

## Investigate the Physical Properties and Transmitted sunlight of PVC/PMMA/ ZnO Nanocomposite Films

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Received 31 October 2022, Revised 11 January 2023, Accepted 17 January 2023

### ABSTRACT

Pure blend (PVC0.3g +PMMA 0.2g) and blend/ZnO nanocomposite films with different amounts were created using the solution casting technique. Different amounts of zinc oxide from (0.001, 0.002, 0.003, 0.004, and 0.005)g were investigated and added to blend polymer with a fixed amount (0.5) g of PVC/PMMA in 15ml tetrahydrofuran (THF). The XRD results demonstrated the amorphous structure of the admixture film and the hexagonal crystal structure of ZnONPs. The ZnONPs in the film were also atomically dispersed resulting in the incorporation of the ZnONPs peaks within the polymer matrix. FESEM image of the mixture and ZnO revealing small white spots scattered on the surface of the mixture with some agglomerates. FTIR spectroscopy data showed no chemical interaction between the polymer blend and ZnONPs. The increasing amounts of ZnONPs improved the absorbance, absorption coefficient, and extinction coefficient of the blend polymer. The blended polymer's permeability and energy gap decreased from 4.48eV to 3.91eV with the increase in the number of ZnONPs in the nanocomposites. The transmitted sunlight intensity was measured through the blended pure polymer films and the blended nanocomposites/ZnO nanocomposites. At the beginning of September 2021, the intensity of transmitted sunlight was measured in Baghdad for a period of 7 days. As can be observed, almost all films have the same ratio of the intensity of transmitted radiation to the intensity of sunlight for all hours and days.

**Keywords:** Blend Polymer, ZnO Nanoparticle, Optical Properties, Transmitted Sunlight.

### 1. INTRODUCTION

Blending at least two distinct polymers with different structures results in the creation of new polymeric materials with improved characteristics [1]. Blending is an alternative, direct, and low cost method for obtaining new polymeric materials with desired qualities. The main benefits of polymer blending are its adaptability, simplicity, inexpensiveness, and the final product's qualities, which may be adjusted to meet the needs of applications that cannot be met by a single polymer [2]. Polyvinyl chloride (PVC) is one of the most essential and widely used thermoplastics polymers due to its numerous advantages, including low flammability, chemical resistance, and low cost (Aouachria et al., 2006). However, PVC has drawbacks such as limited heat stability at processing temperatures, low impact strength, and high melt viscosity [4]. Plasticizers or processing aids are used to compensate for this weakness in PVC. Given its low cost and bulk productivity, polymethyl methacrylate (PMMA) has attracted extensive attention for usage in optical components and optoelectronics systems. Several optical components, including an optical switch, a coupler, a splitter, and a transceiver, have recently been described by researchers [5,6]. PMMA is commonly used as a processing aid for PVC[7]. Zinc oxide nanoparticles (ZnONPs) have intriguing features for

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a variety of applications, including blue light emitting devices (LEDs), photocatalysis, and solar cells. Zinc oxide represents semiconductors as it is a metallic compound with an energy gap of about 3.4 eV in the near UV and crystallizes preferentially in the hexagonal wurtzite type structure [8]. ZnO has gained popularity as an addition in rubbers, plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, batteries, ferrites, fire retardants, and first aid tapes. These properties make polymer/ZnO nanocomposite materials potentially appealing for a variety of applications, including UV shielding, field emission display, gas sensing, and thermoelectricity[9].

Abdelghany *et al.* [10], produced samples of varied mass fractions (PVC/PMMA) and examined their physical characteristics via standard Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), ultraviolet-visible (UV/Vis) spectroscopy and scanning electron microscopy (SEM). A novel method for determining the degree of miscibility was presented, based on spectroscopic quantitative measurement. All of the results indicated that the ratio (70/30 wt. percent) of PVC/PMMA blends should be employed in various practical applications to add adequate dopant. Joseph *et al.* [11], employed a solution casting method to prepare PVC/PMMA/germanium dioxide (GeO<sub>2</sub>) nanocomposite films and demonstrated their capacity to be used as an absorption-dominant shielding material. Mohammed *et al.* [12], reported an increase in AC conductivity after complexing PVC/PMMA with nitrate salts of Cd, Co, Cr, and Mg and forming membrane films by solution casting. As a result, these films have the potential to be used in battery applications and water treatment and filtration processes.

The goal of this research is to improve the optical properties of a PVC/PMMA polymer blend by filling the matrix with ZnONPs and measuring the transmission of these films in sunlight.

## 2. THEORETICAL PART

Beer Lambert's law explains how absorption relates to the properties of an absorbent medium. The law states that the intensity of light passing through a sample decreases with increasing concentration and thickness within a given wavelength. The absorption coefficient is defined as the ratio of the reduction in radiation energy flow to the unit of distance toward wave propagation in the material, which varies based on the type of absorbent material and the wavelength of the incoming wave [13].

The absorption coefficient was computed using Lambert's law, which asserts that the absorbance of a material sample is proportional to its thickness (path length) (*t*), and is expressed as follows:[14].

$$\frac{I}{I_0} = e^{-\alpha t} \quad (1)$$

where  $I/I_0$  is the ratio of the incident wave's transmittance intensity to the incident wave's incidence intensity, representing the electromagnetic wave's transmittance (*T*), and since absorbance (*A*) is represented as:

$$A = \log \frac{I}{I_0} \quad (2)$$

The absorption coefficient can thus be expressed mathematically as [15].

$$\alpha = \frac{2.303}{t} A \quad (3)$$

where  $\alpha$ : is the absorption coefficient. and the thin film transmittance (T) is given by the relationship

$$T = 1 - A - R \quad (4)$$

where R: reflectance and A: absorbance. The equation that links the absorption coefficient to the energy gap is as follows [16].

$$\alpha h\nu = B(h\nu - E_g)^r \quad (5)$$

Where  $h\nu$  is the energy of the incident photon, B is a constant depending on the nature of the material,  $E_g$  is the energy gap and r is a constant whose value is determined by the presence of the transformation, with  $r=(1/2$  and  $3/2)$  for allowed and forbidden direct transitions, respectively, and  $r=(2$  and  $3)$  for allowed and forbidden indirect transitions, respectively. The extinction coefficient (k) can be calculated using the following equation[17].

$$K = \frac{\lambda\alpha}{4\pi} \quad (6)$$

using the Debye-Scherrer equation, the average Crystalline size of ZnO nanoparticles was calculated from the equation below [18].

$$D = 0.94\lambda/\beta \cos \theta \quad (7)$$

Where  $\lambda$  is the wavelength,  $\beta$  is the full width at half maximum intensity (FWHM) in radians, and  $\theta$  is the diffraction angle.

### 3. EXPERIMENTAL PART

PVC is a powder supplied by Sabic from K.S.A, Its chemical formula is  $(C_2H_3Cl)_n$ , and its molecular weight is  $6000 \text{ g mol}^{-1}$ . PMMA is a powder supplied by Didactic Barcelona Espana, Its chemical formula  $(C_5O_2H_8)_n$ , and its molecular weight is  $200,000 \text{ g mol}^{-1}$ . ZnONPs (particle size less than 80 nm) were from China. In this study, pure blend (PVC 0.3g+PMMA 0.2g) and blend /ZnO NP films were made using the casting technique. As a solvent, tetrahydrofuran (THF) with a purity of 99.8% was obtained from (LAB-SCAN, Poland). Pure blend film was made by dissolving 0.5g of polymer in 15 mL of THF. The solution was mixed thoroughly by using a magnetic stirrer to obtain a homogeneous mixture. This mixture was poured into a clean glass Petri dish (diameter of 6 cm) and left to dry for 24 h at a temperature room, to obtain the film. ZnO NPs were added in varying amounts (0.001, 0.002, 0.003, 0.004, and 0.005g) to produce (PVC-PMMA) blend/ZnO nanocomposite films. The thickness of the as-prepared films was (145-148  $\mu\text{m}$ ) and measurements were made by using an electronic digital micrometer (Tesda, Japan). The measurement precision for the range of (0-150 mm) was 0.001mm. The amount of light that reaches the earth's surface varies depending on the season, time of day, location, and other factors. The location of this work was set in Baghdad/Rusafa3. The temperatures for 7 days in a row are shown in Table 1. The illuminance levels were measured with an Auto Digital Luxmeter (China). The temperatures recorded for seven consecutive days are shown in Table 1. The illuminance levels can be measured by Auto Digital Luxmeter (China) from (1/9/2021) to (7/9/2021). The transmitted intensity of sunlight through the films is denoted by ( $I_{\text{sun}}$ ) and the illuminance of sunlight is denoted by ( $I_o$ ). The transmitted intensity of solar radiation was measured from 6 a.m. to 6 p.m. A UV spectrophotometer (T80 Series UV/VIS spectrometer) was used to evaluate all samples' optical properties by measuring UV and vis light with wavelengths between 200 and 900 nm. All films were analyzed by (FTIR) spectroscopy (Bruker-Tensor 27 with ATR unit). The transmission mode

was in the wavenumber range of (4000-400) $\text{cm}^{-1}$ . Through XRD (X'Pert PRO, PANalytical, the Netherlands), the structure of blend polymer and blend/ZnO nanocomposite films were investigated. High-resolution SEM was used to evaluate all film's surface makeup and fractured surface (ZEISS SIGMA VP Field Emission SEM).

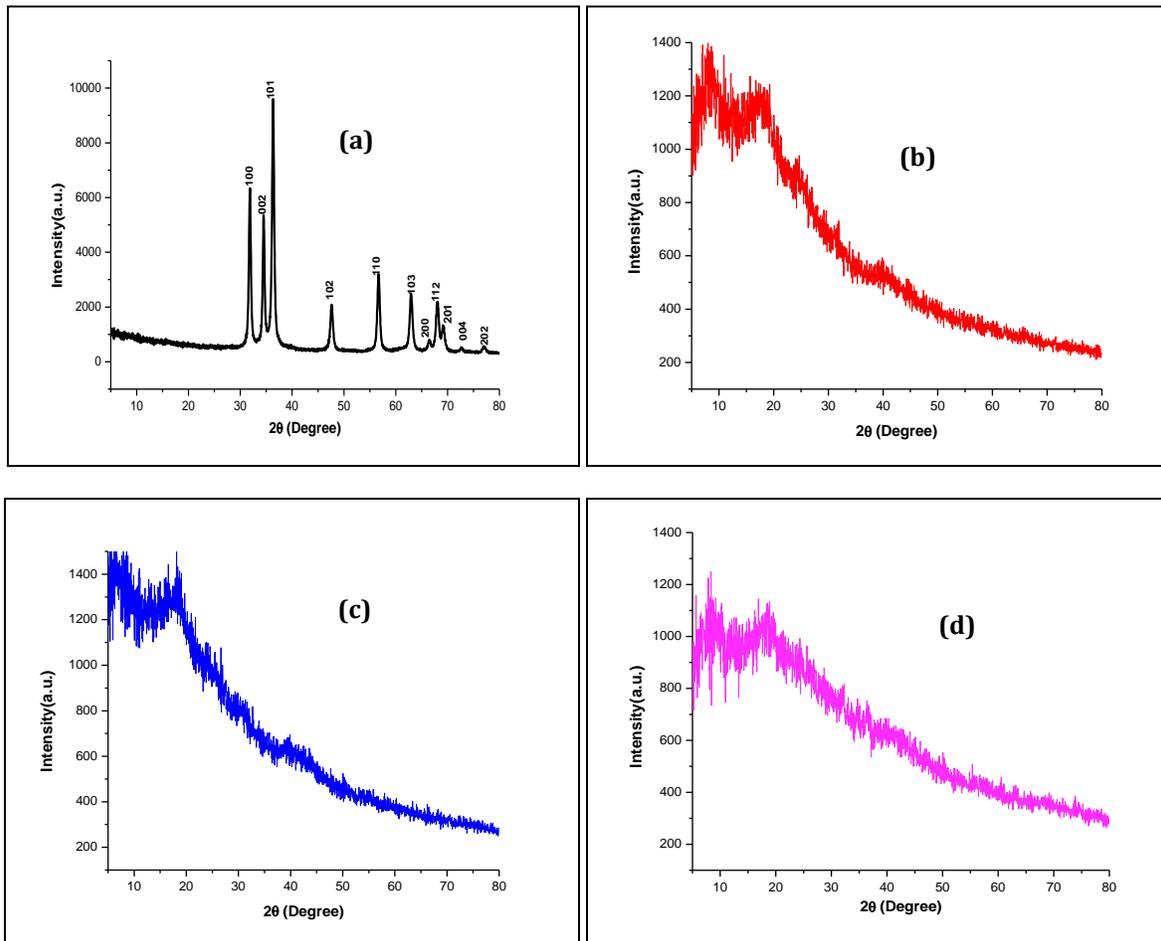
**Table 1** The temperatures for seven consecutive days

Time	Saturday 1 <sup>st</sup> day	Sunday 2 <sup>nd</sup> day	Monday 3 <sup>rd</sup> day	Tuesday 4 <sup>th</sup> day	Wednesday 5 <sup>th</sup> day	Thursday 6 <sup>th</sup> day	Friday 7 <sup>th</sup> day
	Temperature ( $^{\circ}\text{C}$ )						
6AM	27	26	27	26	25	25	24
7AM	29	28	28	28	27	26	27
8AM	30	29	30	31	30	29	29
9AM	32	31	32	33	32	31	32
10AM	34	33	34	35	36	34	34
11AM	36	36	36	36	37	36	36
12AM	37	38	38	38	38	38	38
1PM	39	39	39	39	39	38	39
2PM	39	39	39	39	39	39	39
3PM	39	39	39	39	39	39	39
4PM	39	38	38	39	39	39	38
5PM	38	37	38	38	38	37	37
6PM	37	36	37	36	36	36	36

## 4. RESULTS AND DISCUSSION

### 4.1 XRD Analysis

The XRD analysis of ZnONPs, pure PVC/PMMA blend polymer, and blend/ZnO nanocomposite films with 0.001 and 0.003g of ZnONPs are shown in Figure 1, used to estimate the crystalline structure and crystalline size of these films. The diffraction pattern of ZnO NPs Figure 1 (a) showed many peaks that corresponded to reflection planes. The peaks at  $31.8^{\circ}$ ,  $34.48^{\circ}$ ,  $36.32^{\circ}$ ,  $47.6^{\circ}$ ,  $56.65^{\circ}$ ,  $62.9^{\circ}$ ,  $66.4^{\circ}$ ,  $67.9^{\circ}$ ,  $69.1^{\circ}$ ,  $72.5^{\circ}$  and  $77.0^{\circ}$  were attributed to the (100),(002),(101),(102),(110) (103),(200),(112),(201),(004)and(202) planes, respectively. According to a previous study [19], ZnONPs exhibited a hexagonal crystalline structure because they agree with the International Centre of Diffraction Data reference code (01-089-0510) at both angular position and intensity. The average crystallite size was 16.54 nm, which was calculated through Equation (9), as indicated in Table 2. Figure 1(b)indicated that the pure blend was completely amorphous, in agreement with previous research [20]. The changes in the XRD spectra show that the amount of nanoparticle material caused a change in the microstructure of the polymer, and ZnONPs in the films were also atomically dispersed leading to the incorporation of the ZnONPs peaks within the polymer matrix, as shown in the Figure 1(c, d). At the amount of mixture / (0.003 g) ZnO, the change in XRD spectrum is obvious, as the width and shape of the peak changes when compared to pure mixture and mixture/(0.001 g) ZnO, and this agrees with the previous finding[11].



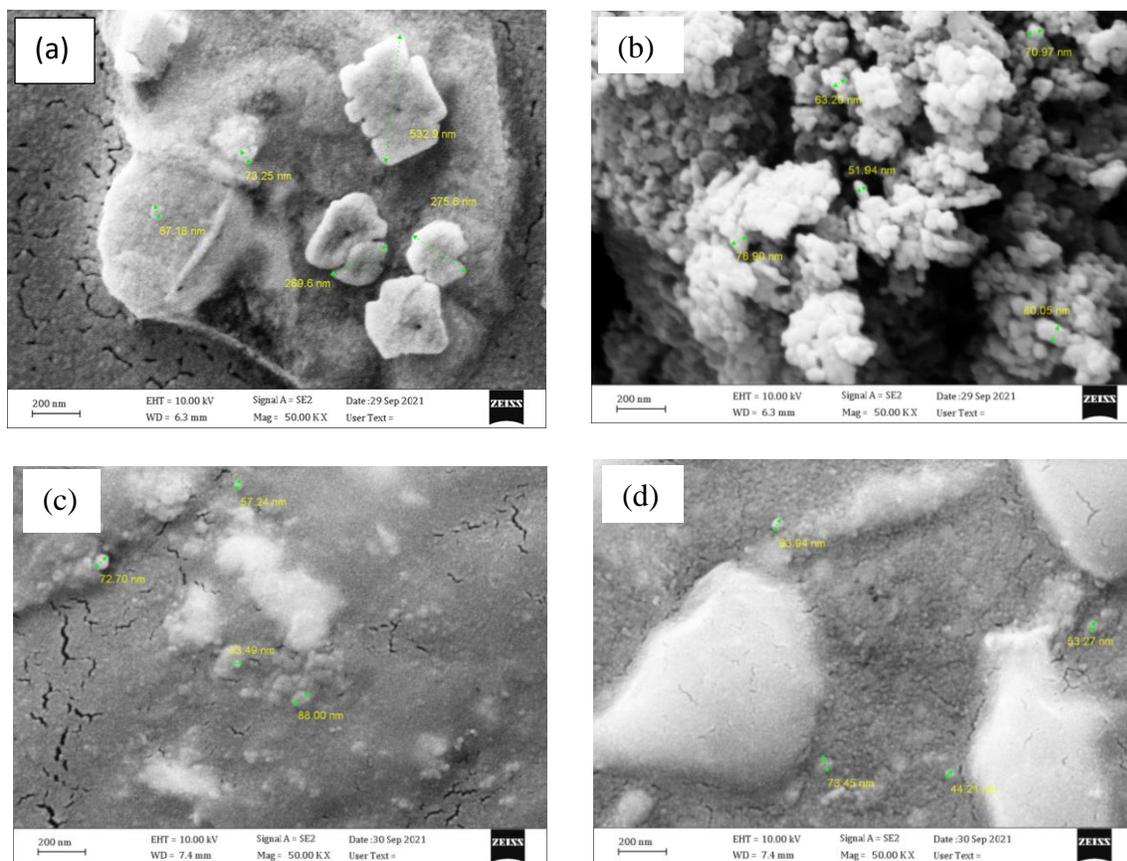
**Figure1.** X-ray diffraction spectra of the (a) ZnO NPs, (b) pure blend polymer, (c) blend/0.001g ZnO, (d) Blend/0.003g ZnO

**Table2** Analysis of XRD and the assignments of various reflections of ZnONPs

2θ° (deg)	FWHM (deg)	Intensity (counts)	d(A°)	(hkl)	D(nm)
31.83	0.456	62.65	2.80911	(100)	18.12
34.48	0.40	52.52	2.59870	(002)	20.79
36.31	0.468	100.00	2.47274	(101)	17.84
47.59	0.57	19.14	1.90930	(102)	15.23
56.64	0.51	32.56	1.62385	(110)	17.70
62.93	0.64	24.44	1.47537	(103)	14.55
66.43	0.56	30.92	1.40614	(200)	16.95
67.92	0.59	20.77	1.3770	(112)	16.23
69.15	0.70	10.34	1.3581	(201)	13.69
72.74	0.60	10.60	1.3004	(004)	16.40
76.96	0.70	20.48	1.237	(202)	14.50

## 4.2 SEM Analysis

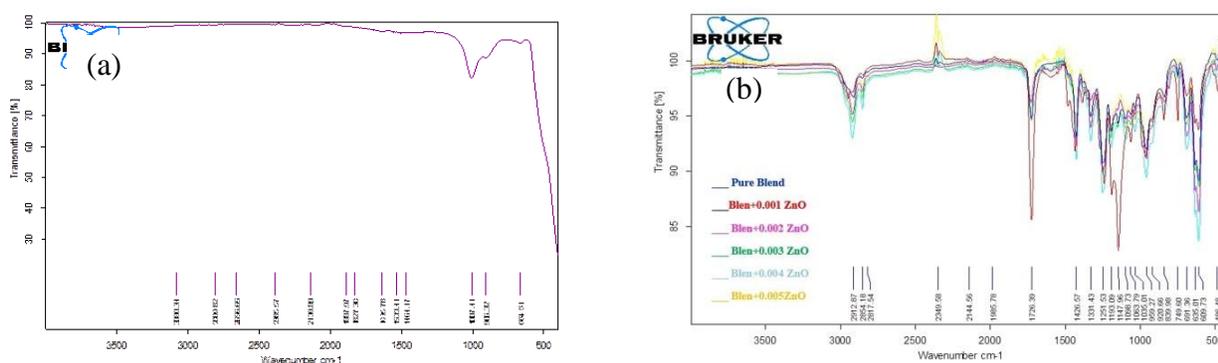
Figures 2 (a, b, and c) show typical SEM images of PVC/PMMA blend film, blend/0.001g ZnO film, and blend/0.003g ZnO film, respectively. Figure 2 (a) demonstrates how the smooth surface of the pure blend polymer was amorphous. As the THF solvent evaporates throughout the preparation process, pores are also spread at the surface, allowing the charge carrier to move readily and fast without the need for a blocking step. This behavior is matched with previous studies[21]. The distribution of ZnONPs within the PVC/PMMA mixture is shown in Figures 2 (b,c). On the blend's surface, there were a few agglomerations and small white spots scattered about. The agglomerations grew as the ZnONPs content increased. The smooth morphology is strictly associated with the interaction or coordination between the two matrixes of PVC and PMMA with nanoparticles. This behavior was remarkably similar to that of the literature[22,23].



**Figure 2.** SEM images for (a) pure blend Polymer, (b) pure ZnONPs, (c) blend/0.001g ZnO, (d) blend/0.003g ZnO

### 4.3 FTIR Spectra

Figure 3(a) shows the FTIR results of ZnONPs, which are  $664.51\text{cm}^{-1}$  for Zn-O and  $906.32\text{cm}^{-1}$  for Zn-OH. The band at  $1007.41\text{cm}^{-1}$  correlates with Zn-OH and  $\text{CO}_2$  was represented by the peak at  $213.89\text{cm}^{-1}$ . This result was in agreement with the literature [24]. Figure 3(b) illustrates the FTIR spectrum of the PVC/ PMMA blend film. The peaks at  $2853.49\text{-}2923.21\text{cm}^{-1}$  are related to the stretching band of aliphatic C-H. At  $1724.55\text{ cm}^{-1}$ , the C=O stretching mode occurred. The peaks at  $840.87\text{-}1064.14\text{ cm}^{-1}$  are strong for all samples of nanocomposites because of the C-O group's stretching mode. At  $1331.42\text{-}1433.97\text{ cm}^{-1}$ , the  $\text{CH}_2$  bending band is observed. The peak at  $2154.62\text{-}2176.53\text{ cm}^{-1}$  was related to C=C wagging. (Table 2). No reactions were found between the blend polymer and ZnO NPs from the FTIR spectra consistent with the literature [25].



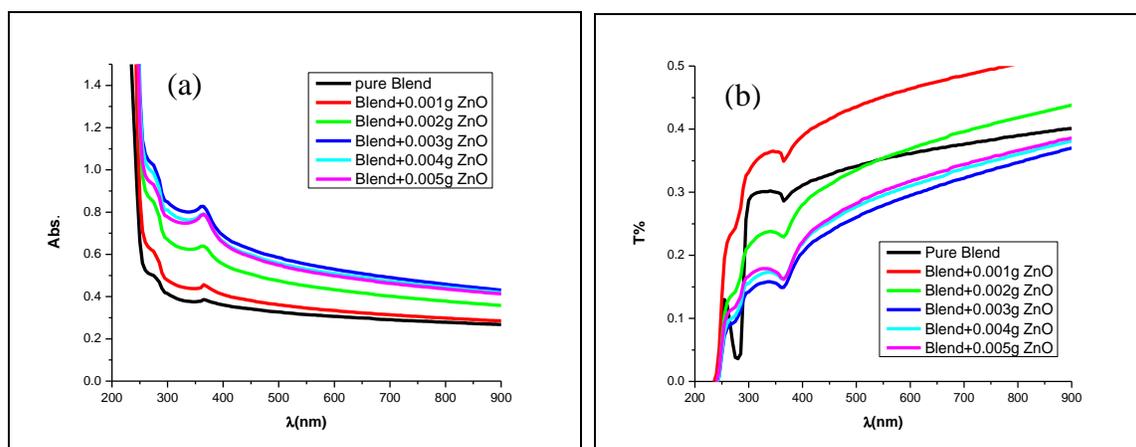
**Figure3.** FTIR Spectra for (a) pure ZnO, (b) blend/ZnO with different amounts of ZnONPs

**Table 3** FTIR spectra data of blend and blend/ZnO nanocomposites

Types of bands	The peaks locations ( $\text{cm}^{-1}$ )	Types of bands	The peaks locations ( $\text{cm}^{-1}$ )
C-H Bending	609.85 749.61	C=O Stretch vibration	1724.45 1979.57
C-O stretching mode	840.87 1064.14	C-H Stretch vibration	2853.49 2923.21
C-H <sub>2</sub> Bending	1331.42 1433.97	C=C Stretch	2154.62 2176.53

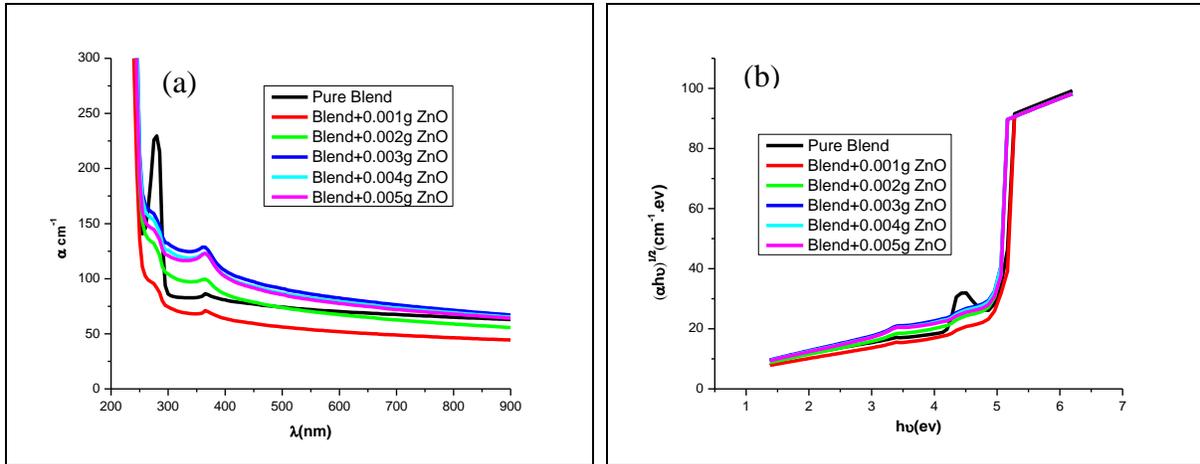
#### 4.4 Optical Properties

The absorption spectra of pure blend and blend/ZnO nanocomposites are illustrated in Figure 4(a). The maximum absorption wavelength of ZnONPs is at 370 nm[26], which was attributed to the intrinsic band-gap absorption of ZnO. The wide peak with the maximum wavelength at 270nm and absorbance at 0.45 is referred to as the blend polymer. This absorption was due to interband transition. These results were consistent with the findings in the literature [27]. The presence of ZnONPs led to an increase in absorption and a decrease in the transmission as the ZnONPs amounts increased, and the reason for the increase in absorbance at 0.003 g instead of 0.005 g was due to the nature and behavior of the polymer. Figure 4(b) shows the transmission spectrum of the pure blend polymer and the blend/ZnO nanocomposites. The permeability of the pure polymer blend was higher than that of the blend/ZnO nanocomposites. Pure polymers and nanocomposites had lower transmittance in the UV range than in the visible range. The attached ZnONPs exhibited an obvious effect. They have a low transmission rate of UV rays, which increases the absorption and decreases the transmittance thereby reducing degradation. The obtained material can be used in several applications, including special containers for preserving medicines and in the structures of some buildings; these results were comparable with those of other studies [21].



**Figure 4.** (a) Absorbance change with wavelength for blend/ZnO nanocomposite.(b)Transmittance variation with wavelength to blend/ZnO nanocomposite

Figure 5 (a) shows the wavelength of the absorption coefficient for all samples containing varying amounts of ZnONPs that could be calculated from Equation (3). The measurements showed that the absorption coefficient for blend/ZnO nanocomposites was lower than  $10^4\text{cm}^{-1}$ , suggesting that it possessed an indirect energy band. This increase could be attributed to the difference in carrier concentration or the presence of higher ground state vibration levels to higher sublevels of the first excited single state [28]. The best amount of blend polymer mixture added was 0.003g of ZnO and this depends on the nature and behavior of the polymer, as shown in Figure 5 (a). Figure 5 (b) shows how the amount of ZnO in the nanocomposites affected the energy band difference. The previous figure indicates that it had an indirect energy band. The energy band gap narrowed with the increase in the number of NPs. In Table 4, the energy band gap decreased from 4.48eV to 3.91eV. Increases in the prohibited energy band gap's local levels resulted in an increase in the incidence of overlap between these levels, leading to a drop in the energy band gap [29].

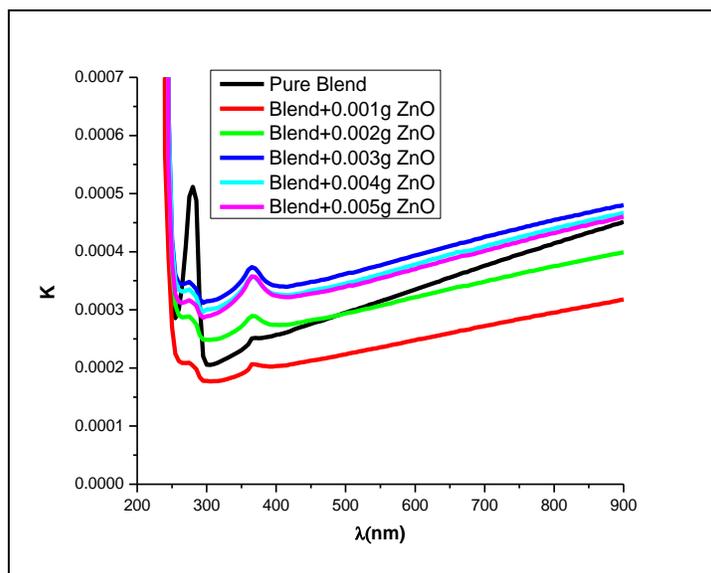


**Figure 5.** (a) Absorption coefficient( $\alpha$ ) variation with wavelength to blend/ZnO nanocomposites (b)  $(\alpha h\nu)^{1/2}$  Energy band gap value to blend/ZnO nanocomposites

**Table 4** Energy band gap value to blend/ZnO nanocomposites

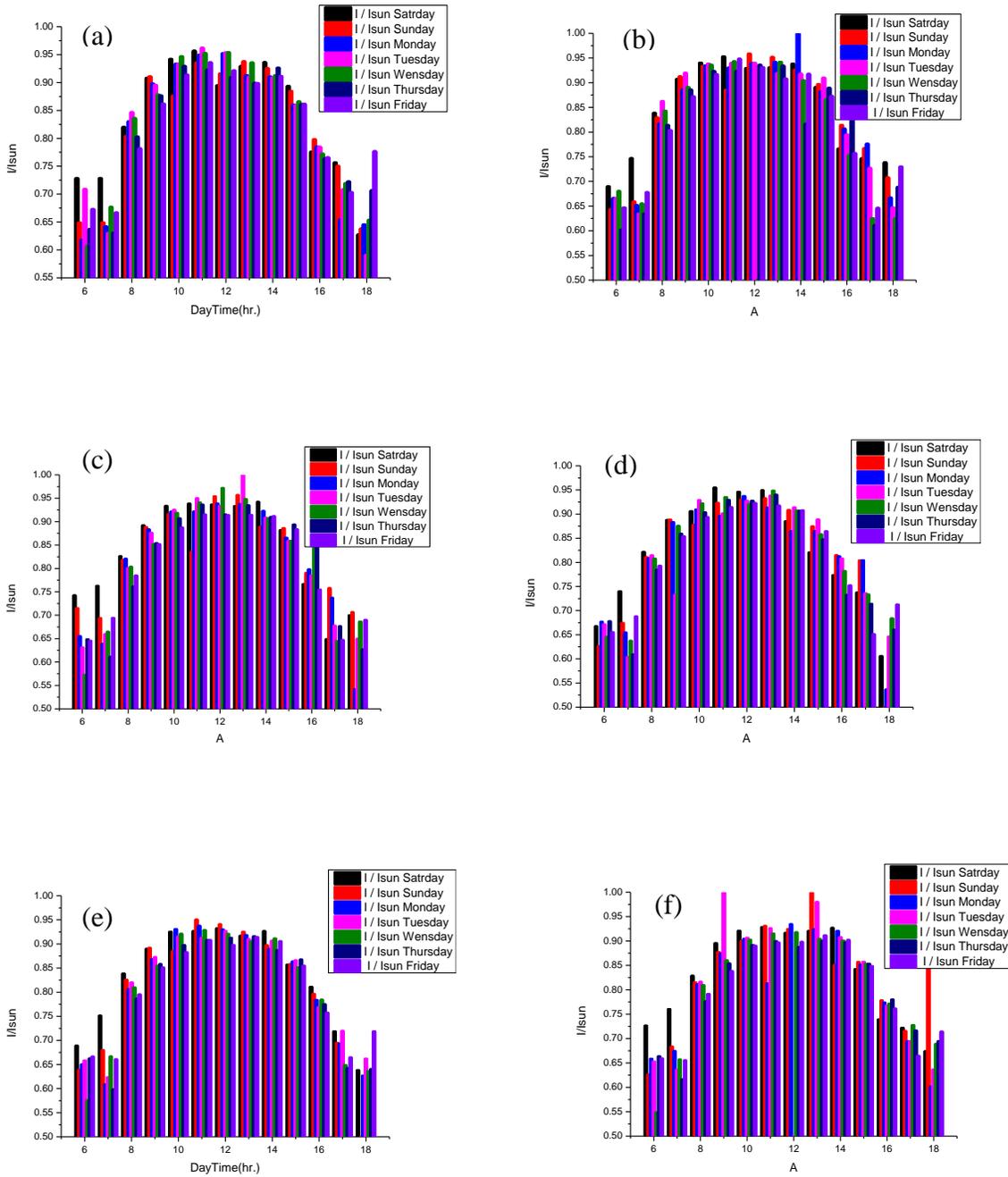
Samples	$E_g$ (eV)
Pure Blend	4.48
blend +0.001 g ZnO	4.38
blend +0.002 g ZnO	4.31
blend +0.003 g ZnO	4.20
blend +0.004 g ZnO	4.025
blend +0.005 g ZnO	3.91

The extinction coefficient of the blend polymer for photon wavelength with varied quantities of ZnONPs was obtained using Equation (5), as shown in Figure 6. The extinction coefficient of polymer blend/ZnO nanocomposites was higher than that of pure polymer blend. The extinction coefficient increased as the ratio of ZnONPs increased, indicating that an increase in the absorption coefficient led to an increase in the number of charge carriers [30].



**Figure 6.** Extinction coefficient variation with wavelength to blend/ZnO nanocomposites.

The amount of solar radiation transmitted by the mixture of pure polymer and nanocomposite/ZnO films is shown in Fig. 7. The levels of solar radiation transmitted to the samples were slightly different. The transmitted solar radiation peaked at 12:00 p.m., after which its intensity began to gradually decrease. Table 1 was calculated and presented for each movie. Almost all films contain the same ratio of radiation intensity depending on the nature and behavior of the polymer material and its transparency toward the incident solar radiation. The reason for the slight difference in radiation intensity is due to the nanomaterials added in a different amount, as shown in Figures 7(a-f). These results were similar to the literature [31].



**Figure 7.** Transmission of sun radiation intensity from (a) pure blend, (b) blend /ZnO(0.001g), (c) blend /ZnO (0.002g),(d) blend ZnO(0.003g),(e) blend /ZnO(0.004g),(f) blend /ZnO(0.005g).

## 5. CONCLUSIONS

Results showed that PVC/PMMA may be successfully doped with ZnONPs. The XRD results revealed the amorphous structure of the admixture film and the hexagonal crystal structure of ZnONPs. The ZnONPs in the film also dispersed atomically resulting in the incorporation of the ZnONPs peaks within the polymer matrix. Using nanoscale SEM, the distribution of ZnONPs within the PVC/PMMA mixture was observed. On the blend's surface, there were a few agglomerations and small white spots scattered about. The PVC/PMMA polymer's surface exhibited an amorphous character and a smooth surface. From the FTIR spectra, it is observed that there is no chemical reaction between the blend polymer and ZnONPs. The findings showed ZnO doped into the PVC/PMMA blend effectively and improved its optical characteristics. The presence of ZnO caused an increase in absorbance and a decrease in transmittance as the amount of ZnO increased. The extinction coefficient was dependent on the ZnO amount, increasing after doping, and as the ZnO amounts increased the optical band gap dropped from 4.48eV to 3.91eV. The solar radiation intensity was measured for seven consecutive days, from 6 AM to 6 PM (13 h), at a rate of 1 h for pure blend and blend/ZnO nanocomposites films. The ratio of the power of transmitted radiation to the intensity of solar radiation was almost constant for all films at all hours and on all days.

## ACKNOWLEDGEMENT

The authors would like to thank the Department of Physics/ College of Science/ Mustansiriyah University ([www.uomustansiriyah.edu.iq](http://www.uomustansiriyah.edu.iq)) Baghdad-Iraq for its support in the present work.

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