East European Journal of Physics. **4.** 364-372 (2024)
DOI:10.26565/2312-4334-2024-4-42 ISSN 2312-4334

STUDIES OF THE IMPACT OF UV ON CMC PVA/ZnO NANOCOMPOSITE FILMS PREPARED WITH A SIMPLE SOLUTION CASTING METHOD

Sarah A. Ibrahim[a], **Abderrazek Oueslati**[b], **Abdelhedi Aydi**[b]*
[a]*Laboratory of Multifunctional Materials and Applications (LaMMA), LR16ES18, Faculty of Sciences of Sfax, University of Sfax, BP 1171, 3000 Sfax, Tunisia*
[b]*Laboratory of spectroscopic characterization and optical materials, Faculty of Sciences, University of Sfax, B.P. 1171, 3000 Sfax, Tunisia*
**Corresponding Author e-mail: aydi_abdelhedi@yahoo.fr*

Received July 27, 2024; revised September 24, 2024; accepted September 24, 2024

The synthesis of nanocomposite films comprising carboxymethyl cellulose/ polyvinyl alcohol (CMC PVA) mixed with zinc oxide nanoparticles (ZnO NPs) through a simple solution casting method is examined. Furthermore, the impact of ZnO NPs and UV-irradiation exposure for varying durations (20,45,75h) on the morphology (FE-SEM) is investigated. The X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, and ultraviolet-visible (UV-Vis) spectroscopy are utilized to analyze the as-prepared films. Furthermore, the field-emission scanning electron microscopy (FE-SEM) images reveal a noticeable change in the morphology of CMC PVA/ZnO nanocomposite films attributed to the significant impact of ZnO nanoparticles and UV exposure. The XRD spectra demonstrate a modification in the amorphous phase of the samples as a result of UV exposure The FTIR analysis reveals that the exposure to UV radiation positively influenced the polymer's structure, as evidenced by notable changes in the infrared peaks. Additionally, the UV-Vis spectroscopy results indicate that longer UV exposure times (75 hours) and the addition of ZnO nanoparticles resulted in improved absorption characteristics within the produced films. The nanocomposite films displayed an adjustable energy gap (Eg) that varied between (4.52 eV and 4.55 eV) as the duration of UV irradiation increased from (20 hours) (75 hours) led to a reduction in the energy gap (Eg) value to (4.50 eV). This phenomenon is believed to be caused by the substantial influence of UV radiation on the development of structural defects. Ultimately, the Energy gap Eg of the nanocomposite films was influenced by the duration of UV. The results demonstrate that there is significant potential for the utilization of CMC/PVA/ZnO nanocomposite films in various crucial optoelectronic applications.

Keywords: *CMC/PVA/ZnO; Nanocomposites Properties; ZnO Nanoparticles; Energy Gap; UV irradiation; X-ray*

1. INTRODUCTION

Over the past few years, there has been a notable surge in the study of polymers with varied optical properties, largely attributed to their extensive range of uses such as sensors and light-emitting diodes. The optical attributes of these substances can be readily modified by managing the levels of fillers. Despite the extensive research conducted on these materials, there is still much to explore and understand [1] Polyvinyl alcohol (PVA) is a polymer with a semi-crystalline structure that is soluble in water. It possesses remarkable film-forming and adhesive characteristics, rendering it highly valuable in various technological, pharmaceutical, and biomedical fields due to its intriguing physical properties. [2] Polyvinyl alcohol (PVA) is a polar polymer with hydroxyl groups linked to methane carbons via a carbon chain backbone. The incorporation of OH groups enable the creation of PVA composites through hydrogen bonding interactions. PVA showcases advantageous traits including a notable charge storage capability, robust dielectric strength, and optical and electrical properties that are modulated by the filler material employed. By incorporating chalcogenide semiconductors and metal oxide semiconductors into PVA, optical properties of the host matrix can be significantly enhanced. Consequently, PVA has emerged as a promising candidate in the fields of electronics and optoelectronics [3]. One of the derivatives commonly used in various industries is carboxymethyl cellulose (CMC). This compound undergoes treatment with chloroacetic acid ($ClCH_2CO_2H$). CMC is utilized in various industries such as cosmetics, paints, pharmaceuticals, mineral processing, food, textiles, ceramic foam, biodegradable films, and paper. It functions as a thickening agent, binding agent, stabilizer for suspensions, and agent for retaining water in these industries [4]. The frequently utilized natural polysaccharide polymer possesses outstanding biodegradability, biocompatibility, and film-forming characteristics. Due to its safety and lack of toxicity, it finds extensive application in the pharmaceutical, food, and packaging sectors [5] The frequently utilized natural polysaccharide polymer possesses outstanding biodegradability, biocompatibility, and film-forming characteristics. Due to its safety and lack of toxicity, it finds extensive application in the pharmaceutical, food, and packaging sectors [6]. Moreover, zinc oxide nanoparticles (ZnO NPs) exhibit versatile properties as a metal oxide, showcasing remarkable electrochemical and physicochemical attributes. These include elevated chemical stability and a wide-ranging absorption spectrum [7]. The wide energy range and stable thermal properties of this material make it exhibit semiconductor characteristics, indicating promising prospects for its utilization in electronic and optoelectronic technologies like solar cells and storage devices. [8,9] Sunlight is made up of a continuous spectrum of electromagnetic energy separated into three major wavelength bands: ultraviolet (5%), visible and infrared

---

Cite as: S.A. Ibrahim, A. Oueslati, A. Aydi, East Eur. J. Phys. 4, 364 (2024), https://doi.org/10.26565/2312-4334-2024-4-42

(45%), and 50%. The UV light region is found between (100-400) nm. International UV radiation is classified as follows by the Commission on Illumination: There are three types of wavelengths: long tidal wave UVA (315-400 nm), UVB (280-315 nm), and UVC (short wave) (100–280 nm) [10]. The impact of UV exposure on the electrical and optical characteristics of solution-processed transparent ZnO films has been a subject of study by Hwai-En Lin and colleagues. Researchers have shown considerable interest in exploring the chemical and physical attributes of CMC/PVA blend materials, including the analysis of CMC/PVA samples, as demonstrated by Al-Muntaser and others. [12]. The Co/ZnO-CMC nanocomposite was thoroughly investigated to analyze its structural, optical, thermal, and electrical characteristics, with a specific focus on its potential utilization in solid-state battery applications. Channa et al. [13]. The hybrid nanocomposite films of PVA/PVP/CMC-ZnO were fabricated through the solution casting technique. [14] The solution casting technique was effectively utilized to fabricate lightweight and elastic polymer nanocomposites of CMC/PVA/ZnO-NPs in a recent study, resulting in enhanced optical properties. ZnO nanoparticles were incorporated as conducting fillers, while a CMC/PVA blend was utilized as the polymer matrix. Various techniques and protocols were examined to systematically analyze the optical and structural characteristics of this composite system. The significance of this study in academia lies in the comprehension of the fundamental nanoscale mechanisms that improve the functional characteristics of composite materials. This research seeks to improve the structural and optical features of CMC/PVA/ZnO nanocomposite-based films through photo-irradiation (UV light) exposure of the as-prepared samples.

2. THEORETICAL PART

The proportion of the incident light beam that is not reflected upon striking a material surface is either absorbed or transmitted through the substance. The amount of beam that is absorbed is influenced by the thickness of the materials and the interaction of photons with them, as stated by the Beer-Lambert Law. Equation (1) establishes the connection between the brightness of the incident light and the light that is transmitted [15].

$$I = I_o e^{-\alpha t} \tag{1}$$

The incident and transmitted light intensities are denoted by (Io) and (I), respectively, the symbol (α) is used to denote the optical absorption coefficient, while (t) is used to represent the thickness of the film. The optical absorption coefficient (α) can be determined from the optical absorption spectrum Equation (2) by using the absorbance relation A = log (Io/I) .[16,17]

$$\alpha = 2.303\frac{A}{t} \tag{2}$$

The energy band gap can be calculated using the following equation, where λ represents the wavelength of the incident light. [18,19]

$$\alpha h\upsilon = B(h\upsilon - E_g)^r \tag{3}$$

Where: E_g: optical energy gap for indirect transition in (eV), B: constant depended on type of material, r: The refractive index is unchanging and can vary between 1/2, 3/2, 2, or 3, contingent upon the specific material and the nature of the optical transition.

Scherer's equation is utilized to estimate the average crystallite size (D). Subsequently, various calculations can be performed based on this estimation. [20,21].

$$D = \frac{K\lambda}{\beta \cos\theta}. \tag{4}$$

The lattice parameter (a) was determined through calculations based on X-ray diffraction findings, utilizing specific mathematical relationships [22]

$$\frac{1}{d_{hkl}^2} = \frac{(h^2+k^2)}{a^2} + \frac{l^2}{c^2}. \tag{5}$$

Where d_{hkl}: is the inter planer distance for a given plane with Miller indices (hkl).

3. EXPERIMENTAL PART

The powdered carboxymethyl cellulose (CMC) was obtained from AVONCHEM, a UK-based company, with an average molecular weight of 67.000 g/mole. The powdered PVA was acquired from Thomas Baker, with an average molecular weight of 14.000 g/mole, and was manufactured in India. Zinc oxide (ZnO) nanoparticles with an average particle size of 22.15 nm were utilized in the fabrication of a CMC/ PVA/ZnO nanocomposite film, which was manufactured in the United States by Sky Spring Nanomaterials, Inc. The combination of CMC and PVA was prepared by dissolving 0.25 g of each polymer in 17 ml of distilled water through the solution casting technique. Subsequently, ZnO NPs powder was added in varying amounts of (0.008) g, along with 8 ml of distilled water, and mixed with the precursor solution of CMC/PVA blend. In order to achieve full dissolution, the precursor solution underwent magnetic stirring for a duration of 24 hours at ambient temperature. The CMC/ PVA/ZnO nanocomposite was then formed by carefully pouring the solution onto glass plates measuring (5) cm in diameter, and subsequently allowing it to gradually evaporate over a period of (5-9) days at room temperature. The outcome of this procedure led to the creation of a consistent layer. The nanocomposite film composed of as-synthesized CMC /PVA/ZnO exhibited a measured thickness of (0.044) µm. Moreover, the as-prepared films were exposed to UV sterlizer (UV -209b) (8) watt (220-275) nm made in China. The sample was exposed to the lamp for durations of 20, 45, and 75 hours, with the distance between the sample and the lamp kept constant for each irradiation time. The T70/T80 Series UV/Vis Spectrometer, a UV-Visible spectrophotometer, was employed to examine the absorption and transmission spectra across the wavelength range of 200-900 nm. The composite characteristics of each film were assessed through FTIR spectroscopy (Bruker-Tensor 27 with ATR unit). The samples' thicknesses were measured utilizing a Japanese-made digital micrometre model (Tasha), which has a measurement accuracy of (0.001) mm and a measurement range of (0-150) mm. Fourier transform infrared spectroscopy (FTIR) was performed on all films utilizing an FTIR spectrometer (Bruker-Tensor 27 type with ATR unit). A completely computerized X-ray diffractometer 106 Materials Science and Modern Manufacturing (XRD; Aeris – Malvern Panalytical's company-made in Holland, the investigation focused on analysing the composition of CMC, PVA polymer, and CMC/PVA/ZnO and ZnO nanocomposite films at Al Khora Company. High-resolution scanning electron microscopy FESEM (Inspect F50-EFI company-made in Holland, the surface composition and the presence of cracks were analysed in pure CMC and CMC/ZnO nanocomposite films by Al Khora Company.

3. RESULTS AND DISCUSSION

XRD, Field Emission Scanning Electron Microscope (FESEM), FTIR, Uv- Visible Spectroscopy and UV irradiation, were performed to examine the structure and morphology of the samples

3.1. X-ray diffraction analysis (XRD)

Display Figure 1 (A) the ZnO nanoparticles' X-ray diffraction pattern. It was evident from the study of the ZnO nanoparticles' X-ray diffraction patterns that they were single-phase in nature [21].

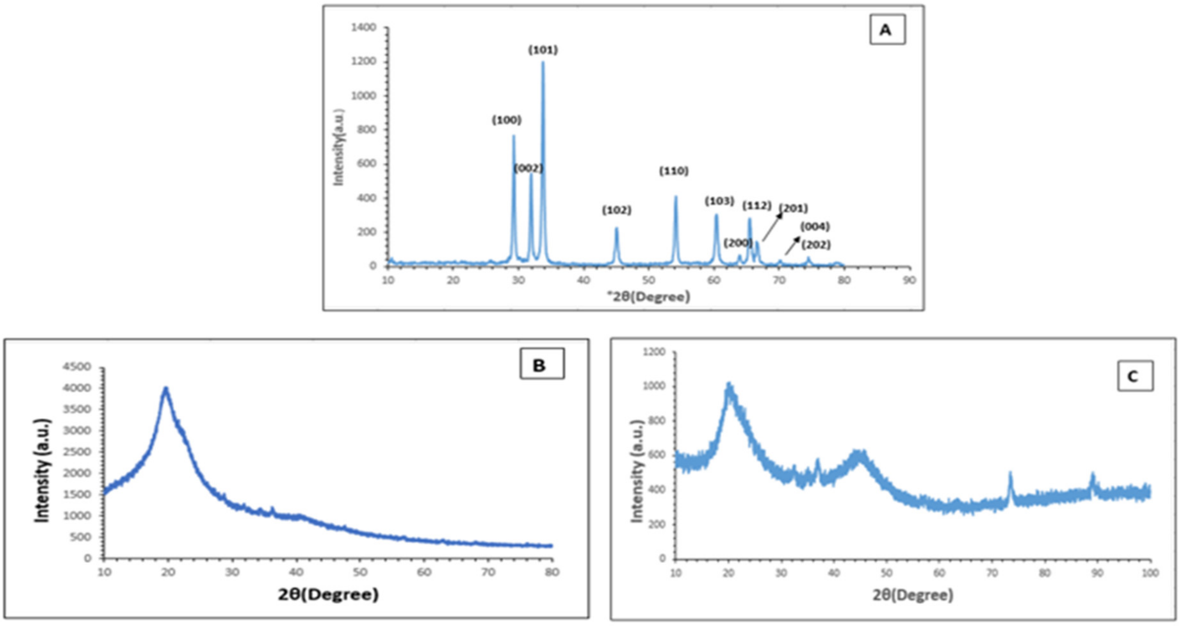

Figure 1. Display the X-ray diffraction patterns of (A) ZnO NPs, (B)CMC/PVA/Zno Nanocomposite Film and (C) CMC/PVA/ZnO Nanocomposite Film after UV-irradiation for 75h

When the peaks for ZnO occur at an angle of $2\Theta = 29.385$, 32.0275, 33.8567, 45.1378, 53.8266, 54.2048, 60.4452, 63.9796, 65.5435, 66.6788, and 74.5686 degrees, the crystalline nature results. With crystal planes (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202), ZnO has a hexagonal crystal structure. The values are in agreement with the data on the International Center of Diffraction Data (ICDD) card No. (36-1451). that agree with research [23,24] The estimated average size of ZnO nanoparticles (NPs) average 25.5203 nm, as determined using equation (4) and presented in Table (1).

In addition, a solitary peak at $2\theta = 19.6314°$ was observed in the X-ray diffraction (XRD) analysis of the PVA/CMC/ZnO nanocomposite film prior to exposure to UV radiation, as illustrated in Figure 1-B, that implies the amorphous structure of the CMC/PVA/ZnO nanocomposite film. The XRD spectrum of the CMC/PVA/ZnO nanocomposite film, as shown in Figure (1-C), demonstrates several peaks at $2\theta = 20.79$, 32.47, 36.89, 45.66,73.47, 49.02, with lower intensity compared to Figure (1-B) after being exposed to UV-irradiation for 75 hours. he results suggest that UV-irradiation has influenced the film by increasing the amorphous phase and reducing its crystallinity. The prolonged UV-irradiation time of 75 hours has led to an increase in disorder and defects in the structure, ultimately causing a reduction in the degree of crystallinity of the film. The two polymers utilized in the present study exhibited characteristics of semi-crystalline materials due to the presence of both crystalline and amorphous regions. Additionally, the broad peak observed in the CMC/PVA/ZnO film may be attributed to the crystalline cellulose structure of CMC [25,26].

Table 1. XRD Parameters for ZnO

	2θ (deg)	**FWHM (deg)**	**Intensity (I/Io)**	**d ($\overset{\circ}{A}$)**	**D (nm)**	**(hkl)**
1	29.385	0.3337	57	3.03709	25.27	(100)
2	32.0275	0.3252	42	2.79228	25.93	002)
3	33.8567	0.3449	100	2.64548	24.45	(101)
4	45.1378	0.4079	19	2.00707	20.67	(102)
5	53.8266	0.1734	4	1.70179	48.64	(110)
6	54.2048	0.365	36	1.6908	23.10	(103)
7	60.4452	0.4134	27	1.53031	20.40	(200)
8	63.9796	0.3933	4	1.45403	21.44	(112)
9	65.5435	0.3686	26	1.42307	22.88	(201)
10	66.6788	0.4067	12	1.40157	20.73	(004)
11	74.5686	0.3107	4	1.2716	27.14	(202)

3.2. Field Emission Scanning Electron Microscope (FESEM)

The technique employed serves to characterize the surface morphology of ZnO nanoparticles, as well as PVA/CMC/ZnOnanocomposite films, both prior to and following 75 hours of UV irradiation, as illustrated in Figures 2(A-B and C) . The FESEM image in Figure (2-A) confirms the formation of ZnO nanoparticles depict dense clusters of particles, indicating their spherical and granular morphology. A higher resolution FESEM image reveals an aggregation of particles with uniform size, suggesting a multidimensional structure. These findings are consistent with previous research conducted by other scholars [27,28] Fig. (2-B) The CMC–PVA/ZnO nanocomposite film displayed small white particles unevenly distributed across the surface of the biopolymer matrix, indicating the presence of ZnO nanoparticles and that the pores were tighter before UV-irradiation. The FESEM image depicted in Fig. (2-C) illustrates a surface that appears rougher due to the significant impact of UV-irradiation on the CMC/PVA/ZnO nanocomposite film. The shape of the film underwent a transformation, resembling a mixture of large and small non-uniform prominent particles.

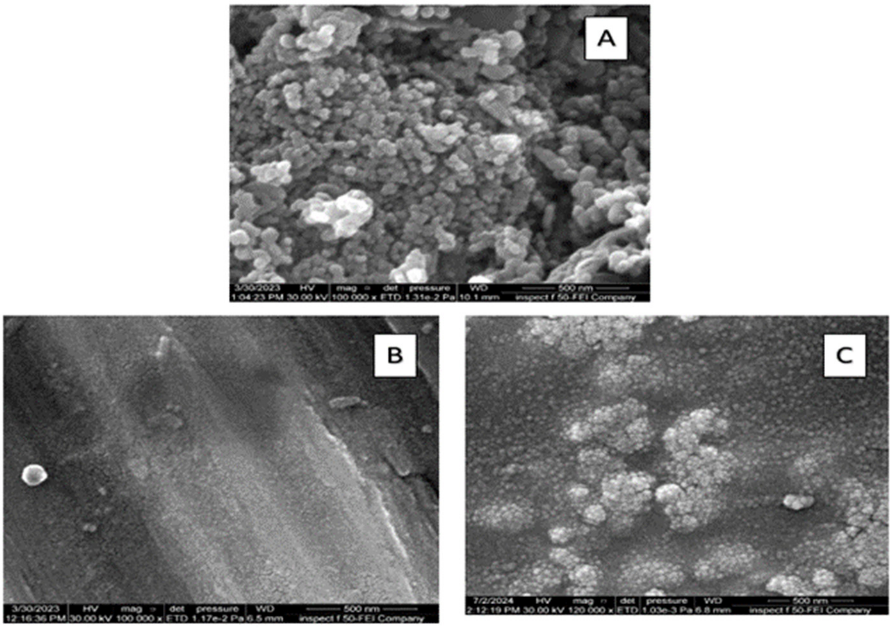

Figure 2. FESEM images for (A) ZnO NPs, (B) CMC/PVA/ZnONanocomposite Film Before UV-Irradiation, and (C) CMC/PVA/ZnO Nanocomposite Film after UV-Irradiation for 75 h

The FTIR spectra illustrating the ZnO thin films that were prepared are displayed in Figure 3.The measurements were conducted at ambient temperature within the spectrum of 500–4000 cm^{-1}. The spectrum of pure ZnO-NPs powder depicted in the analysis of Fig (3-A) involved the use of infrared tests in order to determine the characteristics and quality of the metal NPs. The absorption bands in metals in the fingerprint region, particularly those below 1000 cm^{-1}, were a result of inter-atomic vibrations. Furthermore, the peaks at (708.69 and 1505.58) cm^{-1} indicate the stretching and deformation vibrations of Zn-O, respectively. The recorded metal-oxygen vibrations of the individual metal oxides align with the frequencies reported in existing literature [29]. Moreover, an analysis of the FTIR spectrum of the

PVA/CMC/ZnO nanocomposite film prior to UV irradiation was conducted, as illustrated in Figure (3-B) and Table (2). The CMC and PVA polymers exhibited O-H and C-H stretching modes, respectively, with infrared peaks at (3200-3550) cm^{-1} and (2920) cm^{-1}. Moreover, the composite films displayed a distinct O=C=O stretching mode at (1340-1360) cm^{-1}.

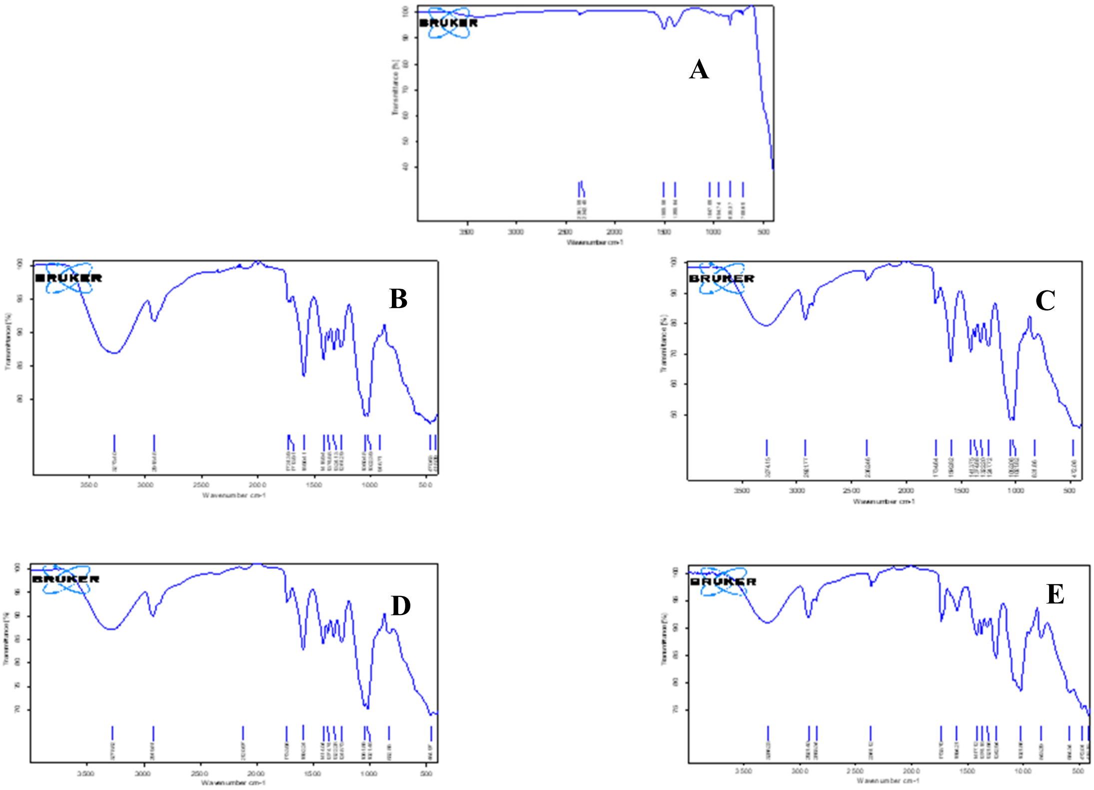

Figure 3. A-F.- The FTIR spectra of (A) ZnO NPs, (B) CMC/PVA/ZnO nanocomposite films before UV-irradiation and (C-E) after UV-irradiation at different times; 20 h, 45 h, and 75 h.

Furthermore, the CMC polymer exhibited an asymmetrical stretching vibration of COO- at (1591.00) cm^{-1}. The blend films contained the C=O carbonyl stretch bond (1733.55cm^{-1}) from vinyl alcohol, along with acetate groups (PVA polymer). The IR absorption bands at (1414.61 cm^{-1}), (1300-1461 cm^{-1}), and (1050-1300) cm^{-1} were designated for the C-H scissoring and C-H bending, as well as C-O stretch of PVA polymer, respectively [5, 30,31]. Based on the findings of the FTIR analysis, it was confirmed through the FTIR spectra that a nanocomposite film of CMC/PVA/ZNO was formed, showing a minor shift in the IR peaks. The polymers and ZNO NPs were effectively mixed together physically without any chemical bonding taking place. It was observed that the presence of ZNO NPs did not alter the IR spectral features of the polymer matrix. These results provide further validation to the conclusions drawn in a previous study [32,33,34]. The influence of UV exposure on the composition properties of PVA/CMC/ZnO nanocomposite films is illustrated in Figs. (3 C-E). The IR absorption bands corresponding to different irradiation times (20 45, 75) are specified in Table (2).

Table 2. FTIR-Characteristic of CMC/PVA/ZnO Nanocomposite Film

Assignments	**Wavenumber (cm^{-1})**		
	After 20h	**After 45h**	**After 75h**
O-H Stretching	3274.15	3278.82	3286.23
C-H stretching	2921.77	2919.81	2921.40 2853.34
C-H, CH2 bending	2362.46	2120.97	2361.12
COO- stretching Carbonyl group	1734.64 1592.82	1733.98 1592.24	1733.70 1594.21
C-H scissoring	1413.75 1322.20	1414.04 1374.74 1322.28	1417.12 1373.15 1321.56
C-O stretch	1247.72 1052.08 1021.82	1248.73 1051.85 1021.45	1242.94 1021.86
1,4--β Glycoside of Cellulos	831.86	832.85	834.29

Figs. 3 C-E show that the IR peaks of OH stretching mode (3200-3550) cm^{-1} were observed for all irradiation times. Vibrational transitions ranging from 4000 to 3275 cm-1 were observed during the time intervals of 20, 45 and 75 hours. The stretching of C-H bonds at 2920 cm-1 was noted in both PVA and CMC polymers, with some variations in wavenumber. Additionally, the absorption related to the single bond character of C=O carbonyl stretching at 1733.61 cm^{-1} was observed in vinyl alcohol and acetate groups (PVA polymer), while the C-O stretch bond (1050-1300 cm^{-1}) was present throughout all irradiation times. New IR peaks were observed at different times of irradiation, including 1592.82 cm^{-1} for 20 h 1592.24 cm^{-1} at 45 h, 1594.21 cm^{-1} at 75h. Additionally, asymmetrical COO-stretching (1591.67 cm^{-1}) and CH scissoring (1300-1461 cm-1) of a carbonyl group were consistently observed throughout the irradiation process. The origin of the IR absorption bands observed can be attributed to the exposure of the samples to UV radiation. Furthermore, after 26 hours of irradiation, A recent IR band at 1417.12 cm^{-1} associated with C-H bending was identified the CC rocking mode was observed at 20, 45, and 75 hours of irradiation. The infrared (IR) findings of PVA/CMC/ZnO nanocomposite films exposed to UV-irradiation for varying durations indicate that the consistent intensities of the aforementioned IR peaks (2919, 1417, 1374, 1322, and 1052 cm^{-1}) changed as the UV exposure time increased. These results can be attributed to the structure of PVA, which consists of parallel chains connected by hydrogen bonds. The impact of UV irradiation on the PVA/CMC/ZnO nanocomposite film is significant, affecting both hydrogen bonding and chain order. The decrease in intensity of these bands under UV radiation suggests that there was no change in the chemical structure, only in the value transmission, and no bond appeared or disappeared. Furthermore, the FTIR spectrum for all samples indicates that there were no chemical interactions between the nanoparticles and polymers, suggesting that only physical reactions occurred.

3.4. Ultraviolet-visible (UV-vis) spectroscopy

The UV-Visible absorption spectra were analyzed for a blend film of CMC/ PVA and a nanocomposite film of PVA-CMC/ZnO, as illustrated in Figure 4 .The UV absorption edge for the CMC/PVA film was observed to be approximately 245 nm, indicating a possible $\pi \rightarrow \pi^*$ electronic transition. This finding is in agreement with prior studies (25-29), thereby affirming the results. The UV absorption edge of the PVA/CMC/ZnO nanocomposite film was measured at 255 nm. There is a significant enhancement in the light absorption intensity of this film in both the UV and visible regions compared to the CMC/PVA blend film spectrum. The incorporation of ZnO NPs into the polymer matrix is believed to be the cause of these results. This conclusion is consistent with findings from prior research [35,5,36].

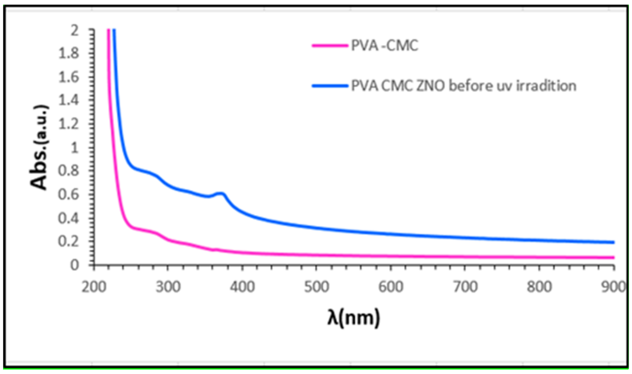

Figure 4. UV- Vis Absorption spectrum for CMC/PVA/ZnO Nanocomposite Films at Different UV-irradiation Times

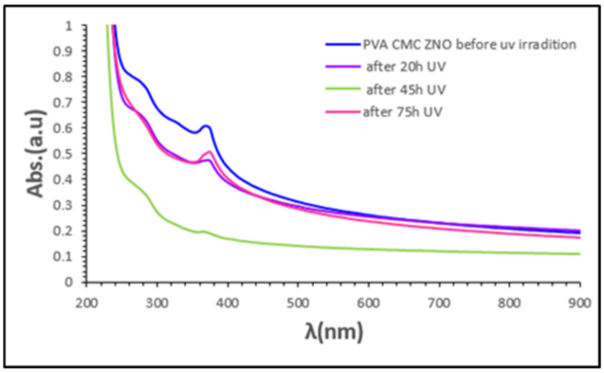

Figure 5. UV- Vis Absorption spectrum for CMC/PVA/ZnO Nanocomposite Films at Different UV-irradiation Times

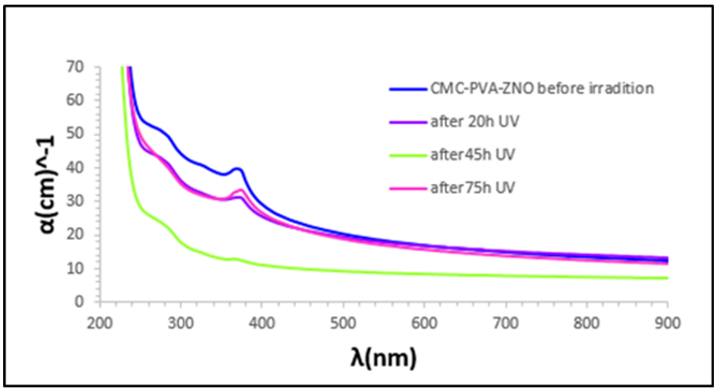

Figure 6. UV-Vis Absorption Coefficient for CMC/PVA/ZnO Nanocomposite Films at Different UV-irradiation Times

Figure 5 illustrates the absorption spectra of CMC/PVA/ZnO nanocomposite films before and after UV irradiation for different durations (20, 45, and 75 hours). The figure shows that the absorption intensity increased with UV-irradiation time compared to the unirradiated sample. This increase was attributed to the higher energy of atoms, resulting in more collisions between incident atoms, leading to decreased transmittance and increased absorbance [35,36] Additionally, A notable shift towards longer wavelengths (from 260 nm to 280 nm) in the absorption edge was detected, accompanied by increased intensity as a result of extended UV-irradiation exposure. The results demonstrate that the UV-irradiation impact led to a reduction in the optical energy band-gap of the synthesized film, as it generated defect levels, consequently enhancing the influence of the defects Moreover, the absorption coefficient (α) for each sample was determined utilizing Equation (2) illustrated in Figure 6.This parameter characterizes the ability of a substance to absorb light of a particular wavelength over a given distance. In cases where the absorption coefficient value was below ($\alpha < 104\ cm^{-1}$), it indicated the presence of an indirect electronic transition [37].

Figure 7 illustrates the variation in the optical energy band gap (Eg) of CMC/PVA/ZnO nanocomposite films before and after exposure to UV radiation. The findings suggest that increasing the UV exposure time from 20 to 75 hours resulted in an increase in the Eg values of the films from 4.43 to 4.55 eV, as outlined in Table 3. Moreover, extending the UV exposure time to 75 hours led to a decrease in the Eg of the film. This phenomenon can be attributed to the rise in disorder within the film due to the emergence of new defect levels in the band-gap of the nanocomposite film, ultimately leading to a narrowing of the Eg [35.37,38]

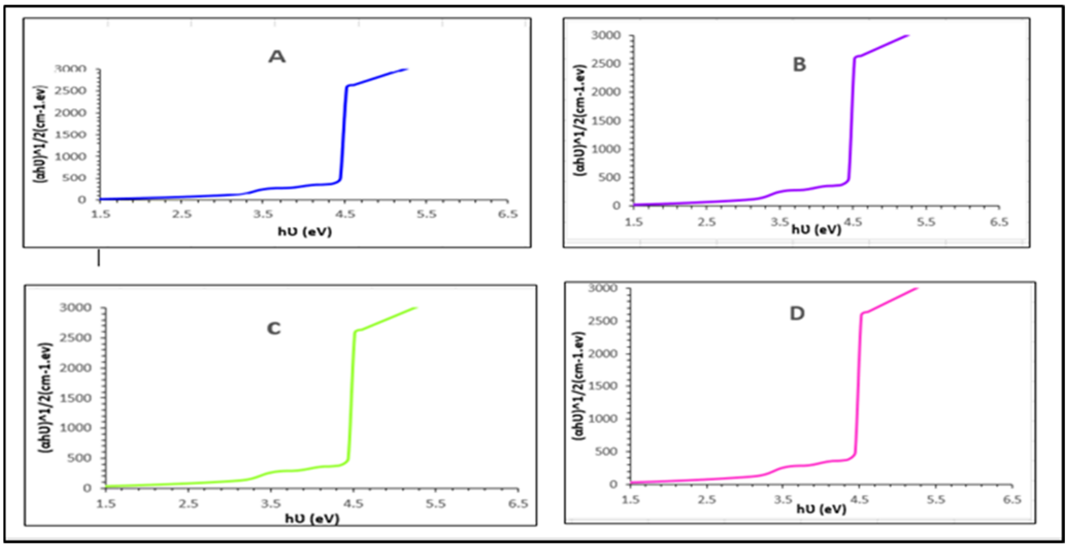

Figure 7. UV-Vis Optical energy gap for CMC/PVA/ZnO(A) CMC/PVA/ZnO Nanocomposite Film Before UV-Irradiation(B) CMC/PVA/ZnO Nanocomposite Film after UV-Irradiation for 20h(c) CMC/PVA/ZnO Nanocomposite Film after UV-Irradiation for 45h(D) CMC/PVA/ZnO Nanocomposite Film after UV-Irradiation for 75h

Table 3. Energy band gap value of CMC/PVA/ZnO Nanocomposite Films

Eg (eV)	UV-irradiation times (h)
4.43	0
4.52	20
4.55	45
4.50	75

CONCLUSIONS

The investigation focused on the synthesized CMC/PVA/ZnO nanocomposite film prepared through a simple solution casting method and the impact of UV-irradiation duration on the resulting films. Analysis of XRD data indicated that the structure quality of the samples was altered by the UV-irradiation time, leading to an increase in their amorphous characteristics. The FESEM images displayed a notable change in the morphology of the nanocomposite films based on the duration of UV exposure. Furthermore, the FTIR spectrum illustrated that ZnO and UV exposure played a beneficial role in the polymer structure by establishing covalent bonds between PVA and CMC. Lastly, The UV-Vis analysis demonstrated an increase in the absorption strength of the nanocomposite films as a result of the notable impact of ZnO NPs and UV exposure. The change in the optical band gap of the films, linked to the length of UV exposure, indicates their potential use in optoelectronic applications.

Funding.
This research received no external funding.

Conflicts of Interest.
The authors declare no conflict of interest.

Data availability statement.
The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Sarah A. Ibrahim, https://orcid.org/0009-0008-6462-3414; **Abdelhedi Aydi,** https://orcid.org/0000-0001-9656-9688

REFRENCES

[1] V.S. Sangawar, and M.C. Golchha, "Evolution of the optical properties of Polystyrene thin films filled with Zinc Oxide nanoparticles," Int. J. Sci. Eng. Res. **4**(6), 2700 (2013). https://www.ijser.org/onlineResearchPaperViewer.aspx?Evolution-of-the-optical-properties-of-Polystyrene-thin-films-filled-with-Zinc-Oxide-nanoparticles.pdf

[2] H.G. Basavaraj, C.G. Renuka, C.A. Harihar, Y. Sangappax, B.L. Rao, and R. Madhukumar, "Physicochemical mechanical and optical properties of polymer inorganic composite thin films: Applications," AIP Conference Proceedings, **2244**, 110009 (2020). https://doi.org/10.1063/5.0009947

[3] E.M. Abdelrazek, A.M. Abdelghany, A.E. Tarabiah, and H.M. Zidan, "AC conductivity and dielectric characteristics of PVA/PVP nanocomposite filled with MWCNTs," Journal of Materials Science: Materials in Electronics, **30**, 15521–15533 (2019). https://doi.org/10.1007/s10854-019-01929-2

[4] A.Y. Yassin, A.M. Abdelghany, and R.S. Salama, and A.E. Tarabiah, "Structural, Optical and Antibacterial Activity Studies on CMC/PVA Blend Filled with Three Different Types of Green Synthesized ZnO Nanoparticles," Journal of Inorganic and Organometallic Polymers and Materials, **33**, 1855–1867 (2023). http://dx.doi.org/10.1007/s10904-023-02622-y

[5] Y.M. Jawad, M.F.H. Al-Kadhemy, and J.A.S. Salman, "Synthesis structural and optical properties of CMC/MgO nanocomposites," Mater. Sci. Forum, **1039**, MSF, 104–114 (2021). https://doi.org/10.4028/www.scientific.net/MSF.1039

[6] H.E. Ali, A. Atta, and M.M. Senna, "Physico-Chemical Properties of Carboxymethyl Cellulose (CMC)/Nanosized Titanium Oxide (TiO_2) Gamma Irradiated Composite," Arab J. Nucl. Sci. Appl. **48**(4), 44–52 (2015).

[7] A.E. Tarabiah, H.A. Alhadlaq, Z.M. Alaizeri, A.A.A. Ahmed, G.M. Asnag, and M. Ahamed, "Enhanced structural, "optical, electrical properties and antibacterial activity of PEO/CMC doped ZnO nanorods for energy storage and food packaging applications,". J. Polym. Res. **29**(5), 1-16 (2022). https://doi.org/10.1007/s10965-022-03011-8

[8] A. Wibowo, M.A. Marsudi, M.I. Amal, *et al.*, "ZnO nanostructured materials for emerging solar cell applications". RSC Adv. **10**(70), 42838-42859 (2020). https://doi.org/10.1039/D0RA07689A

[9] Y. Sun, D. Wen, and X. Bai, "Nonvolatile ternary resistive switching memory devices based on the polymer composites containing zinc oxide nanoparticles". Phys Chem Chem Phys. **20**(8), 5771-5779 (2018). https://doi.org/10.1039/C7CP07887K

[10] A. Svobodova, D. Walterova, and J. Vostalova, "Ultraviolet light induced alteration to the skin.," Biomed. Pap. Med. Fac. Univ. Palacky. Olomouc. Czech. Repub. **150**(1), 25–38 (2006). https://doi.org/10.5507/bp.2006.003

[11] H. Lin, J. Hong, R. Nitta, Y. Kubota, Y. Katanayagi, H. Wagata, T. Kishi, *et al.*, "Effects of UV irradiation on the electrical and optical properties of solutionprocessed transparent ZnO films," Appl. Surf. Sci. **289**, 135–141 (2019). https://doi.org/10.1016/j.mssp.2020.105266

[12] A.A. Al-Muntaser, R.A. Pashameah, K. Sharma, E. Alzahrani, M.O. Farea, and M.A. Morsi. "α-MoO3 nanobelts/CMC-PVA nanocomposites: hybrid materials for optoelectronic and dielectric applications," J. Polym. Res. **29**(7), 1-11 (2022). https://doi.org/10.1007/s10965-022-03134-y

[13] M.M. Abutalib, and A. Rajeh, "Structural, thermal, optical and conductivity studies of Co/ZnO nanoparticles doped CMC polymer for solid state battery applications," Polymer Testing, **91**, 106803 (2020). https://doi.org/10.1016/j.polymertesting.2020.106803

[14] A.A. AlMuntaser, E. Alzahrani, H.M. Abo-Dief, A. Saeed, E.M. Alshammari, A.M. Al-Harthi, and A.E. Tarabiah, "Tuning the structural, optical, electrical, and dielectric properties of PVA/PVP/CMC ternary polymer blend using ZnO nanoparticles for nanodielectric and optoelectronic devices," Optical Materials, **140**, 13901 (2023). https://doi.org/10.1016/j.optmat.2023.113901

[15] K.H.H. Al-Attiyah, A. Hashim, and S.F. Obaid, "Fabrication of novel (carboxy methyl cellulose–polyvinylpyrrolidone–polyvinyl alcohol)/lead oxide nanoparticles: structural and optical properties for gamma rays shielding applications," Int. J. Plast. Technol. **23**(1), 39–45 (2019). https://doi.org/10.1007/s12588-019-09228-5

[16] A. Hashim, and A. Hadi, "Novel lead oxide polymer nanocomposites for nuclear radiation shielding applications," Ukrainian Journal of Physics, **62**(11), 978–983 (2017). https://doi.org/10.15407/ujpe62.11.0978

[17] T.A. Jasim, A.A. Saeed, F.J. Kadhum, and M.F.H. Al-Kadhemy, "Effect of Gamma Irradiation on The Optical Properties of PVA/Ag Nano-composite," GJSR Journal, **8**(2), (2020). http://dx.doi.org/10.1088/1757-899X/928/7/072137

[18] J.D. Patterson, and B.C. Bailey, *Solid-state physics: introduction to the theory*, (Springer Science & Business Media, 2007).

[19] N.A. Darweesh, A.A. Saeed, and M.F. Al-Kadhemy, "Influence of Weathering on Physical Properties and Sun Light Transmitted through PMMA/ Safranin Films for Greenhouse Applications," Mustansiriyah Journal of Pure and Applied Sciences, MJPAS **1**(1), 40-53 (2023).

[20] F.M. Nada, S.A. Hussain, S.K. Muhammad, and A.H.O. Alkhayatt, "Hydrothermally growth of TiO_2 Nanorods, characterization and annealing temperature effect," Kuwait Journal of Science, **48**(3), 1-10 (2021). https://doi.org/10.48129/kjs.v48i3.10417

[21] P.S. Sundaram, T. Sangeetha, S. Rajakarthihan, R. Vijayalaksmi, A. Elangovan, and G. Arivazhagan, "XRD structural studies on cobalt doped zinc oxide nanoparticles synthesized by coprecipitation method: Williamson-Hall and size-strain plot approaches," Physica B: Condensed Matter, **595**, 412342 (2020). https://doi.org/10.1016/j.physb.2020.412342

[22] C. Hammond, *The basics of cristallography and diffraction*, (Oxford, 2001).

[23] T. Ji, R. Zhang, X. Dong, D.E. Sameen, S. Ahmed, S. Li, and Y. Liu, "Effects of Ultrasonication Time on the Properties of Polyvinyl Alcohol/Sodium Carboxymethyl Cellulose/Nano-ZnO/Multilayer Graphene Nanoplatelet Composite Films," Nanomaterials, **10**(9), 1797 (2020). https://doi.org/10.3390/nano10091797

[24] S.L. Perumal, P. Hemalatha, M. Alagara, and K. N. Pandiyaraj, "Investigation of structural, optical and photocatalytic properties of Sr doped ZnO nanoparticles," Int. J. Phys. Sci. **4**, 1-13 (2015). https://doi.org/10.23851/mjs.v34i1.1226

[25] Y. Zahedi, B. Fathi-Achachlouei, and A.R. Yousefi, "Physical and mechanical properties of hybrid montmorillonite/zinc oxide reinforced carboxymethyl cellulose nanocomposites," International Journal of Biological Macromolecules, **108**, 863–873 (2018). https://doi.org/10.1016/j.ijbiomac.2017.10.185

[26] G.A.H.A. Jabbar, A.A. Saeed, and M.F. Hadi AL-Kadhemy, "Optical characteristics and bacterial-resistance ability of PVA/ZnO nanocomposites," Kuwait Journal of Science, **50**(3), 209-215 (2023). https://doi.org/10.1016/j.kjs.2023.03.004

[27] Q.M. Al-Bataineh, A.A. Ahmad, A.M. Alsaad, and A.D. Telfah, "Optical characterizations of PMMA/metal oxide nanoparticles thin films: bandgap engineering using a novel derived model," Heliyon, **7**(1), e05952 (2021). https://doi.org/10.1016/j.heliyon.2021.e05952

[28] M. Anandalli, T.M. Kanakaraj, V. Hebbar, J. Naik, and R.F. Bhajantri, "Physico-chemical properties of PMMA/ZnO nanocomposite capped with 1 chloro-9, 10-bis (phenyl ethynyl) anthracene," in AIP Conference Proceedings, **1953**(1), 30189 (2018). https://doi.org/10.1063/1.5032524

[29] S. Maensiri, P. Laokul, and V. Promarak, "Synthesis and optical properties of nanocrystalline ZnO powders by a simple method using zinc acetate dihydrate and polyvinyl pyrrolidone," J. Cryst. Growth, **289**(1), 102-106 (2006). https://doi.org/10.1016/j.jcrysgro.2005.10.145

[30] S. Hashem, M. Fadhil, and K. Naji, "Study Physical Characteristics of Polyvinyl Alcohol/Carboxymethyl cellulose Blend Films," **55**(393), 298–305 (2022). https://doi.org/10.48129/kjs.20553

[31] H. Helmiyati, Z.S.Z. Hidayat, I.F.R. Sitanggang, and D. Liftyawati, "Antimicrobial packaging of ZnO–Nps infused into CMC–PVA nanocomposite films effectively enhances the physicochemical properties," Polymer Testing, **104**, 107412 (2021). https://doi.org/10.1016/j.polymertesting.2021.107412

[32] V.S. Sangawar, and M.C. Golchha, "Evolution of the optical properties of Polystyrene thin films filled with Zinc Oxide nanoparticles," Int. J. Sci. Eng. Res. **4**(6), 2700-2705 (2013). https://www.ijser.org/researchpaper/Evolution-of-the-optical-properties-of-Polystyrene-thin-films-filled-with-Zinc-Oxide-nanoparticles.pdf

[33] I. Kim, K. Viswanathan, G. Kasi, K. Sadeghi, S. Thanakkasaranee, and J. Seo, "Poly (Lactic Acid)/ZnO Bionanocomposite Films with Positively Charged ZnO as Potential Antimicrobial Food Packaging Materials," Polymers, **11**(9), 1427 (2019). https://doi.org/10.3390/polym11091427

[34] Y. Yao, Z. Sun, X. Li, Z. Tang, X. Li, J.J. Morrell, Y. Liu, *et al.*, "Effects of Raw Material Source on the Properties of CMC Composite Films," Polymers, **14**(1), 1–15 (2022). https://doi.org/10.3390/polym14010032

[35] N.T.T. Thuy, *et al.*, "Green synthesis of silver nanoparticles using plectranthus amboinicus leaf extract for preparation of CMC/PVA nanocomposite film," J. Renewable Mater. **9**(8), 1393–1411 (2021). https://doi.org/10.32604/jrm.2021.015772

[36] A.M. Youssef, *et al.*, "Development and Characterization of CMC/PVA Films Loaded with ZnO-Nanoparticles for Antimicrobial Packaging Application," Der Pharma Chemica, **9**(9), 157–163 (2017).

[37] T.S. Soliman, A.M. Rashad, I.A. Ali, S.I. Khater, and S.I. Elkalashy, "Investigation of Linear Optical Parameters and Dielectric Properties of Polyvinyl Alcohol/ZnO Nanocomposite Films," Phys. Status Solidi Appl. Mater. Sci. **217**(19), 1-8 (2020). https://doi.org/10.1002/pssa.202000321

[38] S. Villarruel, *et al.*, "Changes induced by UV radiation in the presence of sodium benzoate in films formulated with polyvinyl alcohol and carboxymethyl cellulose," Mater. Sci. Eng. C, **56**, 545–554 (2015). https://doi.org/10.1016/j.msec.2015.07.003

ДОСЛІДЖЕННЯ ВПЛИВУ УФ-ВИПРОМІНЮВАННЯ НА НАНОКОМПОЗИТНІ ПЛІВКИ PVA/ZnO, ВИГОТОВЛЕНІ МЕТОДОМ ЛИТТЯ З РОЗЧИНУ

Сара А. Ібрагім[a], Абдерразек Уеслаті[b], Абдельхеді Айді[b]
[a]*Лабораторія багатофункціональних матеріалів і застосувань, Факультет наук Сфакса, Університет Сфакса, Сфакс, Туніс*
[b]*Лабораторія спектроскопічної характеристики та оптичних матеріалів, факультет природничих наук, Університет Сфакса, Сфакс, Туніс*

Розглянуто синтез нанокомпозитних плівок, що містять карбоксиметилцелюлозу/полівініловий спирт (CMC PVA), змішаний з наночастинками оксиду цинку (ZnO NPs) простим методом лиття з розчину. Крім того, досліджено вплив наночастинок ZnO та УФ-опромінення протягом різної тривалості (20, 45, 75 годин) на морфологію (FE-SEM). Для аналізу підготовлених плівок використовуються рентгенівська дифракція (XRD), інфрачервона (FTIR) спектроскопія з перетворенням Фур'є та ультрафіолетова видима (UV-Vis) спектроскопія. Крім того, зображення скануючої електронної мікроскопії з польовою емісією (FE-SEM) показують помітну зміну в морфології нанокомпозитних плівок CMC PVA/ZnO, пов'язану зі значним впливом наночастинок ZnO та ультрафіолетового випромінювання. XRD-спектри демонструють модифікацію аморфної фази зразків у результаті УФ-опромінення. Аналіз FTIR показує, що вплив УФ-випромінювання позитивно вплинуло на структуру полімеру, про що свідчать помітні зміни в інфрачервоних піках. Крім того, результати УФ-видимої спектроскопії вказують на те, що довший час УФ-опромінення (75 годин) і додавання наночастинок ZnO призвели до покращення характеристик поглинання у створених плівках. Нанокомпозитні плівки демонстрували регульований енергетичний зазор (Eg), який змінювався між (4,52 еВ і 4,55 еВ), коли тривалість УФ-опромінення збільшувалася з (20 годин) (75 годин), що призвело до зменшення значення енергетичного зазору (Eg) до (4,50 еВ). Вважається, що це явище спричинене значним впливом УФ-випромінювання на розвиток структурних дефектів. Зрештою, на енергетичний розрив Eg нанокомпозитних плівок впливала тривалість ультрафіолетового випромінювання. Результати демонструють, що існує значний потенціал для використання нанокомпозитних плівок CMC/PVA/ZnO у різних важливих оптоелектронних застосуваннях.

Ключові слова: *CMC/PVA/ZnO; властивості нанокомпозитів; наночастинки ZnO; енергетична щілина; УФ-опромінення; ультрафіолет*