



Physical Properties and Transmitted Sunlight of Polyvinyl Chloride/ZnO Nanocomposite Films

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ABSTRACT

The optical properties of polyvinyl chloride (PVC) and PVC/Zinc Oxide (ZnO) films were considered with different amounts of ZnONPs (0.001, 0.002, 0.003, 0.004 and 0.005) g. Using a Tetrahydrofuran (THF) solution all films be prepared by casting method. XRD results showed the amorphous structure of PVC film and Hexagonal crystalline structure of ZnO NPs, PVC/ZnO nanocomposites appear as pattern of PVC films so the peaks of ZnO don't appear in it. FESEM image of PVC, ZnO and structure of PVC/ZnO nanocomposites seems to have cluster aggregates in different size. FTIR spectra revealed that ZnONPs had no effect on the polymer structure as there are no covalent bonds between PVC and ZnO NPs. Increasing the amounts of ZnONPs was seen to improve the optical properties (Absorbance, absorption coefficient and extinction coefficient) for PVC polymer. PVC polymer transmittance and energy gap decreased from 5.25 eV to 4.98 eV with increasing the amounts of ZnO NPs in nanocomposites. The solar radiation intensity in Baghdad was measured at a rate of 1 hour for the pure PVC films and PVC/ZnONPs for seven consecutive days in a rate from 6 A.M. to 6 P.M. (13 h). As can be observed, all films have the same ratio of transmitted radiation strength to sunlight intensity for all hours and days.

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الخواص الفيزيائية ونفاذية ضوء الشمس لأغشية المترابك النانوي البولي فينيل كلورايد/أكسيد الزنك

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الخلاصة

الكلمات المفتاحية:

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تمت دراسة الخواص البصرية لأغشية البولي فينيل كلوريد (PVC) وأغشية PVC / أكسيد الزنك (ZnO) بكميات مختلفة من أكسيد الزنك النانوي (0.001، 0.002، 0.003 ، 0.004، 0.005) غم. باستخدام محلول تتراهدرو فوران (THF) يتم تحضير جميع الأغشية بطريقة الصب. أظهرت نتائج حيود الأشعة السينية البنية غير المتبلورة لغشاء PVC والتركييب البلوري السداسي لمركبات ZnONPs و PVC / ZnO النانوية تظهر كنمط لأغشية PVC بحيث لا تظهر قمم ZnO فيه. يبدو أن صورة المجهر الإلكتروني الماسح لـ PVC و ZnO وتركييب المتراكبات النانوية PVC / ZnO تحتوي على مجاميع عنقودية بأحجام مختلفة. كشفت أطياف FTIR أن ZnONP ليس له أي تأثير على بنية البوليمر حيث لا توجد روابط تساهمية بين PVC و ZnONPs. شوهدت كميات متزايدة من ZnONPs لتحسين الخواص البصرية (الامتصاصية، معامل الامتصاص ومعامل الخمود) لبوليمر PVC. انخفضت نفاذية بوليمر PVC وفجوة الطاقة من ٥.٢٥ إلكترون فولت إلى ٤.٩٨ إلكترون فولت مع زيادة كميات ZnO NPs في المتراكبات النانوية. تم قياس كثافة الإشعاع الشمسي في بغداد بمعدل ساعة واحدة لأغشية PVC النقية و PVC / ZnONPs لمدة سبعة أيام متتالية من الساعة ٦ صباحًا حتى الساعة ٦ مساءً (١٣ ساعة). كما يتضح، فإن جميع الأفلام لها نفس نسبة قوة الإشعاع الساقط إلى شدة ضوء الشمس لجميع الساعات والأيام.

1. INTRODUCTION

Polymer composites have recently piqued the curiosity of scientists due to their wide range of outstanding qualities, such as their ease of fabrication and flexibility under adverse weather conditions. In many industrial applications, polymers are widely employed from home exterior rain gutter to plasma tubes in the medical field. Polyvinylchloride (PVC) has a vast range of applications. The PVC is a form of polymer that is commonly utilized, and a good candidate polymer for use in a broad range of electrochemical devices, including high energy density batteries, fuel cells, and sensors[1]. The chemical structure of the PVC can be seen in Figure(1) [2]. Nano composites defined as materials made up of Nanosized particles embedded in a matrix of more typical material. This inclusion improves mechanical, optical, electrical and thermal properties.

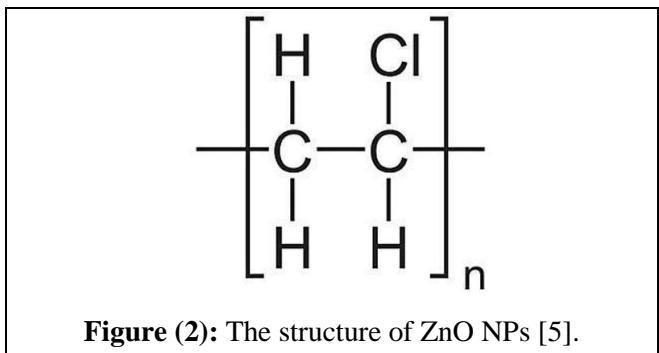
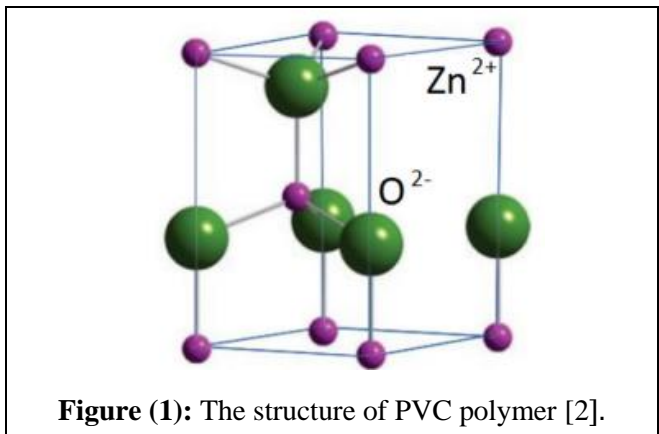
Nanotechnology is a novel technology that has the ability to transform a range of scientific fields. Nanomaterial offer a broad array of

applications based on their size and shape and have major topic in the pure and applied sciences. Nano semiconductors attracted a considerable attention in recent times due to their new characteristics that have applications in optical devices[3]. Zinc Oxide Nanoparticle (ZnONps) has interesting properties for many applications such as blue Light emitting devices (LEDs), photo catalysis, and Solar Cells [4]. The structure of ZnO as in figure (2)[5].

Ultraviolet light (UV) is a type of electromagnetic radiation and it is present in the sunlight, and it constitutes 10% of total electromagnetic radiation output of the sun. It is classified into three groups based on wavelength: UVA (320-400nm), UVB (280-320nm), and UVC (100-280nm). The more intense the radiation is, the more dangerous it might be. Shorter wavelength radiation, on the other hand, has a harder time to penetrating human skin. The sun's UVC rays are the most dangerous, yet they aren't strong enough to enter the earth's atmosphere[6]. Determining the intensity of UV radiation in relation to

stratospheric ozone, clouds, altitude, and sun height (time of day and year), as well as reflection, is one of the most difficult parts of evaluating the impact of UV radiation on polymers. The complexity of the effects might be rather significant. The UV of any kind can cause a photochemical reaction in the polymer structure, which can be advantageous or detrimental to the substance [7].

Numerous studies have been conducted to increase the physical properties of PVC polymers by introducing nanoparticles like ZnONPS In order to enhance their structure. These works are referenced in numerous literatures.[8,9]. For example, Ahmed *et al.* (2010)[10]. studied the optical properties of PVC with amino acetate Benzothiazole complex, their optical results have been analysed in accordance with the theory of phonon that assist direct transition and noticed the relation between energy and doping ratio of inorganic complex is direct. M. Abdul Nabi *et al.* (2014) [11], demonstrates that the doping of ZnO has an impact on the optical characteristics of PVC, increasing absorption and decreasing transmission as the ZnO Increasing amounts. A. Kumar *et al.* (2018)[12], concluded that the dielectric constant increases with the increase of ZnO NPs concentration and obtained surface morphology like sponge at different magnification. Mohammed *et al.* (2020) [13], had showed how to protect PVC films against Photoirradiation with UV light, there are a number of tin complexes valsartan were added. Mohammed et al (2021) [14], evaluated the efficiency of tin compound /PVC films before and after UV irradiation and obtained higher activity for these complex that PVC film alone. The aim of this work is to improve the physical properties of PVC polymer by filling matrix with ZnONPs and measure the transmission of these films under sunlight.



2. THEORETICAL PART

If the light permits to transfer from one medium to another, some energy can be transported. Part of energy will be absorbed and some will be transmitted as the two media interact. The diminishing percentage of incident light energy in length unit to wave propagation within the medium can be equal to the absorption coefficient (α in unit cm^{-1}), which varies with the incident photon energy. When the incident photon energy is lower than the energy wavelength, the photon is transmitted, and the transmittance (T) of the thin film is given by the equation [2]

$$T = 1 - A - R \tag{1}$$

Wherever: R and A is the reflectance and the absorbance of the film. The absorption coefficient is calculated using Beer- Lambert law in the fundamental absorption edge [15].

$$I = I_0 e^{-\alpha d} \tag{2}$$

Where I_0 and I represent the intensity of the incident and transmitted beams, respectively. The thickness of film is d.

If $\left(\frac{I}{I_0}\right) =$ Then $\left(\frac{1}{T}\right) = e^{\alpha d}$ (3)

So that

$\ln\left(\frac{1}{T}\right) = \alpha d, 2.303 * \log_{10}\left(\frac{1}{T}\right) = \alpha d$ (4)

$A = \log_{10}\left(\frac{1}{T}\right)$
(5)

therefore the absorption coefficient can be written as [16].

$\alpha = \frac{(2.303 * A)}{d}$ (6)

In the optical properties, direct and indirect electrical transformations can be illustrated based on the lower position in the conduction band and the upper position point in the valance band.

An important relationship occurs between the forbidden (optical energy gap E_g) and the photon energy gap ($h\nu$), existing in the following equation[17].

$\alpha h\nu = B(h\nu - E_g)^r$ (7)

Where B: Constant whose value is determined by the conduction and valance band properties, r: constant whose value is determined by the transformation existence, where $r = (1/2, 3/2)$ for allowed and forbidden direct transition, Respectively and $r=(2,3)$ for allowed and forbidden indirect transitions, Respectively.

The extinction coefficient (k) may be calculated using the equation below[18].

$K = \frac{\lambda\alpha}{4\pi}$ (8)

Using the Debye-Scherrer equation, the average Crystalline size of ZnO nanoparticles was calculated from equation below.[19]

$D = 0.94\lambda/\beta \cos\theta$ (9)

Where, λ is the wavelength, β is the full width at half the maximum intensity (FWHM) in radians, and θ is the diffraction Bragg angle.

3. EXPERIMENTAL PART

Poly Vinyl Chloride (PVC) is a powder supplied by Sabic, its chemical formula $(C_2H_3Cl)_n$ with molecular weight of 6000 g mole^{-1} . Zinc oxide (ZnO) NPs (particle size 80 nm) supplied from China. Casting technique was used in this work to prepare pure PVC and PVC /ZnO NPs films. Tetrahydrofuran (THF) with a purity of 99.8% from (LAB-SCAN, Poland) was used as a solvent. To make pure PVC film, a 0.5g of polymer was dissolved in 15ml of THF. The solution was then thoroughly stirred using a magnetic stirrer to produce a homogenous mixture. Pour this mixture on clean glass petri dish (diameter 6 cm), and left to dry for 24hr. to obtain film. The amounts of ZnO NPs added to obtain ZnO NPs/PVC films were (0.001, 0.002, 0.003, 0.004 and 0.005) g. The thickness of the prepared films was(135-138) μm and the measurements were done using electronic digital micrometer (Tesda) (Japan), the accuracy of the measurement range (0-150) mm is (0.001)mm. The illuminance of sunlight on surface of earth varies by season, time day, location and other parameters. So in this work, the location was specified in the Baghdad City. The temperatures recorded for seven consecutive days as 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 denoted by (symbol I_{sun}) and the illuminance of Sunlight denoted by (symbol I_0). The transmitted intensity of solar radiation was measured from 6 o'clock (A.M.) to 6 o'clock (P.M.). The optical properties of all samples were tested using a UV spectrophotometer (T80 Series UV/VIS spectrometer) which measures ultraviolet and visible light within the range (200-1100)nm. Fourier transformation Infrared (FTIR) spectroscopy was conducted for all films using (Bruker-Tensor 27 with ATR unit). The transmission mode used in the wavenumber range (4000-400 cm^{-1}). X-ray diffractometer

(XRD; X'Pert PRO, PANalytical, the Netherlands) was used to study the structure of PVC polymer, ZnO NPs and PVC/ZnO nanocomposit films. High-resolution scanning electron microscopy (ZEISS SIGMA VP Field Emission Scanning Electron) characterized the composition of the surface and the cracked surface of all films.

Table (1):The temperatures for seven consecutive days.

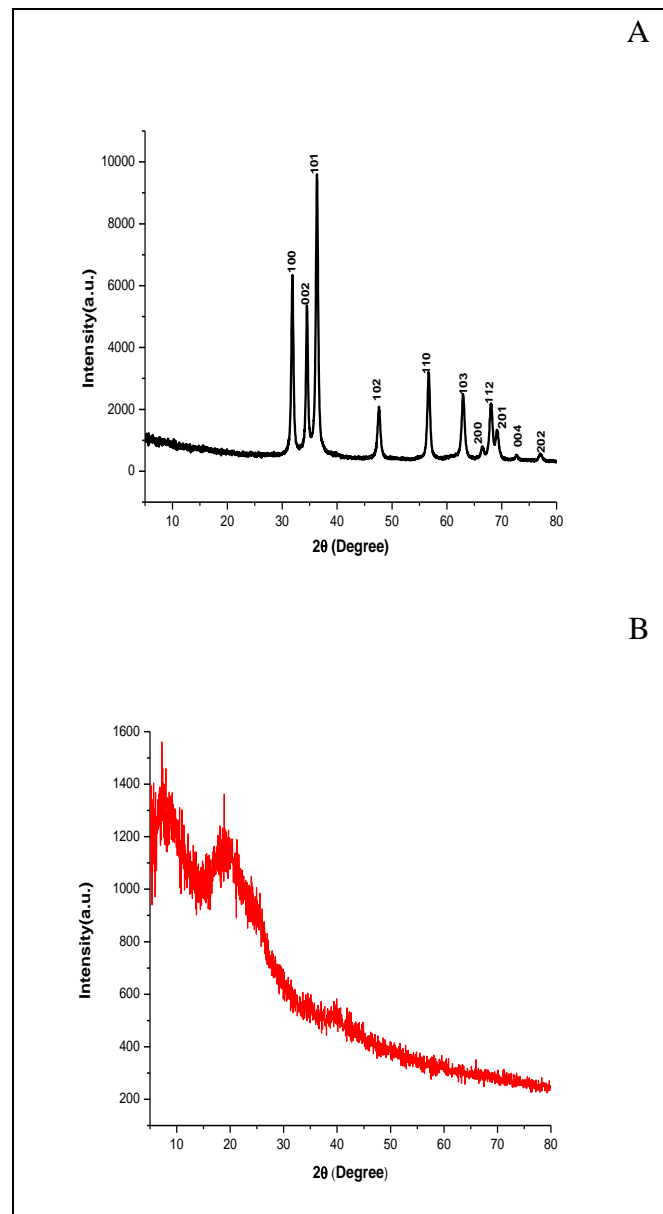
Time (o'clock)	Saturday 1/9/2021	Sunday 2/9/2021	Monday 3/9/2021	Tuesday 4/9/2021	Wednesday 5/9/2021	Thursday 6/9/2021	Friday 7/9/2021
	Temperature (oC)						
6	27	27	26	26	26	25	25
7	29	29	28	29	28	27	28
8	30	30	30	31	30	29	30
9	32	31	32	33	32	31	32
10	34	33	34	35	36	34	34
11	36	36	37	36	37	36	36
12	38	38	39	38	38	38	38
13	39	39	39	39	39	38	39
14	39	39	39	39	39	39	39
15	39	39	39	39	39	39	39
16	39	38	38	39	39	39	38
17	38	38	38	38	38	38	38
18	37	37	37	37	37	37	37

4. RESULTS AND DISCUSSIONS

4.1 XRD Analysis

Figure (3-A,B,C,D) shows XRD morphology of ZnONPs, pure PVC polymer, and PVC/ZnO With two amounts of ZnO NPs 0.001g and 0.003g, respectively to estimate the crystalline structure and crystalline size of these films. From Figure (3-A), XRD pattern for ZnONPs has diffractions peaks at angles ($2\theta^\circ$) of (31.8° , 34.48° , 36.32° , 47.6° , 56.65° , 62.9° , 66.4° , 67.9° , 69.1° , 72.5° , 77.0°) which match the reflection from (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202), respectively. This matched with

hexagonal Zinc Oxide structure's crystal planes are shown in Figure (2). These values of all diffraction peaks matched with joint committee on powder Diffraction standards (JCPDS) Card No.(000-0036-1451) [20]. The XRD information presented in Table (2) using Debye-Scherrer equation eq. (9) to calculate crystalline size of ZnONPs and the average crystallite size is 16.788 nm. The XRD pattern for figure (3-B) revealed amorphous structure that agreed with many researches [21]. The observed diffraction peak in the PVC/ZnONPs polymer X-ray diffraction spectra vanished with increased doping. The ZnONPs peaks were fused and/or eliminated, as seen by the XRD spectra within the diffraction halos of the figures (3-C, D).



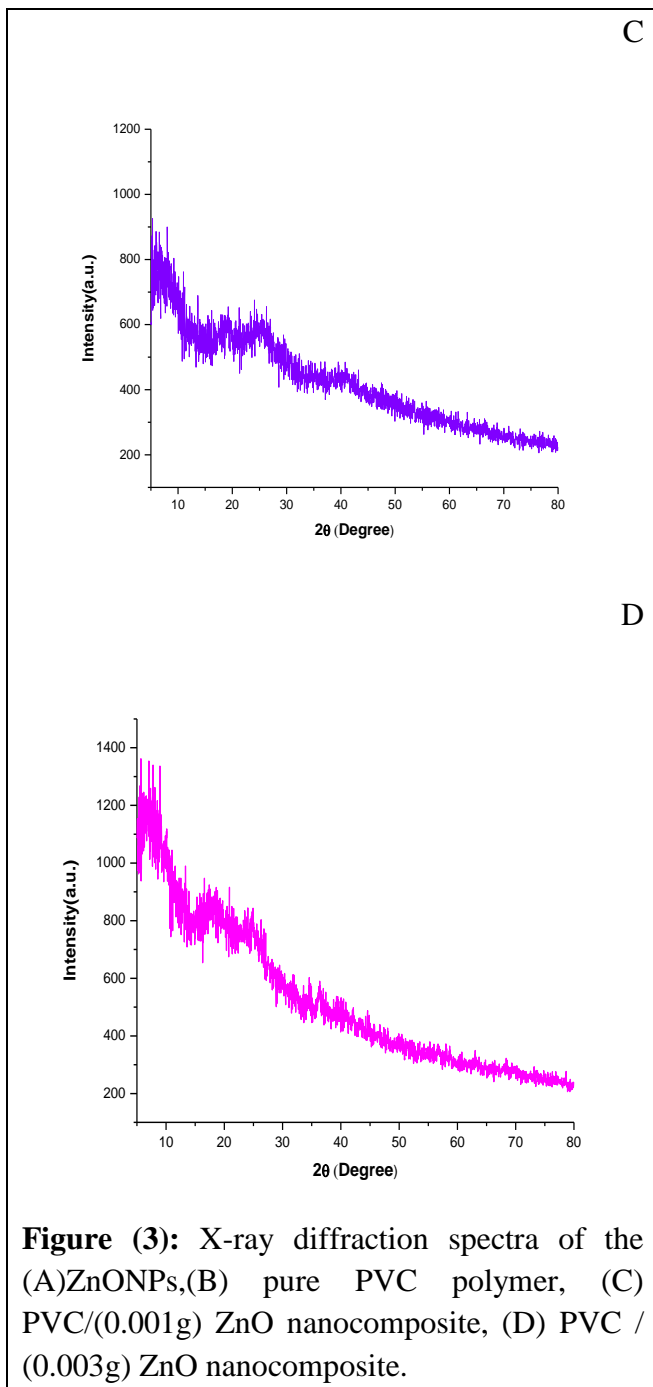


Figure (3): X-ray diffraction spectra of the (A)ZnONPs,(B) pure PVC polymer, (C) PVC/(0.001g) ZnO nanocomposite, (D) PVC / (0.003g) ZnO nanocomposite.

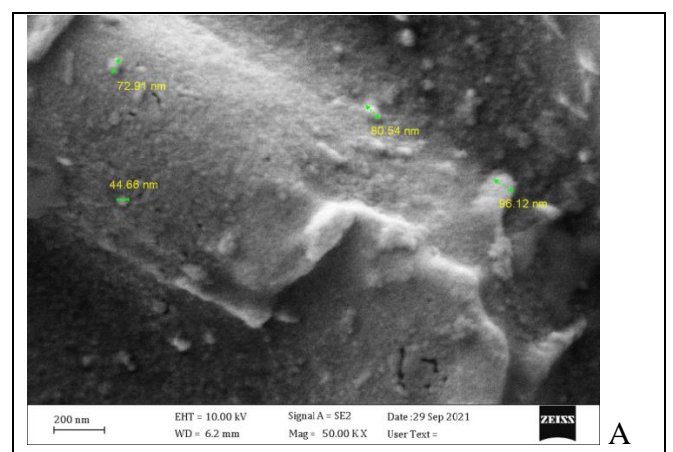
Table (2): Analysis of XRD and the assignments of various reflections of ZnO.

$2\theta^\circ$	FWHM (deg)	Intensity (counts)	$d(\text{\AA})$	hkl)	D(mm)
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	22.68	1.3770	(112)	16.23
69.12	0.70	23.34	1.3581	(201)	13.69

4.2 SEM Analysis

Figure (4-A,B,C,D) shows typical SEM images of (PVC, ZnO, and PVC/ZnO), respectively. Figure (4-A) illustrated morphology of pure PVC film, it has been noticed smooth, flat more homogeneous surface. This was comparable with research[22], and agreed very well. Figure (4-B) depicts the morphology of ZnO NPs, which appears to be an agglomeration of uniform size and a multidimensional structure. This matched with planes formed by its hexagonal structure as appeared by results of XRD pattern, figure (3-A). These results matched with researches[23]. Figures (4-C,D) represent morphology of ZnO (0.001g)/PVC and ZnO (0.003g)/PVC films, respectively. It will be seen that ZnO NPs dispersed in PVC matrix, perhaps presence of uniform growth. This is agreement with research[24]. Increasing the amount of ZnO NPs led to appear cluster aggregates in PVC with different sizes.



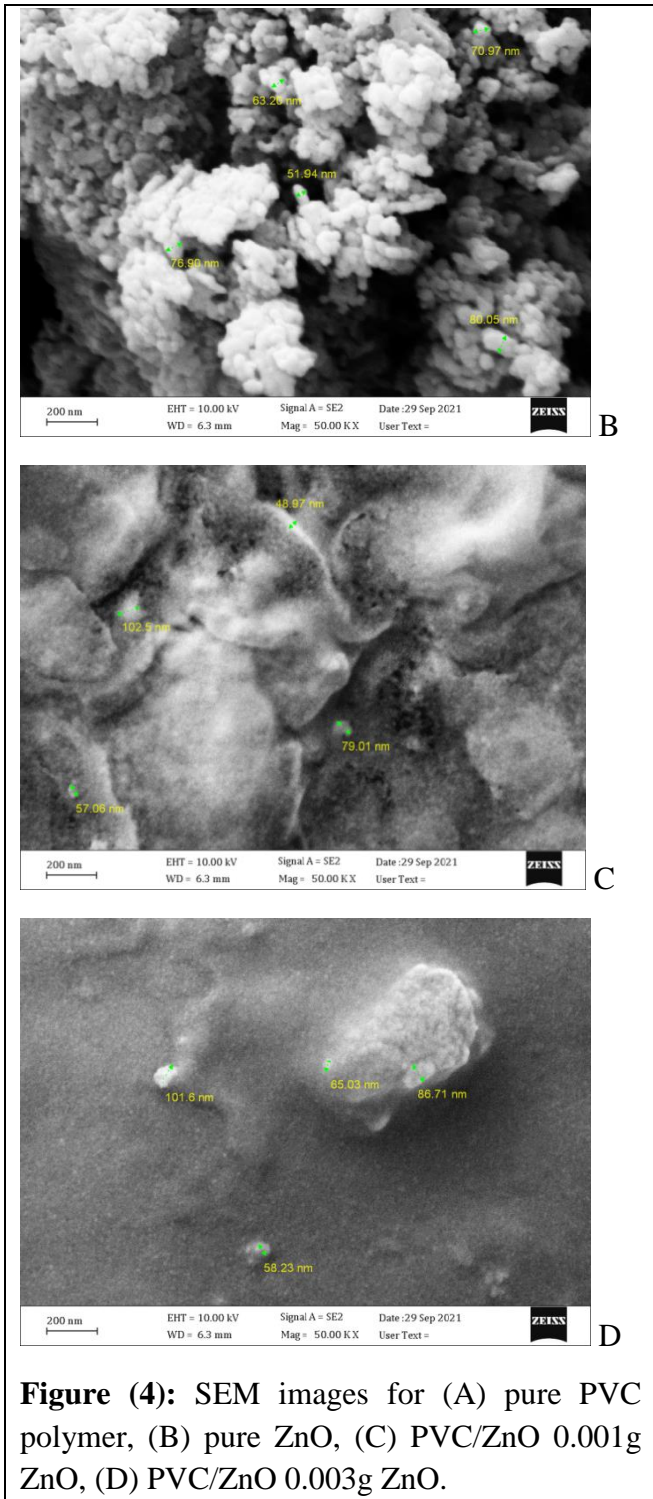


Figure (4): SEM images for (A) pure PVC polymer, (B) pure ZnO, (C) PVC/ZnO 0.001g ZnO, (D) PVC/ZnO 0.003g ZnO.

4.3 FTIR Spectra

Figure (5-A) shows the FTIR result of ZnONPs, which indicated 664.51cm^{-1} for Zn-O and 906.32cm^{-1} for Zn-OH. The band at 1007.41cm^{-1} correlates to Zn-OH as well. The peaks at 2139.89cm^{-1} were CO_2 levels. This is agreed upon by researchers[25,26]. A single bond connects a CH_2 group with a CHCl unit in each vinyl chloride monomer. This single bond, which connected those groups in the vinyl

chloride molecule with a permanent double bond . Figure (5-B) illustrated FTIR spectrum of PVC film. The peaks ($2816.11\text{-}2967.14\text{ cm}^{-1}$) were associated to C-H stretch Aliphatic. At (1721.14 cm^{-1}), the C=O stretch mode happens. Because of the stretching mode of the C-O group, the peaks at ($921.49\text{-}957.22\text{ cm}^{-1}$) are strong for all samples of nanocomposites.. At (1330.88 cm^{-1}), in band the CH_2 bending mode happens. Peak at (609.74 cm^{-1}) was related to C-Cl. Table (3) noticed that there are no chemical reactions between the PVC polymer and ZnONPs from the FTIR spectra.

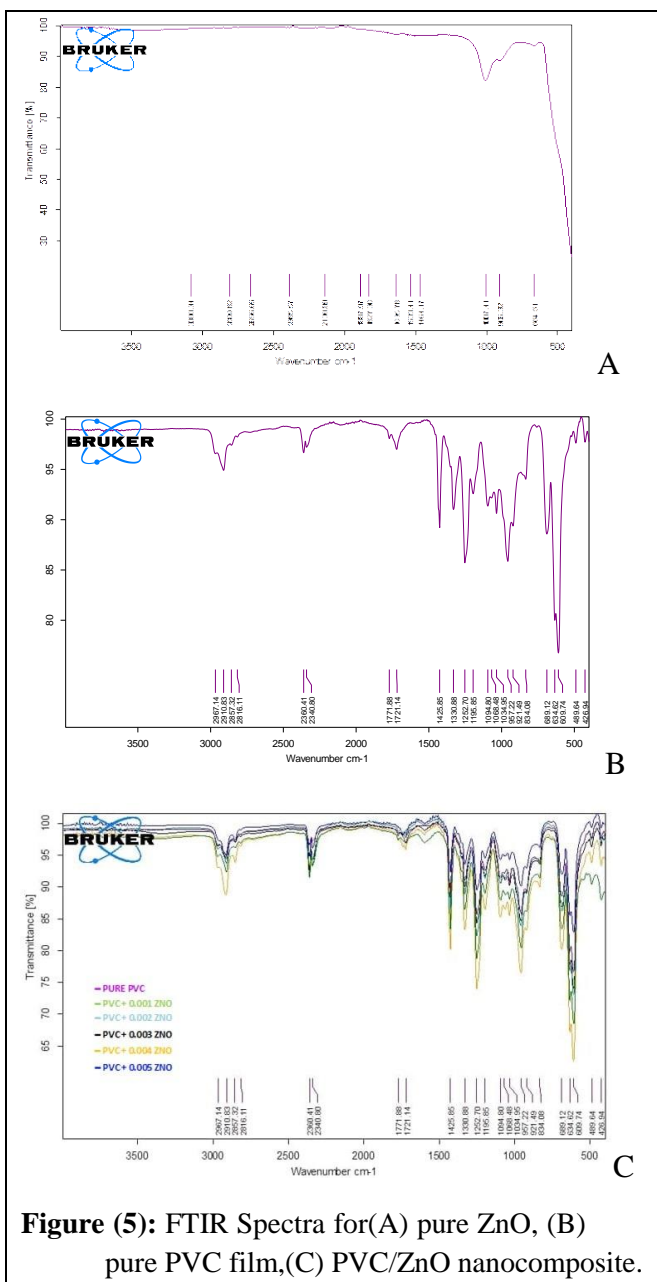


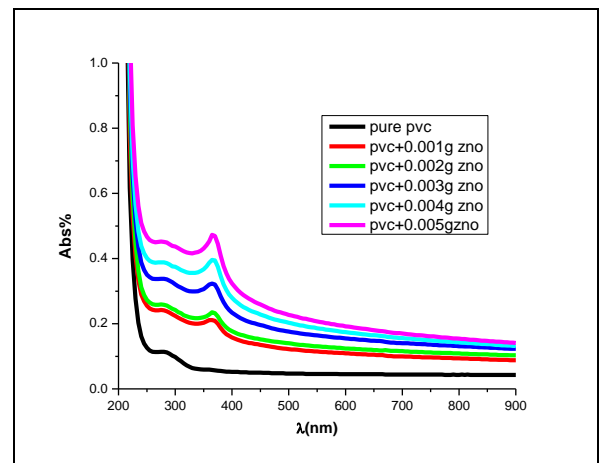
Figure (5): FTIR Spectra for(A) pure ZnO, (B) pure PVC film,(C) PVC/ZnO nanocomposite.

Table (3): FTIR spectra data of PVC and PVC/ZnO nanocomposite.

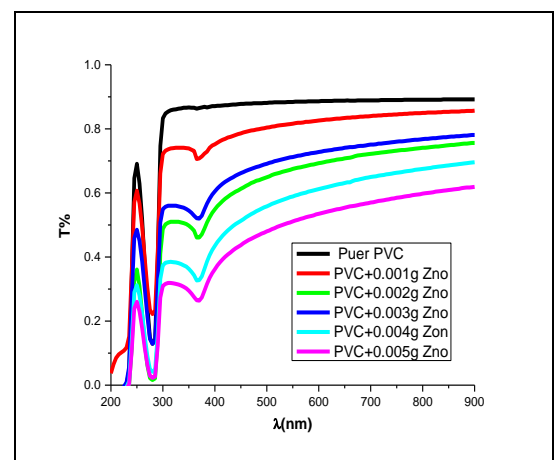
Types of bands	Description of band	The peaks location(cm^{-1})
C-H (625-970) cm^{-1}	Bending	634.62, 689.12, 834.08
C-Cl (600-800) cm^{-1}	Stretching	746.90
C-O (880-1000) cm^{-1}	stretch mode	921.49, 957.22
C=C (1630-1643) cm^{-1}	Stretch	1631
C-H2 (1300-1380) cm^{-1}	Bending	1330.88
C=O (1550-1750) cm^{-1}	Stretch vibration	1721.14
C-H (2800-3000) cm^{-1}	Stretch vibration	2816.11, 2857.32, 2910.83, 2967.14

4.4 Optical Properties

The absorption spectra of pure PVC and PVC/ZnO nanocomposites are illustrated in Figure(6). The maximum absorption wavelength of ZnO NPs is at (370nm) that can be noticed to intrinsic band-gap absorption ZnO that agreed with research [27]. There was a wide peak with maximum wavelength of (280nm) and absorbance of (0.12) which refers to PVC Polymer. This absorption is due to interband transition. These results matches with research[28]. The presence of ZnONPs causes an increase in absorption and a decrease in transmission as the amount of ZnONPs increases. Figure (7) shows the transmitted spectrum of pure PVC polymer and PVC/ZnO nanocomposites. The transmittance of pure PVC polymer is higher than that of PVC/ZnO nanocomposites. Pure polymers and nanocomposites have a lower transmittance in the UV field than in the visible range. The effect of appended ZnO nanoparticles is evident; they have a very low UV transmission. Transmittance has decreased when ZnO amounts has increased this matched with Ref[29].



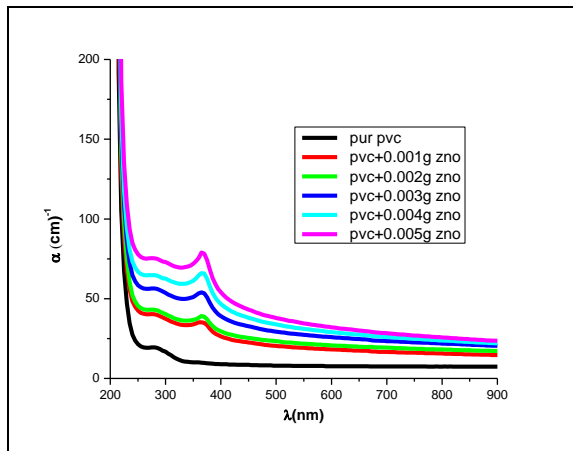
Figure(6): Absorbance change with wavelength for PVC/ZnO nanocomposite.



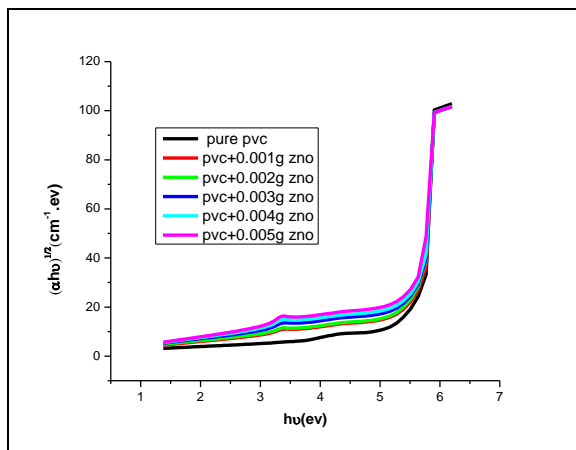
Figure(7): Variation of transmittance with wavelength for PVC/ZnO nanocomposites.

Figure (8) demonstrates the relationship between the absorbance coefficient and wavelength for all samples with various amounts of ZnONPs. From this Figure, it was noted that the absorption coefficient increases with the increase in the amount of ZnONPs. This increase could be explained by the difference in carrier amounts or by the presence of more carriers moving from the ground state's higher vibrational levels to the first excited singlet state's higher sublevels[30]. Measurements show that the absorption coefficient of the PVC/ZnO nanocomposites has amounts that are lower than (10^4 cm^{-1}) indicating that they possess an indirect energy range. Figure (9) shows how the amount of zinc oxide in the nanocomposites affects the energy band difference. The energy band gap narrowed with the increase of the amount of nanoparticles

as in Table 4. As the energy band gap decreased from 5.25eV to 4.98eV, the decrease in the value of the energy band gap is associated with higher local levels of the forbidden energy band gap [31].



Figure(8): Absorption coefficient spectra of samples PVC/ZnO nanocomposites.



Figure(9): $(\alpha h\nu)^{1/2}$ Variation with photon energy to PVC/ZnO nanocomposites.

Table(4): Value of the energy band gap for PVC/ZnO nanocomposites.

Samples	E_g (eV)
Pure PVC	5.25
PVC- 0.001g ZNO	5.22
PVC- 0.002g ZNO	5.20
PVC- 0.003g ZNO	5.16
PVC- 0.004g ZNO	5.12
PVC- 0.005g ZNO	4.98

From equation (8) the extinction coefficient of the PVC polymer for photon wavelength with different amounts of ZnONPs was calculated as shown in Figure (10). A graph shows that the extinction coefficient increases as the ratio of ZnO NPs increases, referring to an increase in the number of charge carriers as a result of an increase in the absorption coefficient. [32]. Figure (11) represents the measurement of the sun radiation intensity transmitted from pure polymer PVC and PVC/ZnO NPs films. It was observed that the transmitted sun radiation intensity is almost the same in the samples or slightly different at some time. It is clear from the Figure that the highest transmitted sun radiation intensity is at a time (12 o'clock.) after which the intensity begins to decrease gradually. Depending on the table (1), the temperatures in the seven consecutive days in Baghdad from the beginning of September 2021 are approximately equal for the period from 6 am to 7 pm (13 hr). For each film, the ratio of solar radiation intensity with films present (symbol I) to solar radiation intensity without films present (symbol I_0) was computed and plotted, Almost all films have the same radiation intensity ratio as shown in the Figures (6-A, B, C, D, E, F) This was comparable with research[33].

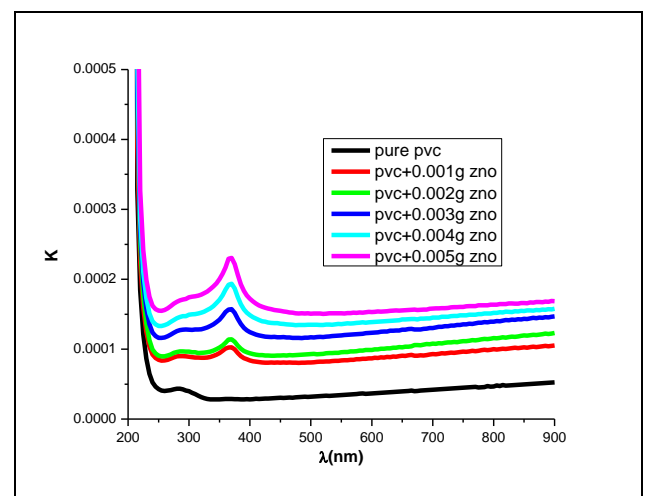
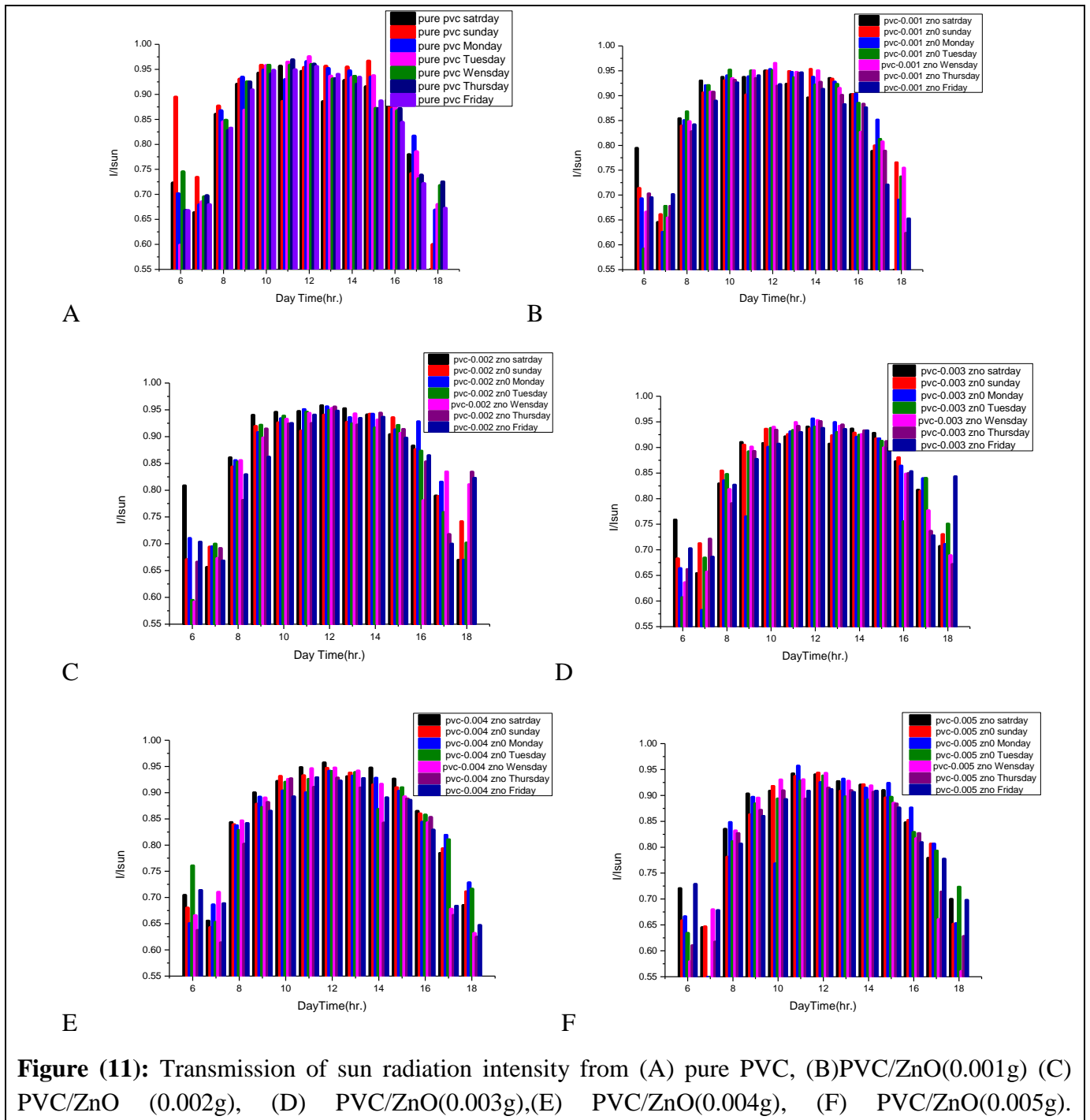


Figure (10): Extinction coefficient variation with wavelength to PVC/ZnO nanocomposites.



5. CONCLUSIONS

The results indicate that increasing the amount of ZnONPs incorporates the ZnONP peaks and/or the total disappearance within the PVC diffraction halos into the experimental results of the XRD assay. The differences in the XRD spectrum show that the doping of the nanoparticles changed the polymer microstructure, and the XRD data also revealed the hexagonal crystal structure of ZnONP, which was inferred by (SEM). that ZnONPs are dispersed in the PVC matrix. Increasing the

amount of ZnONPs gave rise to cluster aggregates in PVC of different sizes . However, the ZnO nanoparticles can effectively dope PVC and enhance its optical properties. Absorption increases and permeability decreases with increasing the amount of zinc oxide. The absorption coefficient and the extinction coefficient show the dependence on the amounts of zinc oxide, which increases after ingestion with increasing amounts of zinc oxide. The optical bandgap decreases with increasing filler amounts from 5.25 eV to 4.98 eV. The

intensity of solar radiation was measured at a rate of one hour for pure PVC and PVC/ZnONPs films for seven consecutive days, from 6 a.m. to 6 p.m. (13 hr.). It is reasonable to deduce that the ratio of transmitted radiation strength to solar radiation intensity for all films is the same at all times and on all days.

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