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Diode Laser Irradiation Effects on Physical Properties of Titanium Dioxide Nano Fillers Doped Polyvinyl Alcohol Films

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ABSTRACT

Study effect of diode laser (wavelength 650 nm) irradiation for different irradiant times (0.25, 0.5, 1.00, 3.00, and 4.00 hrs) on the physical properties of titanium dioxide (TiO$_2$) possess particle size of 15.7 nm doped polyvinyl alcohol (PVA) films were experimentally investigated. The solution casting process has been utilized to create as-prepared TiO$_2$/PVA nanocomposite films. Ultraviolet-Visible (UV-Vis) spectroscopy investigates the samples' optical characteristics by analyzing optical absorption spectra in a wavelength range of (200 - 900 nm) at room temperature (RT) of 300 K. The PVA matrix could be used to describe the influence. All optical constants produced artificially through laser radiation, like absorption, refraction index, extinction coefficient and complex dielectric constants, have decreased with increasing radiation times. On the contrary of optical energy gap they increased with increasing radiation times, according to the study's findings. TiO$_2$ Nanoparticles (NPs) additions significantly impacted the PVA host's optical characteristics. When FTIR-spectrum regarding the TiO$_2$/PVA nanocomposite films was examined in various ratios of irradiation times, the peak positions or bonds did not change; instead, they became smaller or larger as the irradiation time increased.

Keywords: Diode laser, Optical Properties, PVA polymer, Titanium dioxide Nano-fillers.

1. INTRODUCTION

Substances are subjected to a variety of physical and chemical changes when they are subjected to electromagnetic radiation. A significant advantage of combined circuit production and control qualities is the capability to employ the laser to impact a small, precise spot [1]. The contact of organized polymer films with laser radiation is a topic for various academics. The laser has changed the thermal and optical features of polymers and complex polymers, like band-gap and crystallinity [2]. Nanomaterials have recently attracted much attention for both commercial and academic research [3]. Due to their outstanding characteristics, like their huge surface area, small size, strong interactions, quantum confinement impact, etc., Nanoparticles (NPs) (such as SnO$_2$, ZnO, TiO$_2$, etc.) might improve the polymer's performance by adding a small amount [4]. Due to its desirable optical and physical qualities, processability, high hydrophilicity, superior chemical resistance, and biological compatibility, poly (vinyl alcohol) (PVA) is a significant and appealing polymer [5, 6].

PVA was a tasteless, translucent powder that was either cream or white that was intended for food use. PVA was beneficial in the manufacturing, medical, commercial, and food industries and was utilized to produce various goods, including resins, lacquers, food-contact packaging materials, and surgical threads [7]. The most significant ones were N-Methyl Pyrrolidone (NMP), Dimethyl Sulfoxide (DMSO), and Ethylene Glycol (EG), soluble in water [8]. Because of its hydrophilic characteristics and compatible construction, this polymer has been widely employed in conjunction with other polymer compounds, like bio-polymers and other polymer materials with hydrophilic capabilities, to enhance the films' mechanical properties [9].

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Additionally, PVA was applied as a lubricant for the solutions of contact lenses, in sustained-release oral formulations, and in trans-dermal patches for viscous originations like ophthalmic items [10].

Additionally, various nanomaterials were employed to prepare inorganic/organic nanocomposites. TiO_2 NPs were one of such inorganic fillers that were widely used. It enjoys a distinctive status due to its exceptional transparency for visible light, hydrophilicity, high refractive index, strong stability, and UV absorption. Because of its low cost and high catalytic activity, TiO_2 has long been recognized as a material with a strong oxidation capacity which can be used for photo-electrochemical cells [11], air or water purification [12], and to reduce organic pollutants that kill germs [13, 14]. A new class of innovative materials has also been created using TiO_2 NPs because of their unique and attractive dielectric, optical, and photo-catalytic capabilities resulting from size quantization [15, 16].

The casting process, which is majorly utilized in the fabrication of organic / inorganic nanocomposite materials, is one of the recent manufacturing techniques for various nanocomposite structures. The benefit of this approach is that the mixture process may be performed at room temperature and that organic polymers could be introduced at the first stage while the solution's particles are still in their dispersion state. Inorganic particles added to polymer matrices give composite materials new chemical and physical properties that are very different from traditional materials [17-19].

The research on the interaction regarding laser irradiation with filler-doped polymer structures is the focus of many researchers. The excellent dispersion and particle size of TiO_2 NPs in the polymer matrix are crucial due to all such vital needs. The impact of a half-hour of (He-Ne) laser irradiation on the optical characteristics of the dichromium trioxide thin films was studied by Daham et al. in 2010 [20]. As a result of the irradiation process, the absorption edge related to the irradiated films was altered to a longer wavelength (red-shift), and their optical band gap was lowered. Al-Kadhemy et al. (2014) researched the effects of He-Ne laser irradiation for a range of radiation periods on the optical characteristics of PVA membranes doped with methyl orange; films were created using a casting approach [21]. The refractive index, coefficient of extinction, optical energy gap, and complex dielectric constants have all been impacted by laser radiation, as seen by the absorption and transmission spectra of all as-prepared samples. This effect decreased with the increase in radiation times.

Preparing TiO_2/PVA nanocomposite films and examining the effects of diode laser irradiation with various irradiation periods on the physical characteristics of TiO_2 nano-fillers doped PVA films are the study of the main goals.

Recently, adding TiO_2 NPs has been one of the most important strategies to promote the physical and mechanical properties of PVA thin films attributes due to high power and large superficies area nanofillers [22-25]. PVA Polymer matrices embedded by TiO_2 nanofiller have been studied widely due to their diverse applications in the purification of air and water, batteries, and coatings, due to special photo-chemical features of the mixture have been used in solar cells [26] and used for food packaging [27,28], the mixture is used to enhance the sensing properties and analytical performance of electrochemical sensor technology detecting antibiotics in water [29]. Using the laser to irradiate a fixed and small patch is used to dominate crystallinity, allowing for TiO_2/PVA polymer degeneration adjustment to use in industrialization optical waveguides, photonics, and integrated circuits [30, 31]]. In addition, PVA/ TiO_2 nanoparticle film are non-toxic, inexpensive, and has a wide range of frequencies of ultraviolet (UV) filter properties so that they can be used as an anti-bacterial film in medical environments [32]. Thin films of PVA within embedding TiO_2 nanoparticles display high chemo-mechanical permanence and can availably defend against microorganisms and foodborne allergens in the existence of UV irradiation [33].

In this paper the results show there is a big effect of radiation time on most optical characteristic as obviously in energy gap and absorption; as energy gap property: the energy gap increases as radiation time increases this confirm that there is a distortion happening in PVA structure (free radical, bond rupture, etc) which lead to perversion of the valence band and therefore to cause to change in energy levels.

As absorption property, the peaks still in the same wavelength 275 nm but a decreasing in value in conjunction with the increasing of radiation time. The results are the same for the rest of the optical characteristics.

The Fourier Transform Infrared spectroscopy (FTIR) results of TiO_2/PVA films for various irradiation times show stability in the bonds between materials represented by wavenumber comparing with transmittance quantity which show a change by increasing the values of transmittance proportion with increasing of radiation time this means the relative increment of elevation of transmittance peak to measure quantitatively the decrease of density of functional group.

2. EXPERIMENTAL

2.1 Materials

PVA has been purchased from DBH Chemical LTD Pooled England. The chemical formula for PVA was $[C_2H_4O]_n$ with a molecular weight of 14000 g/mole and density of 1.19-1.31 g/cm³. PVA was used as granular white color to transform to colorless after being dissolved in distilled water. Titanium dioxide (TiO_2) nanoparticles have been supplied by Intelligent Materials Pvt. Ltd, United States, with a particle size of 15.7 nm, which was used as white color powder and dissolved in distilled water.

2.2 Preparation of TiO_2/PVA Nanocomposite Films

In a nutshell, TiO_2/PVA films were created by the dissolution of 0.5 g of the PVA in 10 ml of refined, hot water. The mix has been constantly heated at a temperature of 80 °C with magnetic stirring for 4 hrs. To prevent the NPs from agglomerating, an adequate weight percentage of TiO_2 NPs (0.7 %) was introduced to 10 ml of hot distilled water and magnetically stirred vigorously for 3 hrs. To achieve excellent dispersion with no agglomeration, the as-prepared blend precursor was combined with PVA solution and magnetically stirred for 2 hrs. After blowing and shaking out any remaining air bubbles, the final PVA/TiO_2 mixture was cast on a glass Petri dish and left to dry. At a thickness of about 50 μm, as-prepared films have been evaluated. Film thicknesses were evaluated using an identical amount of total materials and a glass Petri dish of the same size. TiO_2/PVA nanocomposite film was exposed with the use of a 650 nm diode laser and a 10 mm focal-length lens for focusing laser light on as-prepared samples. Using a UV-Vis spectrometer (T70-80), the absorption and transmission spectra were examined in the wavelength range from (200-900 nm). Because of this, irradiation times were measured in the range of 0, 0.25, 0.5, 1.00, 3.00, and 4.00 hrs.

It's important to reveal the major features of TiO_2 nanoparticles, polymer PVA, and the effect of ratio irradiation times. The transmittance mode is used for all (FTIR) spectra. FTIR spectrometer was used in the wavenumber range of 400 cm^{-1} - 4,000 cm^{-1}. The films' thickness has been measured using a digital micrometre (Tesha Version) with a precision of 0.001 mm over a range of 0 – 150 mm

3. RESULTS AND DISCUSSIONS

Figure 1 illustrates the UV-Vis. absorption spectrum, A for TiO_2/PVA nanocomposite films before and after laser radiation with dissimilar radiation times. The absorption peak of TiO_2/PVA nanocomposite films begin to show at wavelength of 275 nm with an intensity value of around 0.205; this peak was started to decrease with increasing irradiation time. Furthermore, a major absorption peak was disappeared at the irradiation time of 4 hrs. As a result of the embrittlement of polymer surface, which makes it of a higher liability to the corrosions and polymer surface has become uneven. Which is why, light scattering increased on the polymer surface and the amount of the transmitted light through polymer decreases following the irradiation.
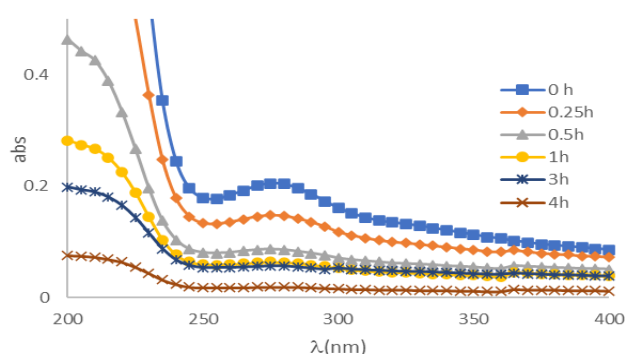
Figure 1. Absorption spectra of TiO_2/PVA nanocomposite films irradiated by diode laser (650 nm) at various times (0, 0.25, 0.5, 1.00, 3.00, 4. 00) hrs.

The transmission spectrum, T of TiO_2/PVA nanocomposite films prior to and post laser radiation with dissimilar radiation times was illustrated in Figure 2. Figure 2 confirms that the spectrum behavior has been inverse spectrum of absorption of the as-prepared samples.
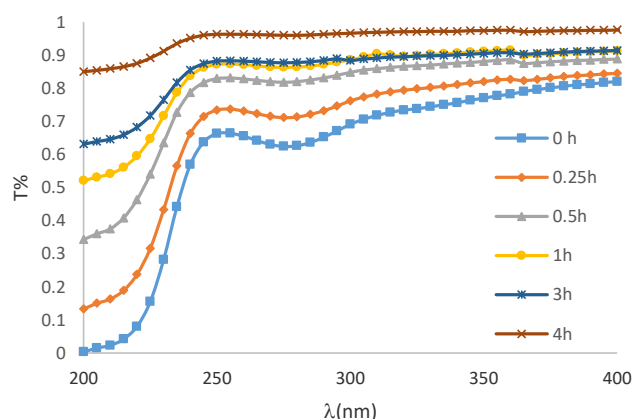

Figure 2. Transmission spectra of TiO_2/PVA nano-composite films for

different irradiation times

The reflection spectrum, *R* of the TiO_2/PVA nanocomposite films prior to and post laser radiation with dissimilar radiation times was demonstrated in Figure 3. Reflectance values were calculated from Equation (1):
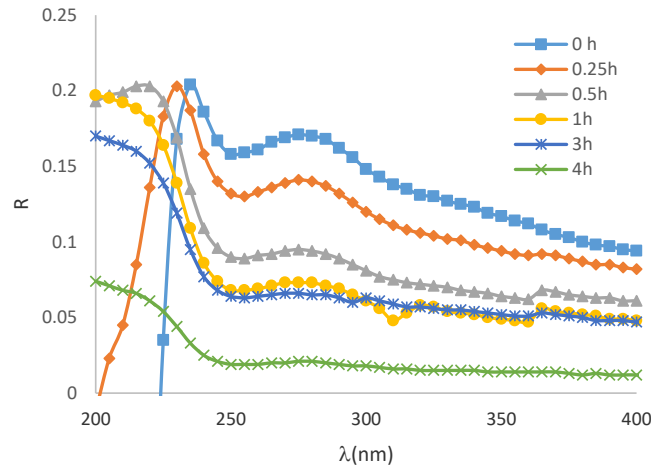
$$R + A + T = 1 \tag{1}$$

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Figure 3. Reflection spectra of the TiO$_2$/PVA nano-composite films
for various irradiation times

The optical absorption coefficient, α calculated from Equation (2), and depended directly on absorbance and inversely with thickness of films, t, and its value provides evidence about the electronic transition nature.

$$\alpha = \frac{2.303\,A}{t} \qquad\qquad (2)$$

In the case where values of absorption coefficient $\alpha > 10^4$ cm^{-1}) at higher energy values, direct electronic transitions are likely to occur and the energy momentum of the photon and electron will be preserved. On the contrary, indirect electronic transitions were caused by modest absorption coefficient values $\alpha < 10^4$ cm^{-1} at low energies. The absorption coefficient for TiO$_2$/PVA films as they were formed was shown in Figure (4). Results showed that indirect electronic transitions were considered to occur when the absorption coefficient value is less than 10^4 cm^{-1}.
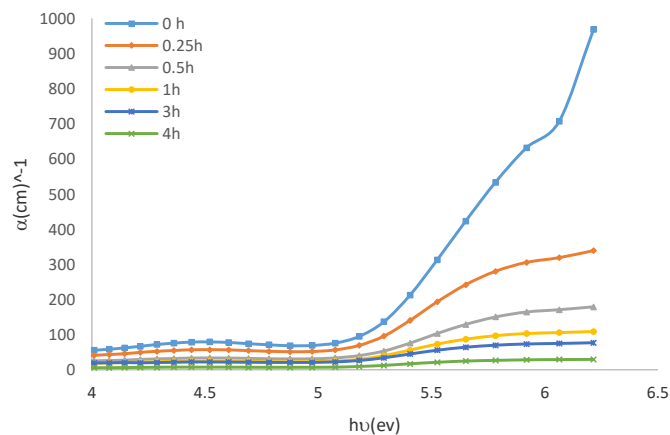

Figure 4. The relation between absorption coefficient and photon energy of TiO2/PVA films for different irradiation times.

The relation between the absorption edge, $\alpha h\nu^{/2}$ (where ν is the radiation's frequency and h is Planck's constant) and photon energy for TiO_2/PVA nanocomposite films before and after laser radiation with dissimilar radiation times —representing indirect allowed and prohibited transitions, respectively — is also can be seen from Figure (5). Values for energy-gap have been shown in Table 1. The results show the increase of the optical energy gap with increases irradiation time of laser beam maybe attributed to the arising grade of disorder in the film where formation some defects in some localized levels
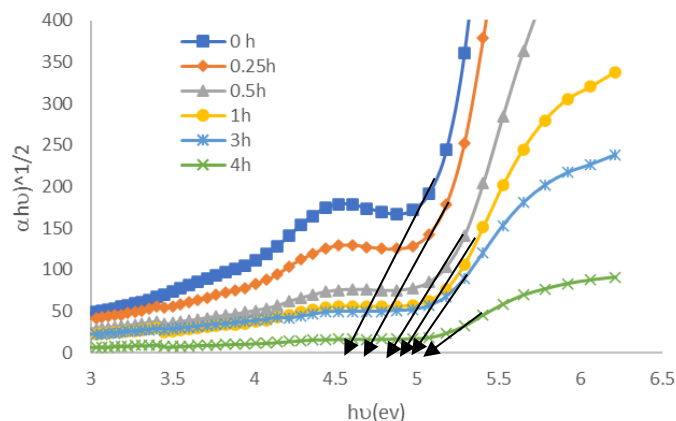

Figure 5. The correlation between the photon energy and $(\alpha h\nu)^{1/2}$ of TiO_2 /PVA nanocomposite films for different irradiation times.

Table 1 Optical energy-gap for TiO_2 /PVA films prior to and post laser radiation for altered times.

Irradiation Times (hrs)	**0**	**0.25**	**0.5**	**1**	**3**	**4**
E_g (eV) of TiO_2/PVA films	4.58	4.65	4.75	4.81	4.95	5.032

Optical constants like extinction coefficient, K and refractive index, n were estimated according to Equations (3) and (4), respectively and illustrated in Figures (6) and (7). Those two factors decline with influence of the increase of the laser radiation time up to definite point were increased. Extinction coefficient was proportional to absorbance and affected by radiation time as showed in Figure (6). Whereas, refractive index was depended on reflectivity, and its values were evaluated in the range of 2.4 to 2.6 for all films as exposed in Figure (7). The enlarged in the refractive index to be high value designate that the composite is absorbing material.

$$K = \frac{\alpha\lambda}{4\pi} \qquad\qquad (3)$$

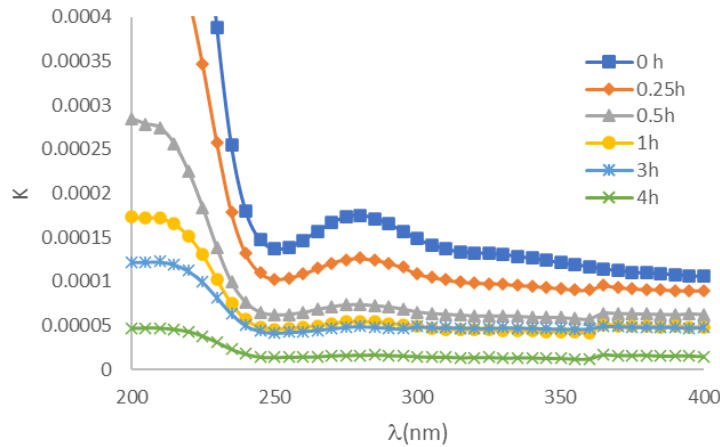$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \qquad\qquad (4)$$

Figure 6. The correlation between extinction coefficient and the wavelength of TiO$_2$ /PVA films for different irradiation times.
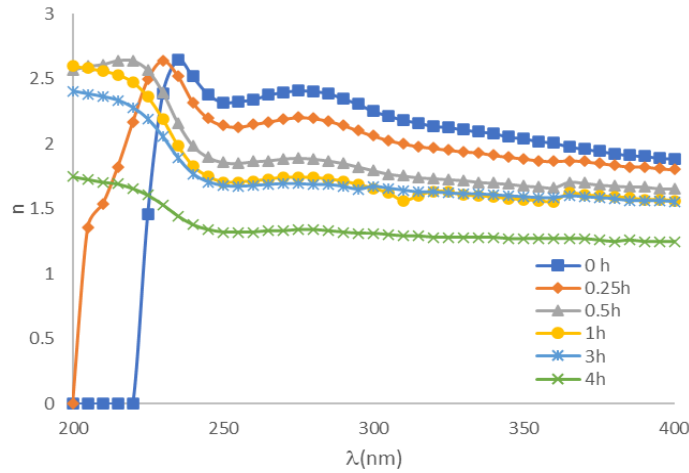

Figure 7. The correlation between refractive index and the wavelength of TiO$_2$/PVA films for various irradiation times.

Furthermore, values of complex dielectric constant, ε^* defined the optical characteristics of as-prepared samples were calculated in the following Equation (5):

$$\varepsilon^* = \varepsilon_r + i\varepsilon_i \qquad (5)$$

where ε_r and ε_i denote real and imaginary dielectric constant portions, respectively and determined via the following equations:

$$\varepsilon_r = n^2 - K^2 \qquad (6)$$

$$\varepsilon_i = 2nK \qquad (7)$$

These complex dielectric constants were plotted as shown in Figures (8) and (9), respectively. The findings of Figures (8) and (9) reveal that the real and imaginary portions of dielectric constant values of irradiated films were less than that of un-irradiated TiO$_2$/PVA films. These

results could be a result of the distinguished changes in the stoichiometry and internal strain of as-prepared films. The ε_r behavior was similar to the n behavior, due to the fact that the extinction coefficient, K^2 is very small compared to refractive index, n^2 value. In contrast, behavior of ε_i is dependent upon variation of K, which means that the real dielectric constant ε_r portion is larger compared to the dielectric constant's imaginary portion ε_i of as-produced samples.
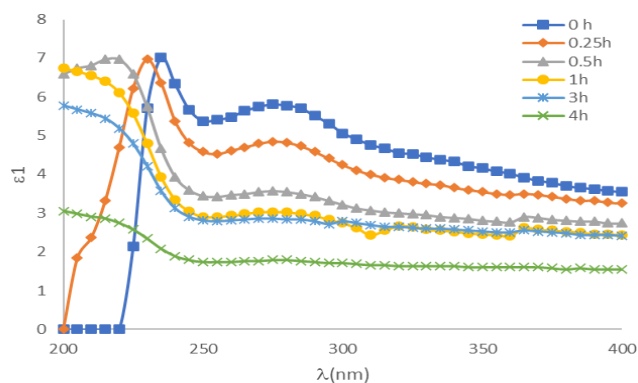

Figure 8. Correlation between the real dielectric constant and the wavelength of TiO$_2$/PVA films for different times of irradiation.
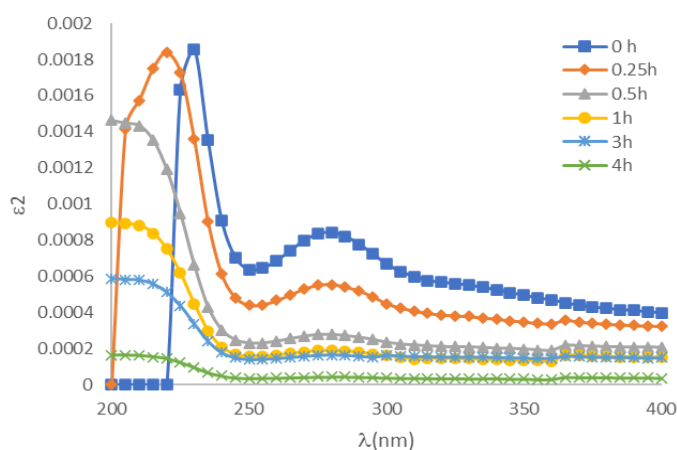

Figure 9. Correlation between the imaginary dielectric constants of the TiO$_2$/PVA films for different radiation times.

Figure (10) displays the pure PVA film's FTIR spectrum. Peaks corresponding to C-H appeared in the transmittance bands for film at 837 cm^{-1}, 834 cm^{-1}, and 2911 cm^{-1} out-of-plane [34, 35]. The asymmetric vibration regarding the C-H band is what causes the peaks at 1631.78 cm^{-1} and 3400 cm^{-1} in spectra. The stretching vibration related to the C-O band causes peaks in the spectrum at 1088.35 cm^{-1}, 1243.88 cm^{-1}, 918.9 cm^{-1}, and 924.68 cm^{-1}, while stretching vibration of the C=O band occurs at 1731.35 cm^{-1} [35]. The asymmetric bending vibration of the C-CH$_3$ bond is characterized by the transmittance between 1423 cm^{-1} and 1430 cm^{-1}. O-H had displayed abroad bands around 3285 cm^{-1}. This outcome is consistent with Jalil M.S [36].
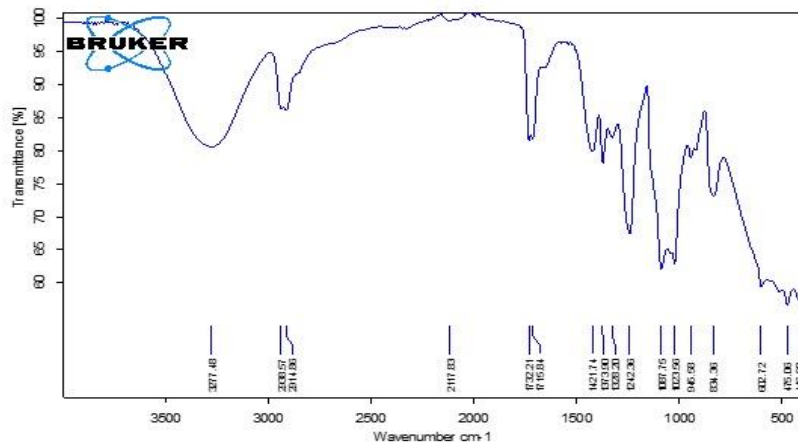
Figure 10. FTIR Spectrum for pure PVA film

The FTIR spectra for Pure TiO_2 Nanoparticles Powder particles size of 15.7 nm are shown in Figure (11). FTIR transmittance spectrum peaks between 3800 – 3000 cm^{-1}. A broad band has been noticed, associated with the stretching hydroxyl that represents water as the moisture. Peaks at 435.91 cm^{-1}, 466.77 cm^{-1} to 700 cm^{-1} showed bending and stretching mode of Ti-O-Ti, this is matched with results obtained Akil D.S. and Shehap A.M. [37].
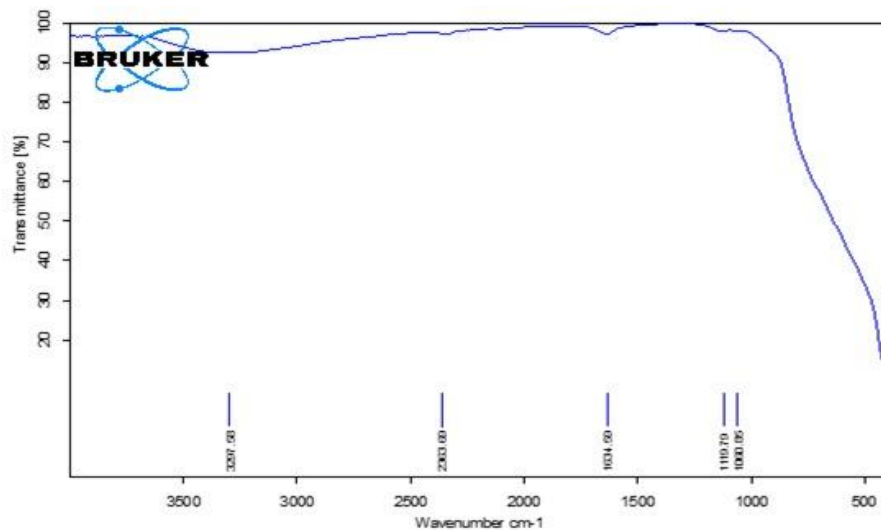

Figure 11. FTIR Spectrum for pure TiO$_2$ Nanoparticles Powder.

The FTIR spectra was taken to the films of mixture PVA and doping with particles sizes of TiO_2 equal to 15.7 nm with weight of 0.007 g as shown in Figure (12). It was noted that the peaks at 3400 cm^{-1} and 1631.78 cm^{-1} referred to stretching and bending vibration of –OH group. The peak at 2939.94 cm^{-1} in the spectra is a result of the asymmetric vibration of C-H band. The peaks 1024.10 cm^{-1}, 834 cm^{-1} are stretching vibration of C-H and out of plane, respectively. The peaks are at 1243.88 cm^{-1}, 1088.35 cm^{-1}, 924.68 cm^{-1}, and 918.9cm^{-1}, In spectra result from stretching vibration of C-O band and 1731.35 cm^{-1} appears the stretching vibration of C=O band. Peaks at 435.91 cm^{-1}, 466.77 cm^{-1} to 700 cm^{-1} showed Ti-O-Ti bending and stretching mode, this has been matched with results obtained by Kavitha B. et al [38]. In Figure (13), all samples show the same

peaks behavior but they differ in intensity of transmittance, the intensity increased with increasing the amount of irradiation time as shown for example at wavenumber 3280.64 cm^{-1} the intensity of transmittance increased from 84 to 93 for irradiation times 0 h and 0.5 h, respectively.

In comparison between Figure (12) and Figure (13), before and after mixing the TiO_2 with PVA; some new bonds were appears belong to the host and the peaks become more sharpness than before mixing up.

FTIR measurements are performed to investigate the vibrational bands of the nanocomposites and intermolecular bonding between PVA matrix and TiO_2 NPs.

In investigation of FTIR-spectrum of TiO_2/PVA nanocomposite films in different ratios of irradiation times, there was no change in the peak positions just bigger or smaller values with increase of times irradiation.

Introducing TiO_2 NPs into PVA matrix enhances the thermal stability of the thin films and improves their electronic and optical properties. This evidently contributes positively to the technology of the fabrication of new generation of optoelectronic devices and thin-film transistors.
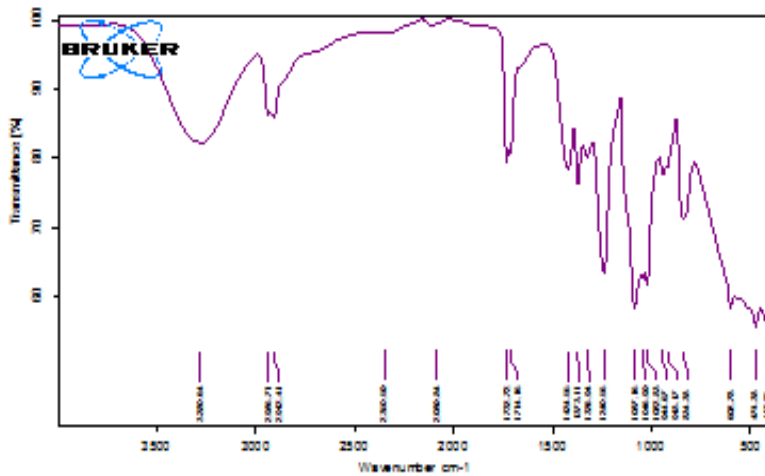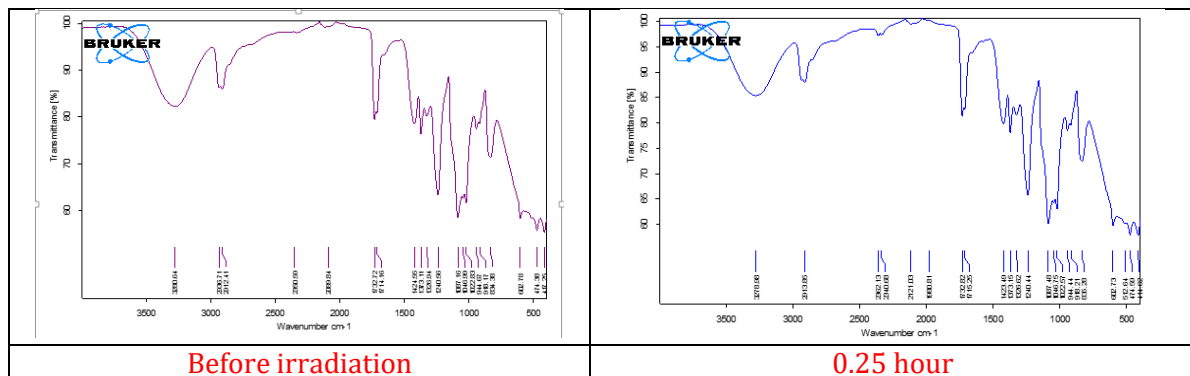

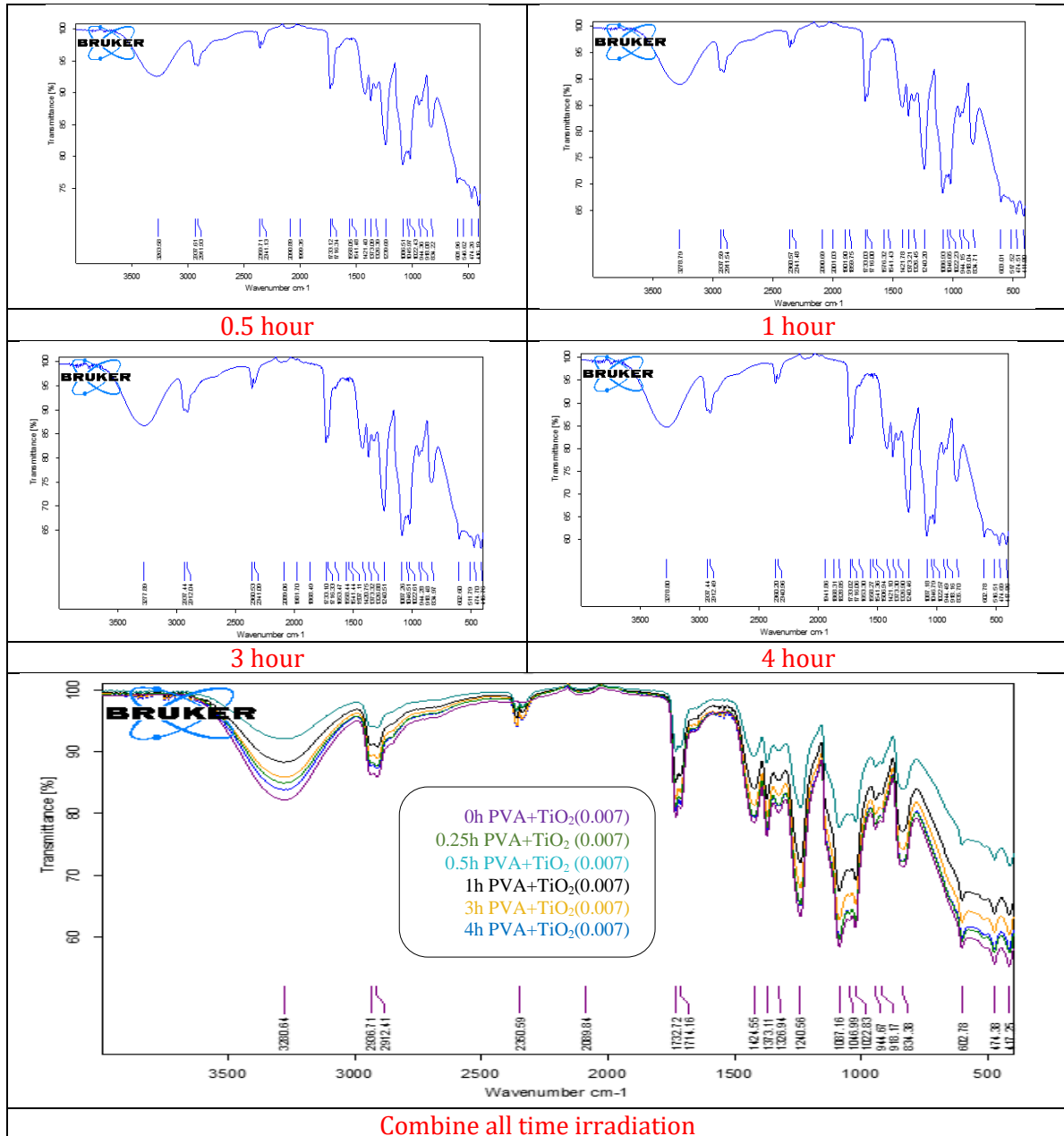**Figure (12).** FTIR Spectrum for TiO_2 size equal to 15.7 nm with weight of 0.007 g/PVA Films

| Before irradiation | 0.25 hour |

Figure (13). FT-IR spectrum for TiO₂/PVA films in various irradiation time.

4. CONCLUSIONS

In the presented work, after PVA films with TiO_2 doped have been made using a simple casting method. The effects of various diode laser irradiation times (0, 0.25, 0.5, 1.00, 3.00, and 4.00 hrs) on the optical properties regarding TiO_2/PVA nanocomposite films were investigated. According to experimental findings, the amount of time that films are exposed to laser irradiation has a significant impact on their transmittance, absorbance, reflectance, and all other optical constants. Additionally, when laser radiation durations increased, reflectance (R), absorption, and absorption coefficient (α) decreased, as did the extinction coefficient (K), refractive index (n), the

imaginary and real parts of the dielectric constant. inverse of that the band energy gap (Eg) value increase as irradiation time increase due to some disorder in electronic levels. There has not been any change in peak positions in the analysis of FTIR-spectrum regarding the TiO_2/PVA nanocomposite films at various irradiation times; instead, the values got smaller or greater as the number of exposures increased.

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CONFLICTS OF INTEREST
All authors have declared no conflict of interest.

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