and its nanocomposites, either linear optical like transmittance, absorbance, reflectance, or nonlinear optical such as nonlinear refractive index and nonlinear absorption, should be getting more interest to determine (Nagaraja et al., 2013) suitable materials for nonlinear applications.

In the current work, the nanocomposites of PMMA/ZnO, as foils have been successfully prepared by using the casting method. Chloroform was used as the solvent for PMMA, which was not used in the previous literatures (Chen et al., 2003; Lee et al., 2006; Azlovare et al., 2008; Kulyket et al, 2009; Sreeja et al., 2010; Azlovare et al., 2011; Kulyket et al, 2011; Jeejuet al., 2012; Haripadnamet et al., 2012), in spite of having important parameters (Wagner, 1987; Qian et al., 2010; Baker et al., 2010). The linear optical properties of the samples were evaluated. To the best of our knowledge, there was no report published to describe the preparation of PMMA/ZnO nanocomposites as foils for that purpose.

MATERIALS AND METHOD

Nanocomposites PMMA/ZnO of the different ZnO concentration were prepared by two steps, firstly; the PMMA solution was prepared by adding chloroform (CHCl3) to Poly (methyl methacrylate) (PMMA) which supplied by (Sigma-Aldrich). To prepare 5wt % of the PMMA / chloroform solution, 0.064 ml of chloroform should be used for every 5mg of PMMA, so 80 mg of PMMA was dissolved in 1.024 ml of chloroform, by using the sonicator for 15 minutes, and followed with magnetic stirrer (angular velocity 400 rpm and time one hour at room temperature) used to help dissolve and prevent agglomerates.

Secondly, Zinc Oxide (ZnO) was purchased from (Sigma-Aldrich), nanoparticles (50<size<100nm), with concentrations of (1-15 wt. %) added to a mixture of PMMA/chloroform. Then, the sonicator was used for 15min to disperse nanoparticles in the solution. The solution was then stirred at room temperature for one hour by a magnetic stirrer (angular velocity 400 rpm) to get the homogeneous solution. By using the casting method, the solution was casted uniformly on the glass Petri dish (diameter = 9 cm), and the aluminium square template (3x3 cm) was put inside it, at room temperature. After one hour the template was removed, and 30 min later the film was removed as
foil easily. After that the foil was kept at room temperature for one day to be solid. Later, the foils of pure PMMA and of nanocomposites (PMMA/ZnO) of different concentrations were collected.

The transmittance, absorbance and reflectance spectra values of the present samples were measured using UV-Vis spectrophotometer (PerkinElmer instruments-Lambda 900 UV/VIS Spectrometer). The samples were checked by FT-IR spectroscopy, Brand: Perkin Elmer, Range: 4000 cm$^{-1}$ – 650 cm$^{-1}$, Resolution: 4 cm$^{-1}$. The photoluminescence (PL) spectra of the samples were recorded using a Perkin-Elmer LS-55 (Perkin-Elmer Co., USA) luminescence spectrometer with a xenon lamp.

RESULTS AND DISCUSSION

FTIR Analysis:

FTIR spectra, as the transmittance mode, of the PMMA/ZnOnanocomposites prepared as foils in the range 650– 4000 cm$^{-1}$ are shown in figure 1. The bands at 2992 and 2951 are assigned to the CH$_2$, C–O–CH$_3$, and CH stretching vibrations (Ramesh et al., 2007). A strong peak at 1727 cm$^{-1}$ appeared due to the presence of the ester carbonyl group stretching vibration of PMMA. Compared to the standard PMMA FT-IR spectrum, the peak shifts to short wave number. The main reason is that PMMA can coordinate with Zn$^{2+}$ ions on the surface of the ZnOnanoparticles, then form delocalized bonds (Gowri et al., 2010). Meanwhile the bands at 1433 cm$^{-1}$ appeared to the stretching vibrations of C=O and −O−CH$_3$ groups of PMMA (Pawde and Deshmukh, 2009). A small band at 1346 cm$^{-1}$ may be due to a −CH$_3$ group. Peaks at the range between 1260 and 1146 cm$^{-1}$ can be explained owing to the C–O (ester band) stretching vibration. There are bands at 978 and 737 cm$^{-1}$ that are due to the bending of C–H (Gowri et al., 2010). Besides that, the literatures indicated that ZnO nanoparticles have the stretching and bending bands. However they are appeared to be suppressed, with one of them were revealed between 360 cm$^{-1}$ and 420 cm$^{-1}$ (Chilvery et al., 2014) or near 420 cm$^{-1}$ (Latif et al., 2012) or at 486 cm$^{-1}$ and 480 cm$^{-1}$ (Rajagopalan and Khanna, 2013) or near 438 cm$^{-1}$ (Gowri et al., 2010).

UV-Vis Spectroscopy:

![Fig. 1: FTIR spectra of PMMA/ZnO of different concentration of ZnO nanoparticles.](image)

![Fig. 2: Transmittance spectra of PMMA/ZnO of different concentration of ZnOnanoparticles.](image)
Figure 2 shows the UV-Visible transmittance spectra of PMMA and PMMA/ZnO nanocomposites as foils. The pure PMMA foil, (0 wt. %), has high transparency in the visible range, but relatively lower than it in UV range. The effect of adding nanoparticles of ZnO in PMMA is clear; they have very low transmittance in UV region that decrease with increasing content of ZnO in nanocomposite. Although, ZnO nanoparticles have lower absorption spectrum in the visible region, the transmittance of PMMA/ZnO for this spectral region declined with the increasing of ZnO concentration that is due to the smoothness of the surface which seems as a specular surface that causes the high reflectivity and lead to the low transmittance for the visible range. In addition, the scattering of ZnO nanoparticles could cause the loosing of incident intensity in this spectral range (Junlin et al., 2010).

**Fig. 3:** Absorbance spectra of PMMA/ZnO nanocomposites of different concentration of ZnO nanoparticles.

Figures 3 shows the UV-Visible absorption spectra of PMMA and PMMA/ZnO nanocomposites as foils. The Pure PMMA , (0 wt. %), has low absorbance in both UV as well as visible region, but the PMMA/ZnO nanocomposites have high absorbance in the UV region, and indicates the absorption peak at 375 nm that belongs to behavior (Al-Taa’y et al., 2014) of ZnO nanoparticles, which means it is able to absorb the UVA range (320-400 nm). The peak of the absorbance increased when the content of ZnO nanoparticles increased that was due to the nano-size of ZnO that increase the surface area, so the strong absorption derived (Yahya and Rusop, 2012).

**Fig. 4:** Reflectance spectra of PMMA/ZnO nanocomposites of different concentration of ZnO nanoparticles.

Figure 4 shows the UV-Visible reflectance spectra of PMMA and PMMA/ZnO nanocomposites as foils. PMMA (pure) sample has low reflectance in the UV and visible regions. All samples show the increase of the reflectance when the concentration of ZnO was increased in the visible region. However, they showed the decreasing reflectance with increasing of concentration of ZnO in the UV region.
Linear absorption coefficient (α):

The linear absorption coefficient (α) for foil samples was calculated by (Ellingson and Heben, 2013):

$$\alpha = \frac{1}{d} \ln \left( \frac{1-R}{T} \right)$$  \hspace{1cm} (1)

where \(d\) is the thickness of foils determined by using a digital micrometer at different places in each foil and an average was taken, around 70 μm. \(T\) is the transmittance and \(R\) is the reflectance obtained from the data of UV-Vis spectroscopy.

Figure 5 shows the absorption coefficient \(\alpha\) spectra of PMMA pure (0 wt.% ) and PMMA/ZnO nanocomposites as Foils. \(\alpha\) depends on the wavelength of light that was actually absorbed. The highest value of \(\alpha\) was showed in the UV region, but less than it was observed at the visible region.

Extinction coefficient (K):

The extinction coefficient (K) was calculated by (Sangawar and Golchha, 2013):

$$K = \frac{\alpha \lambda}{4\pi}$$  \hspace{1cm} (2)

where \(\alpha\) is the linear absorption coefficient and \(\lambda\) is the wavelength.

Calculation of Energy Gap (Eg):

The value and nature of energy gap (Eg) depend on the linear absorption coefficient (α). To determine (Eg), can use the relation (Al-Ammar et al., 2013):

$$(\alpha h\nu)^m = A (h\nu - E_g)$$  \hspace{1cm} (3)

where \(\alpha\) is the absorption coefficient, \(h\nu\) is the frequency, \(h\) is Planck’s constant and \(E_g\) 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 two for direct allowed, 2/3 for direct forbidden, 1/2 for indirect allowed and 1/3 for indirect forbidden transition [Sangawar and Golchha, 2013; Al-Ammar et al., 2013].
The value of $m$ decides the nature of the energy gap or the transition involved. Few of the literatures revealed that the determining of index ($m$) depend on the value of absorption coefficient (Mustafa, 2013). Another literature (Dorranianet al., 2012) indicates that the estimation of ($m$) was obtained from the slope of the graph between log ($\alpha$) and log ($h\nu$). However, in general, the graph between ($\alpha h\nu$)$^m$ and photon energy ($h\nu$) was plotted, then the value of index $m$ which gives the best linear graph was chosen (Al-Ammar et al., 2013).

By using Tauc’s plot, the value of the band gap ($E_g$) was calculated from the graph of ($\alpha h\nu$)$^2$ versus ($h\nu$). The value of $E_g$ will be given by extrapolating the linear portion of the curve to the $h\nu$ - axis.

Figure 7 demonstrates the relationship between ($\alpha h\nu$)$^2$ and photon energy ($h\nu$) of PMMA/ZnOnanocomposites as Foils. From the results, the values of the energy gap decreased with the increasing of the weight percentage of ZnO nanoparticles as stated clearly in Figure 8. The proportional of energy gap with a weight percentage of ZnO nanoparticles are inversely, so the increasing of nanoparticles generates a new energy level between the valence band and the conduction band. The value of energy gap which satisfies in the larger amount of the weight percentage of ZnO(15wt%) equals to (4.55 eV), while its value in PMMA(Pure) equals to (5.08 eV).

![Figure 7](image1.png)

**Fig. 7:** ($\alpha h\nu$)$^2$ and photon energy ($h\nu$) of PMMA/ZnOnanocomposites.

![Figure 8](image2.png)

**Fig. 8:** Energy gap as a function of the concentration of ZnO% in nanocomposites.

**Refractive index ($n$):**

The refractive index ($n$) was calculated by (Sangawar and Golchha, 2013; Al-Ammar et al., 2013):

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2}$$

where $R$: Reflectance, $n$: linear refractive index, $K$: extinction coefficient. When $K^2 \ll (n-1)^2$, so

$$R = \frac{(n-1)^2}{(n+1)^2}$$

$$n = \frac{(1 + R^{1/2})}{(1 - R^{1/2})}$$

Figure 9 describes the change in the refractive index ($n$) for PMMA/ZnOnanocomposites as foils as a function of wavelength. The value of Refractive index of PMMA (pure) is around(1.5) in the visible region which correspond with its known value. While $n$ increased with the increasing of the weight percentage of ZnO nanoparticles in the visible spectrum, that behaviour was different at the UV region when $n$ decreased with the increasing of the weight percentage.

![Figure 9](image3.png)
Fig. 9: Refractive index (n) as a function of wavelength for PMMA/ZnO nanocomposites.

**Photoluminescence (PL) Spectra:**

PL spectra results of nanocomposites PMMA/ZnO as Foils in the wavelength range from 350 to 800 nm are shown in Figure 10. Excitation Xenon lamp at 325 nm was used. There is no peak in the curve of PMMA (Pure). However the narrow and very strong peaks, especially, at the high concentration of ZnO nanoparticles are observed in UV region at around 385 nm in the ZnO/PMMA which increased with the increasing of ZnO contents. The UV emissions are attributed to the exciton recombination of the ZnO nanoparticles. Beside that, there is a broad peak in the visible region, centring at around 590 nm, that is clear in high concentration of ZnO nanoparticles (10wt% and 15wt%). The visible emissions are due to the defects such as the oxygen vacancies (Liu et al., 2004). The 15wt% of ZnO nanocomposite satisfied maximum emission, that due to the transferring of high energy from the nanoparticles to the polymer (Yahya and Rusop, 2012). The intensity at the UV peak is higher than that found at the visible peak in all samples except 15 wt % ZnO. All the emission bands for PMMA/ZnO nanocomposites were placed above the pure PMMA bands. Those results corresponded to a PL spectrum of ZnO that is, generally, showing narrow UV emissions from the exciton states and one or more broad visible emissions from the defects (Kulyk et al., 2011; Djurisic and Leung, 2006; Kim et al., 2008).

Conclusion:

Foils of the pure PMMA and nanocomposites PMMA/ZnO with the different concentrations of ZnO nanoparticles have been prepared. The foil thickness was 70 μm. UV-Visible tests showed low transmittance and high absorbance for UV radiation by PMMA/ZnO nanocomposites depending on the content of ZnO. All nanocomposites have an absorption peak at a wavelength of 375 nm which belong to ZnO nanoparticles, which increased with the increasing of the ZnO concentration. All samples showed the increase of the reflectance when the concentration of ZnO increased in the visible region. However, they showed the decreasing of the reflectance with the increasing of concentration of ZnO in the UV region. The values of the energy gap decreased with the increasing of the weight percentage of the ZnO nanoparticles. The refractive index increased with the increasing of the weight percentage of the ZnO nanoparticles in the visible spectrum, but that behaviour was different in the UV region when it decreased with the increasing of the weight percentage of ZnO. The PL spectra showed narrow UV emissions from the exciton states and one broad visible emission from the defects.
Acknowledgment

The authors would like to acknowledge the contribution and the financial support by the Malaysian Ministry of Higher Education and Universiti Kebangsaan Malaysia under research grant (FRGS/1/2013/SG02/UKM/01/1).

REFERENCES


Kulyk, B., V. Kapustiany, O. Krupka and B. Sahraoui, 2011. Optical absorption and...


