Effect of Amounts of Titanium Dioxide Nanoparticles on FTIR Spectra and Optical Properties of Poly Vinyl Alcohol Films

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Abstract

In this paper, thin films of pure PVA, TiO_2 /PVA with various amounts of TiO_2 nanoparticles (0.007, 0.01, 0.02 and 0.03) g have been acquired by solution casting method. FTIR spectra for all samples measured in transmission mode. The effect of adding TiO_2 nanoparticles is seen by changing changing transmittance whereas the behavior of the spectrum of PVA is unaffected. The optical characteristics were assessed across a wavelength range of (200-800) nm. The findings from the experiment indicate that the absorbance of TiO_2 /PVA films rose as the quantity of TiO_2 nanoparticles increased. There is one peak of absorption spectrum for pure PVA at (275 nm) with intensity (0.113). UV-visible analysis revealed a significant improvement in the UV protection capabilities of the hybrid films following the incorporation of TiO_2. The energy gap values decreased as the amount of TiO_2 nanoparticles increased, ranging from (5.15 to 4.90) eV.

Keywords: TiO_2 Nanoparticles, PVA Films, FTIR Spectra, Optical Properties, Energy Gap.

Introduction:

Polymers are widely found in nature; polymers may either be completely synthetic or naturally occurring. There are a large number of man-made polymers consisting of various families: elastomers, plastics, adhesives, textile, fibers, and synthetic rubbers etc. Each family itself has subgroups: Enzymes, proteins and nucleic acids are polymers of biological origin. DNA are polymers of personage nucleic acids [1]. A polymer is a large molecule made up of hundreds or thousands of atoms that is formed by connecting one, two, or occasionally more monomers into chains or networks [2]. The long-chain structure of a polymer is related to its particular qualities. Molecular weight and structure directly follow physical characteristics [3]. The polymer known as Poly Vinyl Alcohol (PVA) has garnered significant attention due to its several desirable properties, particularly in relation to various pharmacological and biological applications [4]. The medical, food, industrial, and commercial sectors have all utilized it to create a variety of end products, including resins, surgical threads, lacquers, and materials for food packaging that are frequently used in conjunction with food [5]. Poly Vinyl alcohol was utilized as a transparent, white or cream-colored, granular powder that had no taste or odor for use in food. It is soluble in water, N-methyl Pyrrolidone (NMP), Dimethyl Sulfoxide (DMSO), and Ethylene Glycol (EG) in the greatest amount [6].

The group of transition metal oxides is referred to as titanium dioxide (TiO_2). TiO_2 occurs in nature in four recognized polymorphs: rutile (tetragonal), brookite (orthorhombic), anatase (tetragonal), and TiO_2 (B) (monoclinic). Two more high-pressure forms have been synthesized from the rutile phase in addition to these polymorphs. These are Cotunnite with PdCl2, Baddelleyite with ZrO_2, TiO_2 (II) with the α-PbO2 structure, and TiO_2 (H) with hollandite. The anatase and rutile are primarily produced as microcrystalline minerals in the chemical sector. Octahedral joined at the vertices can be used to generate anatase; in rutile, the edges are linked. Rutile is the most stable phase at all temperatures and pressures below 60 kbar, as demonstrated by thermodynamic simulations, when TiO_2 (II) becomes the favorable phase [7]. In many applications, titanium dioxide (TiO_2) is utilized as a self-cleaning and self-disinfecting material for surface covering. However, because of its nontoxicity, photo-induced super-hydrophobicity, and antifogging effect, TiO2 is also useful in the purification of our environment [8]. These qualities have been linked to the removal of germs and dangerous organic pollutants from water and air, as well as to the creation of surfaces that can clean or sterilize themselves in places like medical facilities [9].

Saleh A.F. et al (2014) [10], used chemical spray pyrolysis technique to prepare thin films of titanium dioxide TiO_2 pure and TiO_2: PVA polymer on a glass substrate preheated at (350 ˚C) for TiO_2 pure, and at (160 ˚C) for TiO_2: PVA. With spray rate 3Sec. /1min, and thickness (250 nm). The optical properties measurement explained the effect of adding PVA on transmittance, absorbance, refractive index, absorption coefficient and electronic transitions of prepared thin films. And their results observed that filling of PVA generally increased optical properties. Vishwas M. et al (2014) [11], outlined the impact of different TiO_2 nanoparticle amounts (5, 10 and 15 mg) on the mechanical, electrical, and optical characteristics of poly vinyl alcohol (PVA) films. The transmittance of the un-doped (PVA) films was high in the visible range and fell as the TiO_2 concentration increased. Poly vinyl alcohol (PVA) doped with titanium dioxide nanoparticles at several weight percentages (1.25, 2.5, 5, 7.5, 10 TiO_2/PVA) were made utilizing the sonification and casting processes, as investigated by Shehap A.M. and S. Akil D. (2016) [12]. These materials' structural characteristics were investigated using FTIR, UV-visible, and X-ray diffraction. The XRD pattern showed that when the TiO_2 concentration rose, the amorphous domain in the PVA polymer matrix grew. FTIR tests were used to analyze the dopant's skin tone in relation to the polymer. The spectra of absorption for UV-visible light showed irregular changes of the absorption for high doping samples in UV range (7.5, 10 TiO_2 /PVA). Absorbance, transmittance and reflectance spectra were used for the determination of the optical constants. The results indicated that the optical band gap decreased with increasing TiO_2 content, while the refractive index increased to high value for the composites of high dopant.

Mahdi B. and Rouabah F. (2023) [13]. This work is focused on the preparation and characterization of poly (vinyl alcohol)/silica gel/Nano-TiO_2 , and the study of titanium dioxide (TiO_2) nanoparticles (from 1 to 5%) on the properties of poly vinyl alcohol (PVA)/silica films. This new material was prepared by the sol-gel method using (poly vinyl alcohol) powder with Tetraethyl Orthosilicate (TEOS) as a precursor source of silica. ourier transform infrared (FTIR), water absorption, water contact angle, ultraviolet-visible spectrometry (UV-visible), and thermogravimetric analysis (TGA) were used to characterize the hybrid films obtained. The PVA/SiO_2 /Nano-TiO_2 films were successfully synthesized. Owing to the FT-IR Analysis, the chemical bonds have clearly shown that the PVA backbone is linked to the (SiO 2 -TiO_2) network. UV-VIS tests indicated that the hybrid films' UV shielding properties were drastically enhanced as a result of the addition of TiO_2.

The work's goal is to investigate how various TiO_2 nanoparticle concentrations affect PVA films' optical characteristics and FTIR spectra.

Experimental work

PVA films doped with TiO_2 nanoparticles were fabricated through the solution casting method [14]. A granular powder of PVA with a molecular weight of 14000 g/mole, obtained from BHD Chemicals Ltd, was dissolved in 10 ml of hot distilled water (~55°C). The solution was continuously stirred magnetically for a duration of 3 hours until a homogeneous viscous solution was obtained. Subsequently, the solution was poured into a glass petri dish with a diameter of 10 cm and left at room temperature (~30°C) for a period of 7 days to allow for the slow evaporation of the solvent. To prepare TiO_2 nanoparticles/PVA composite films with varying amounts of TiO_2 nanoparticles (particle size: 45.7 nm), different quantities of TiO_2 powder (0.007, 0.01, 0.02, and 0.03 g) were mixed with 10 ml of hot distilled water for each sample. Then, 2 ml of the TiO_2 nanoparticles solution was added to the PVA solution to obtain TiO_2/PVA films with a particle size of 45.7 nm. The same method of preparation as described above for the PVA film was followed.

The digital micrometer of type Tesha (0.001) mm was utilized to measure the thickness of the samples, ensuring a measurement exactness within the range of 0 – 150 mm. This micrometer is manufactured in Japan. Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted using the Bruker-Tensor 27 instrument equipped with an ATR unit. The UV-Visible spectrophotometer employed for measuring the transmittance and absorbance spectra of all samples belonged to the T70/T80 series.

Results and Discussions

FTIR spectrum was taken to the films of mixture PVA (0.5g) and doping with particles size of TiO_2 (45.7) nm with amount (0.007, 0.01, 0.02 and 0.03) g and doping with ratio (2 ml) of TiO_2 as shown in Fig. (1). The transmittance bands for film have peaks corresponding to C-H appeared at 834 cm^{-1}, 837 cm^{-1} and 2911 cm^{-1} out-of-plane [15,16]. The presence of peaks at 3400 cm-1 and 1631.78 cm-1 in the spectra can be attributed to the asymmetric vibration of the C-H band. On the other hand, the peaks observed at 1243.88 cm^{-1}, 1088.35 cm^{-1}, 924.68 cm^{-1}, and 918.9 cm-1 in the spectra indicate the stretching vibration of the C-O band. Additionally, the peak at 1731.35 cm^{-1} corresponds to the stretching vibration of the C=O band [15]. The transmittance observed around 1423 cm^{-1} and 1430 cm^{-1} is characteristic of the asymmetric bending vibration of the C-CH_3 bond. Furthermore, a broad band around 3285 cm^{-1} is observed, which corresponds to the O-H bond. These findings are consistent with the results reported by Jalil M.S. [17]. Moreover, the peaks observed at 435.91 cm^{-1}, 466.77 cm^{-1}, and 700 cm^{-1} indicate the bending and stretching modes of the Ti-O-Ti bond, which aligns with the results obtained by Kavitha B. et al [18].

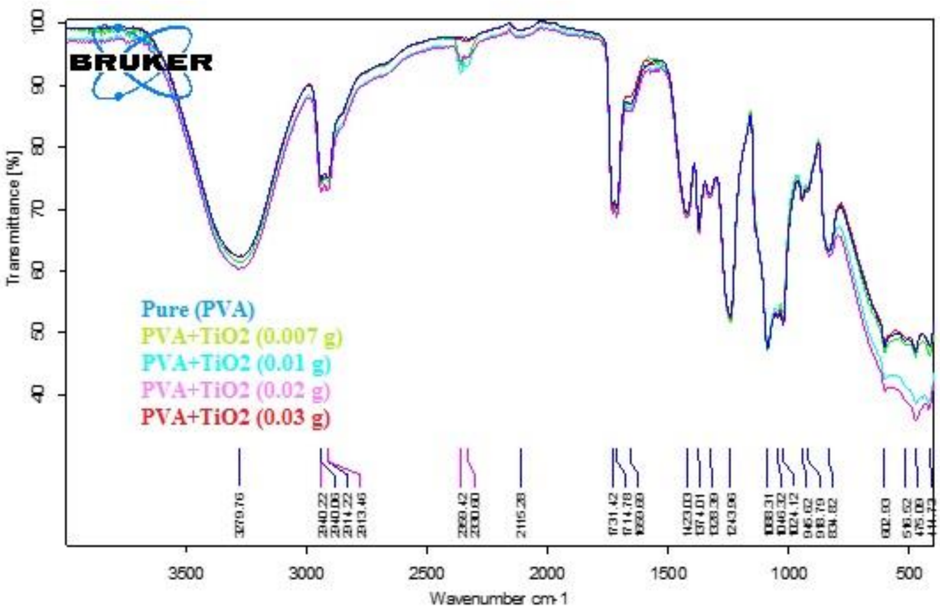

Fig. (1) FTIR spectra for pure PVA and TiO_2/PVA with different amounts of TiO_2

The transmittance spectra for pure PVA and Nano TiO_2/PVA with different amounts of TiO_2 were illustrated in fig. (2). It is obvious that the transmittance for pure PVA is larger than TiO_2/PVA films in UV region, because theTiO_2 nanoparticles particles absorb and scatter light from PVA film. Fig. (3) illustrates the absorption spectra for all samples. There is one peak of absorption spectrum for pure PVA at (275 nm) with intensity (0.113). The intensity of this peak increased with increasing the amount of TiO_2 nanoparticles, but decreased at the amount (0.03 g) of TiO_2 and the maximum absorption wavelength for TiO_2/PVA Films at the amount is (285) nm [11and 13].

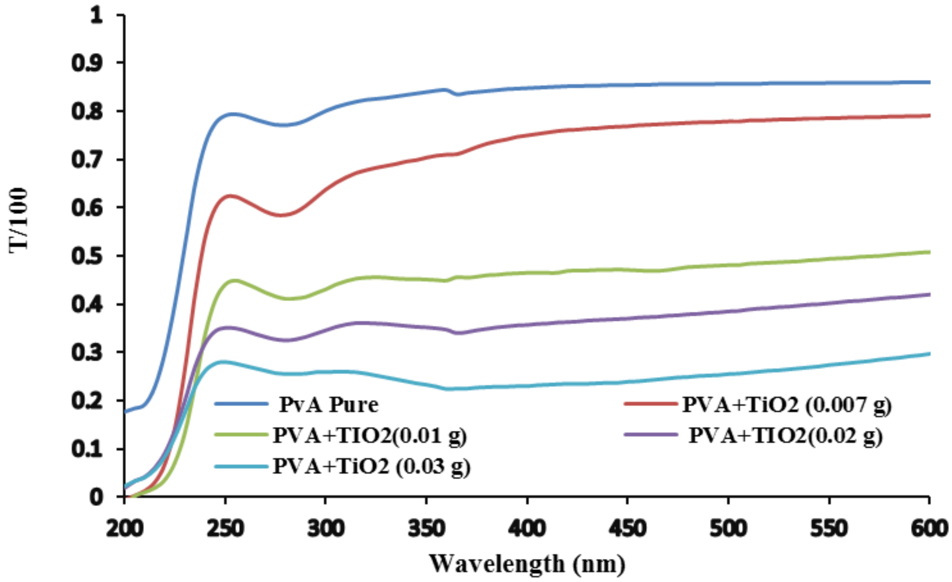

Fig. (2) Transmittance spectra for pure PVA and TiO_2/PVA Films with different amount of TiO_2 nanoparticles

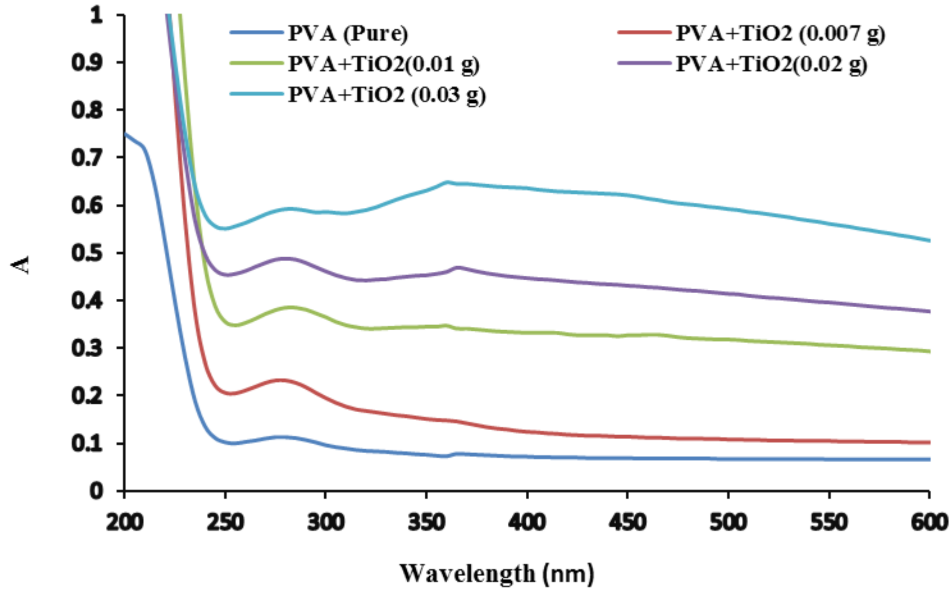

Fig. (3) Absorbance spectra for pure PVA and TiO_2 /PVA Films with different amounts of TiO_2 nanoparticles

The absorption of coefficient (α) is characterized as the capability of a material to absorb the light of a specific wavelength [19]:

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

(1) Where (A) is the absorption of the material, and (t) is the thickness of the sample in (cm). To calculate optical energy gap from eq. (2) [20]:

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

(2)

Where

hυ: photon energy

E_g : Optical energy gap

B: A constant relating to the nature of matter.. For allowed indirect transitions, the constant is denoted as n = 2, while for forbidden indirect transitions, the constant is n = 3. Equation (1) is utilized to calculate the absorption coefficient, which serves as an indicator of the electronic transition's characteristics. It is evident from Figure (4) that the absorption coefficient values are less than $\alpha < 10^4$ cm^{-1}, indicating a clear investigation of indirect electronic transitions. The energy gap value for allowed transitions can be determined using equation (2), as depicted in Figure (5). Table (1) presents the energy band gap for indirect allowed transitions, which decreases with an increase in the amount of TiO_2, as observed by Saleh A.F. et al [10] and Shehap A.M. and S.Akil D. [12]. This behavior can be attributed to the emergence of new energy levels within the band gap, facilitating the efficient movement of electrons from the valence band to localized levels, ultimately transitioning into the conduction band [21].

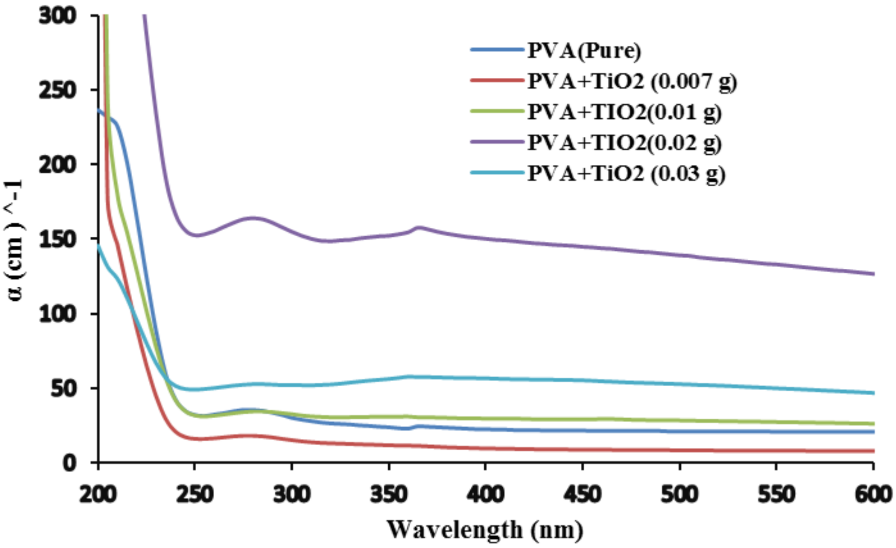

Fig. (4) Absorption coefficient for PVA and TiO_2/PVA films with different amounts of TiO_2 nanoparticles

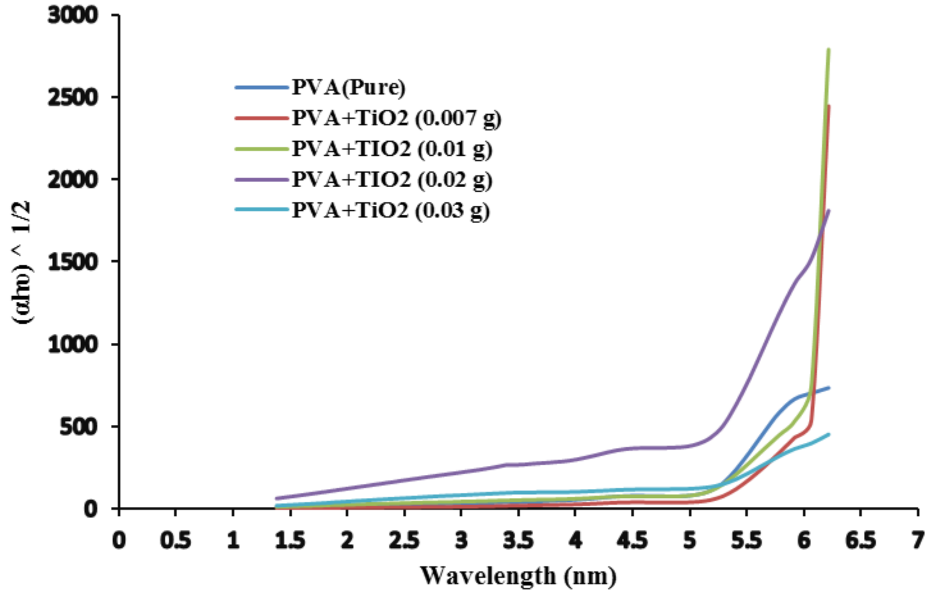

Fig. (5) The allowed indirect transition for PVA and TiO_2/PVA films with different amounts of TiO_2 nanoparticles

Table (1) Optical properties of Pure PVA and TiO_2/PVA films with different amounts of TiO_2 nanoparticles

Substance	λ(nm)	Intensity	Thickness (cm)	Energy gap (eV)
Pure (PVA)	275	0.113	0.0073	5.15
PVA+TiO_2 (0.007 g)	280	0.232	0.02925	5.40
PVA+TiO_2 (0.01 g)	280	0.385	0.02565	5.55
PVA+TiO_2 (0.02 g)	280	0.488	0.00685	5.00
PVA+TiO_2 (0.03 g)	285	0.255	0.02580	4.90

The index of refraction of a material, denoted by the parameter (n_o), is defined as the ratio of the velocity of light in vacuum to the velocity of light in the sample [22, 23].

$$R = \frac{(n_o - 1)^2 + K_o^2}{(n_o + 1)^2 + K_o^2} \quad (3)$$

Also, (k_o) The calculation of the extinction coefficient was performed by utilizing equation (4).

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

When k ⇉ Zero

$$R = \frac{(n_o - 1)^2}{(n_o + 1)^2} \quad (5)$$

$$n_o = \frac{(1 + R)^{1/2}}{(1 - R)^{1/2}} \quad (6)$$

The reflection spectrum, as computed using equation (5) and depicted in Figure (6), indicates that the reflection for pure PVA is minimal at a wavelength of 280 nm. By analyzing the reflection spectrum, the refractive indices were determined using equation (6) and are presented in Figure (7).

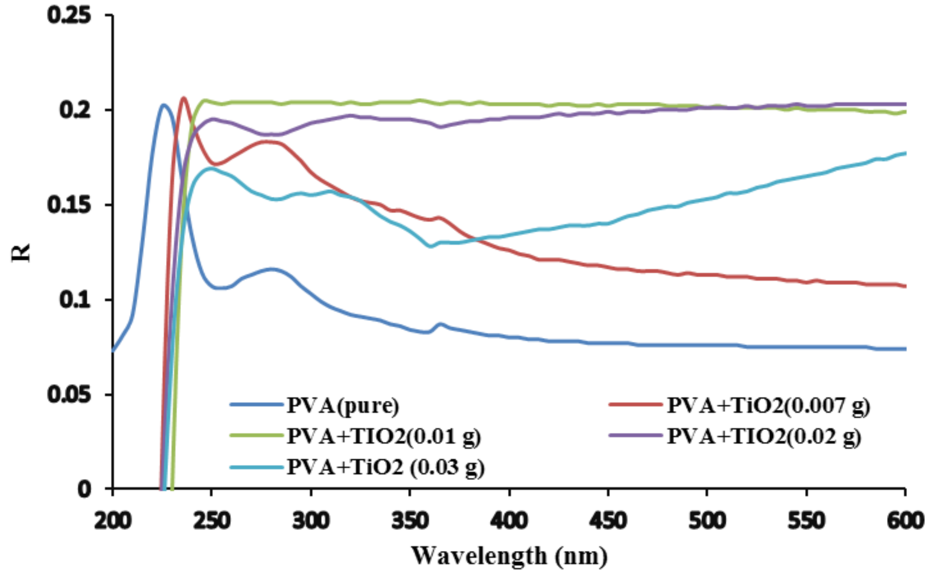

Fig. (6) Reflection spectrum for PVA and TiO_2/PVA films with different amounts of TiO_2 nanoparticles

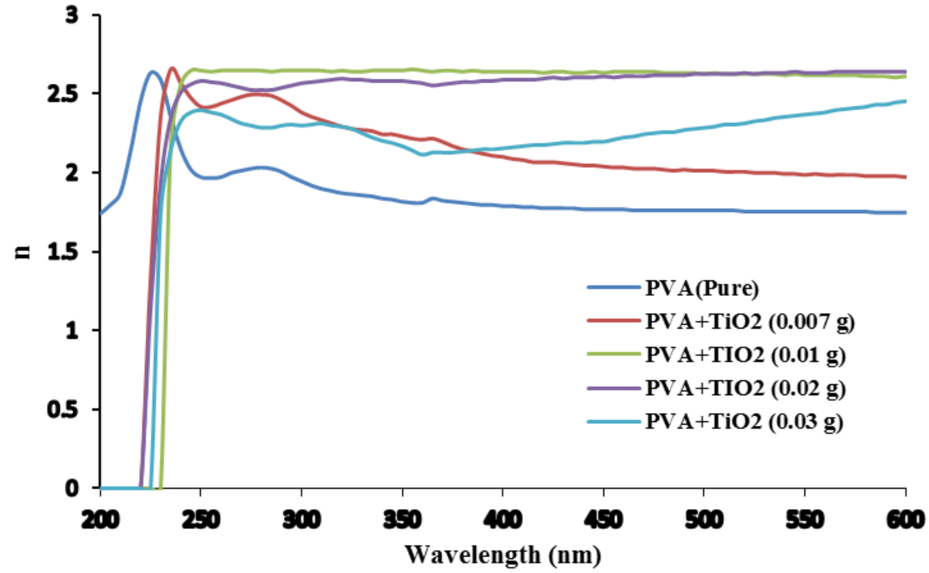

Fig. (7) Refractive index for PVA and TiO_2/PVA films with different amounts of TiO_2 nanoparticles

The Dielectric constant is characterized as the reaction of the material across the incident electromagnetic field. The dielectric constant of compound (ε) is partitioned into two types real (ε_r), and imaginary (ε_i). The equations were employed to ascertain the values of the real and imaginary components of the dielectric constant (ε_r and ε_i) [24].

$$\varepsilon_r = n_o^2 - K_o^2 \tag{7}$$

$$\varepsilon_i = 2\, n_o K_o \tag{8}$$

The extinction coefficient obtained from equation (4) along with the real and imaginary dielectric constants derived from equations (7) and (8) were calculated and graphed in Figures (8) to (10), correspondingly.

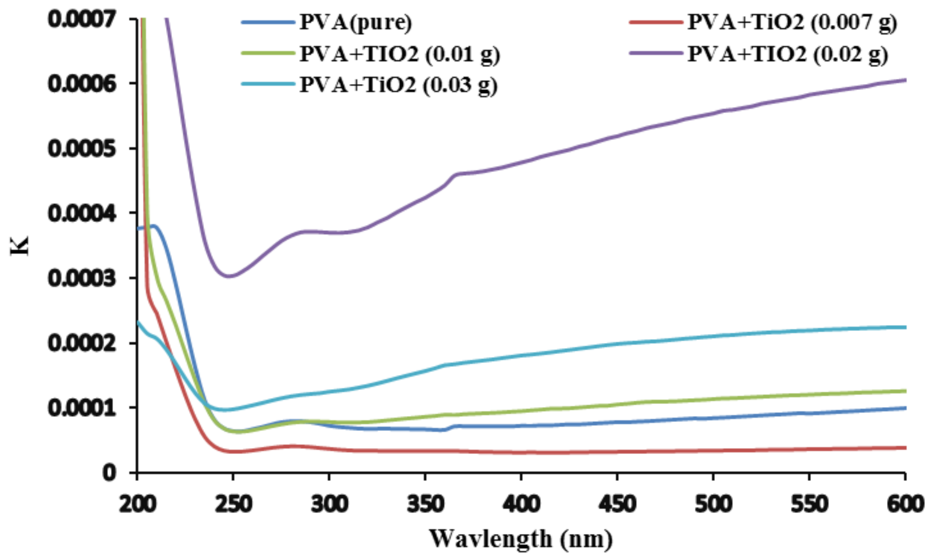

Fig. (8) Extinction coefficient for PVA and TiO_2/PVA films with different amounts of TiO_2 nanoparticles

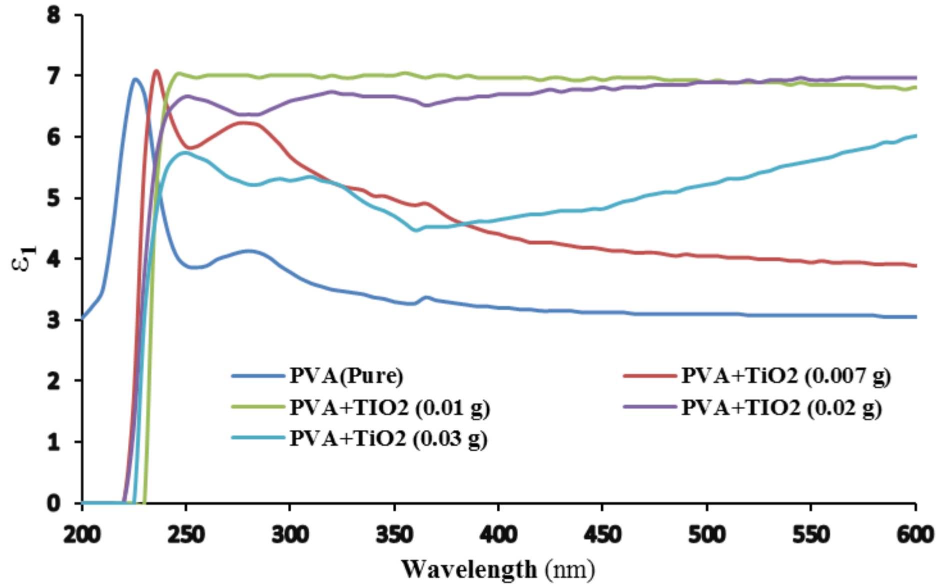

Fig. (9) Real dielectric constant for PVA and TiO_2/PVA films with different amount of TiO_2 nanoparticles

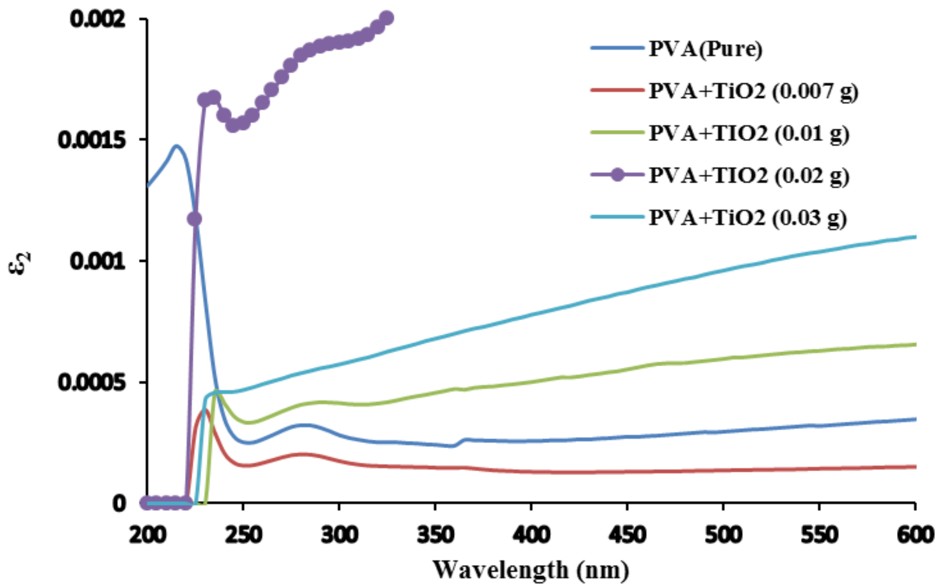

Fig. (10) Imaginary dielectric constant for PVA and TiO_2/PVA films with different amounts of TiO_2 nanoparticles

Conclusion

The FTIR spectra of all samples exhibit similar peak patterns, although variations in transmittance intensity are observed, with intensity levels rising as the quantity of TiO_2 nanoparticles increases. The introduction of TiO_2 nanoparticles influences the optical properties, resulting in a decrease in the energy gap, ranging from (5.15 to 4.90) eV. Titanium oxide nanoparticles are crucial in altering the optical characteristics of PVA, enhancing its suitability for various applications. There are numerous applications where this technology can be advantageous, such as in optoelectronics, photovoltaics, laser systems, photovoltaic cells, sensors, photocatalytic mechanisms, light filters, and ultraviolet light detectors, among others.

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مستخلص البحث:

في هذا البحث، تم تحضير الاغشية الرقيقة لبوليمر فينيل الكحول النقي وبوليمر بولي فنيل الكحول المطعم بجسيمات التيتانيوم النانوية بكميات مختلفة (0.007، 0.01، 0.02. و0.03) غرام بطريقة صب المحلول. أطياف FTIR لجميع العينات المقاسة في وضع النفاذية. تأثير إضافة جزيئات جسيمات التيتانيوم النانوية يظهر بوضوح من خلال تغيير النفاذية بينما لم يتأثر سلوك طيف بوليمر بولي فينيل الكحول. تم قياس الخصائص البصرية في مدى الطول الموجي (200-800) نانومتر. أظهرت النتائج التجريبية أن امتصاصية أغشية PVA/ TiO_2 تزداد مع زيادة كمية جزيئات جسيمات التيتانيوم النانوية. توجد قمة واحدة لطيف الامتصاص لـ PVA النقي عند (275 نانومتر) وبكثافة (0.113). بينت اختبارات UV-VIS إلى أن خصائص الحماية من الأشعة فوق البنفسجية للأغشية المطعمة قد تم تعزيزها بشكل كبير نتيجة لإضافة جسيمات التيتانيوم النانوية. انخفضت قيم فجوة الطاقة مع زيادة كمية جزيئات ثاني أكسيد التيتانيوم النانوية من (5.15 إلى 4.90) إلكترون فولت.

الكلمات المفتاحية: جسيمات التيتانيوم النانوية، اغشية بولي فينيل الكحول، اطياف FTIR، الخصائص البصرية، فجوة الطاقة.