The Effects of Additive TiO_2 Nanoparticles on the Optical properties of DCM Doped with PVC Thin Films

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Abstract: In this work thin films containing laser dye (DCM) doped with (PVC) were prepared using casting method. Titania (TiO_2) nanoparticles also were synthesized using sol-gel technique. Different titania nanoparticle densities (0.882×10^{20}, 1.765×10^{20}, 2.648×10^{20} and 3.530×10^{20} cm^{-3}) were co-doping with dye doped polymer to study the effect of this addition on the optical properties and electronic transition energy gaps in cases of both direct and indirect transitions, Absorbance spectra were measured using Spectrophotometer. Absorption and extinction coefficients as well as the refractive indices have been obtained the spectra of absorbance at the strong absorption region. It was observed from results that the allowed direct electronic transitions energy gap was decreasing from 2.22 to 2.175e.V with the increasing of titania nanoparticles density and the allowed indirect electronic transition energy gap decreasing from 2.19 to 2.13e.V.

Keywords**:** Thin films, Cast method, Optical properties, Poly Vinyl chloride(PVC), DCM, TiO_2 nanoparticle.

1.Introduction

Polymer are substances made up of recurring structural unites, each of which can be regarded as derived from a specific compound called a monomer. In other mean a polymer is a chemical compound where molecules are bonded together in long repeating chains. These materials have unique properties and can be tailored depending on their intended purpose [1]. Over 30 years polymers were considered as a futuristic new material that would lead to the next generation of electronic and optical devices[2] due to the different optical properties of polymers, it has applications in sensors, light-emitting diodes and solar cells[3].These materials have several advantages such as easy processing, low cost, flexibility ,high strength and good mechanical properties [4]. A thin film is a layer of material having thickness of the order of few nanometers .The properties of thin films differ significantly from those of bulk due to surface and interface effects [5].Polymer blend represents very important field in processing of new materials which has better properties in comparison with the pure polymers. Polymer thin film technology has made tremendous advancement in the last decade because of the range of technological applications [6,7] . The preparation of polymer films containing dispersed metallic clusters or metallic nanoparticles has been of great interest[4]. In the last years, the polymer doped with metal oxide nanoparticles have been studied as alternative materials for optical applications, including planar waveguide devices and micro optical elements [8].The polymers modified by metal oxide nanoparticles have been prepared by sol-gel process, by polymerization of monomer containing nanoparticles and by dispersing of nanoparticles in a polymeric matrix. The presence of nanoparticles in polymer improves the mechanical, electrical and optical properties of the material and it is possible to control these properties including the refractive index by concentration [9].Titanium dioxide nanoparticles have grasped a great attention their worldwide due to their potential applications. TiO2 nanoparticles have a special place because of its good stability, high refractive index**,** hydrophilicity, UV absorbance , nontoxicity and excellent transparency for the visible light[10]. TiO_2 nanomaterials are so far used in many technological applications as a photocatalyst, photovoltaic material, gas sensor, optical coating, structural ceramic, electrical circuit varistor, biocompatible material for bone implants, and spacer material for magnetic spin valve systems etc. [11]. Two effects of TiO2 are commonly known; first the high refracting index and the associated effect of light scattering and second the degradation effect on polymer matrices[12]. Polymerization of Vinyl chloride (monomer) results in the production of poly Vinyl chloride or PVC, which is its abbreviated name. Pure PVC is white in color .PVC is one of the most used plastic materials in the world , It is economical and highly resistant to chemicals , by adding some additives ,it can be made ductile and elastic. PVC is used for making a variety of products across industries because of its cheap price, easy processing and chemical properties .It is widely used for making construction profiles , medical devices , roofing membranes ,credit cards ,electric cables, sheets, children`s toys, sewerage pipes, gas pipes , clothing and furniture. Around 50 percent of PVC manufactured is used in construction [13].In this study TiO_2 nanoparticles were prepared using sol-gel method, and then co-doped with the mixture of DCM laser dye and PVC polymer solutions to obtain the final samples. One of the important organic materials that used in this study is the fluorescent dyes, which are organic molecules with aromatic ring structures. The organic laser dye used in this work is DCM, [2-[2-[4-(dimethyl amino) phenyl] ethenyl]-6-methyl-4H-pyran-4-ylidene]-propanedi nitrile and the chemical formula is $C_{19}H_{17}N_3O$, which mixed with TiO_2 nanoparticles synthesized via sol-gel method and doped with PVC polymer of the chemical formula $(C_2H_3Cl)n$ to prepare thin films [14].

2. Materials and Experimental Method

Laser dye solutions were prepared by dissolving the required amount of the DCM dye in THF in order to obtain the final concentration of dye solution was $5x10^{-3}$ mol/liter. Titanium dioxide nanoparticles were prepared by using the sol-gel method. A 10ml titanium alkoxide, as the raw material, was mixed with 40 ml of 2-propanol in a dry atmosphere conditions. This mixture was then added dropwise into another mixture consist of 10 ml distiller water and 10 ml 2-propanol.In order to investigate the effect of pH upon the sample properties, hydrochloric acid or ammonium hydroxide was added, which adjusted the acidity-alkalinity of the gel the value of pH3. A yellowish transparent gel was formed after one hour stirring and the obtained gel then dried at 105^{o}C for several hours until it turned into a yellow block crystal. Calcinations of the synthesized materials were carried out at 500°C for six hours in a furnace.

To prepare PVC doped with DCM thin films, firstly dissolving 0.0225gm of DCM in 15ml THF solvent and stirrer about 30 minutes to obtain homogenous solution, then 3gm of PVC was dissolve in 50ml of THF for one hours vigorous stirring to get the polymer solution. To synthesis the final thin films, 1ml of DCM solution mixed with 5ml of PVC solution and casting on glass substrate at room temperature. TiO_2 nanoparticles densities were obtained as (0.882×10^{20} , 1.765×10^{20}, 2.648×10^{20} and 3.530×10^{20} cm^{-3}) were suspended in THF solvent and added to the mixture of DCM-PVC. The final films labeled as (A, B, C and D) as the nanoparticles density increasing respectively.

Thin films thickness was measured using the optical interferometer method employing He-Ne laser 0.632µm, with incident angle 45° . The optical absorption and transmission spectra of DCM doped with PVC thin films were recorded using UV-VIS double beam spectrometer in the wavelength range from 190 to 1100 nm.

3.Results and Discussions

The final films labeled as (A, B, C and D) as the nanoparticles density increasing (0.882×10^{20} , 1.765×10^{20}, 2.648×10^{20} and 3.530×10^{20} cm^{-3}) respectively .The absorption spectra for PVC doping with DCM and TiO_2 nanoparticles thin films at room temperature shown in figure (1). It is clearly shown that appear single peak at 502nm and it is obviously that the absorbance increases with increasing titania nanoparticles density increasing, this is refer to increase the number of titania nanoparticles that is denominate and decrease the role of polymer or due to aggregates such as dimmers.

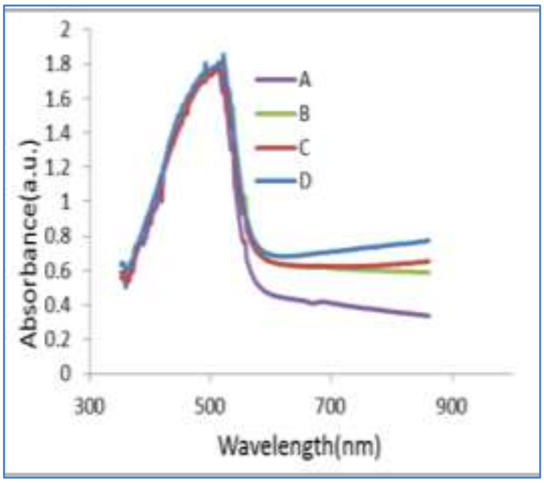

Fig.(1): Absorbance spectra for PVC doped with DCM thin films mixed with different particle density of TiO_2.

Reflectance spectra for prepared thin films were recorded at room temperature and illustrated in figure (2). One can observe from the reflectance spectra that the increasing in the nanoparticles density leads to decrease the intensity of reflection, it is suggested that the presence of titania nanoparticles in starch-based polymer improved the UV-shielding property of the polymer.

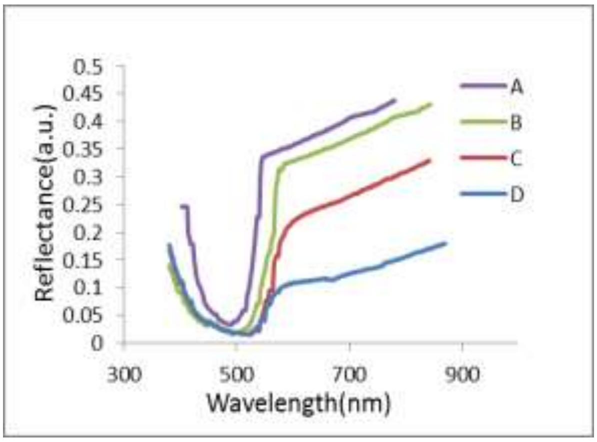

Fig.(2): Reflectance spectra for PVC doped with DCM thin films mixed with different particle density of TiO_2.

The absorption coefficient (α) was calculated by using the equation [15]

$$\alpha = \frac{2.303}{d} A \qquad (1)$$

Where A is absorbance and d is thickness of the thin film. Figure (3) shows the absorption coefficient for PVC doped with DCM thin films mixed with different particle density of TiO_2.The absorption coefficient of final films increased sharply in the UV and visible region range, and then decreased gradually in the end of visible region because it is inversely proportional to the transmittance. This can be linked with increase in grain size and it may be attributed to the light scattering effect for its high surface roughness [16].

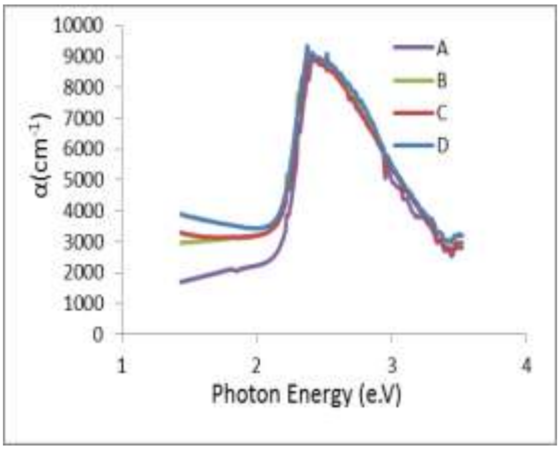

Fig.(3): Absorption coefficient spectra for PVC doped with DCM thin films mixed with different particle density of TiO_2.

From the reflectance data, the refractive index (n) of the thin films calculated from the equation [17,18]

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \qquad (2)$$

Where R is reflectance .

Figure (4) shows the variation in refractive index of PVC doped with DCM thin films mixed with different particle density of titania nanoparticles in the wavelength range of (300-900) nm. The increase in the titania particle density results in a decrease in the refractive index in the visible region and the refractive index increases as the wavelength increases in the infrared range. This trend shows an increase of the value of refractive index with higher particle density. The increase may be attributed to higher packing density of the films and hence caused change in the refractive index[19].

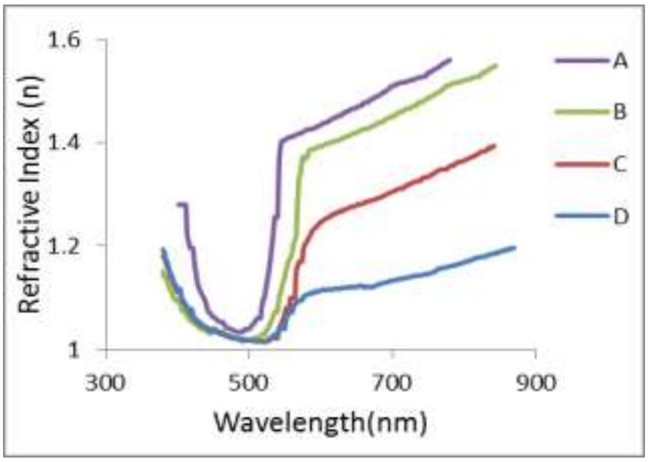

Fig.(4):Refractive Index against the Wavelength

The extinction coefficient K is directly related to the absorption of light and related to absorption coefficient by the equation [20]

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

The curves of extinction coefficient for PVC doped with DCM thin films are shown in figure (5). It is observed that the excitation coefficient behaves in the same behavior of absorption coefficient because of its association with the previous relationship, where the extinction coefficient increasing with increasing of particle density.

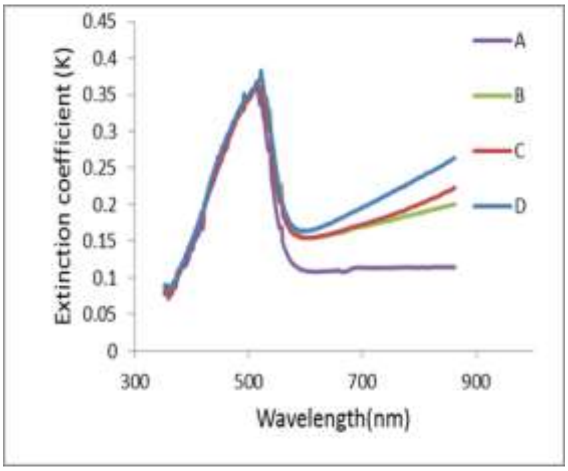

Fig.(5): Extinction coefficient against the wavelength

Figure (6) shows the variation of optical conductivity as a function of wavelength for different titania nanoparticle densities. The optical conductivity(σ) is calculated by using equation [21]

$$\sigma = \frac{\alpha n c}{4\pi} \quad (4)$$

From figure (6), one can see that the optical conductivity increased with increasing wavelength. This suggests that the increase in optical conductivity is due to electron exited by photon energy, and the optical conductivity of the films increased with increasing of particle density. High absorption of thin film behavior is due to the photon-atom interaction this effect increased the optical conductivity.

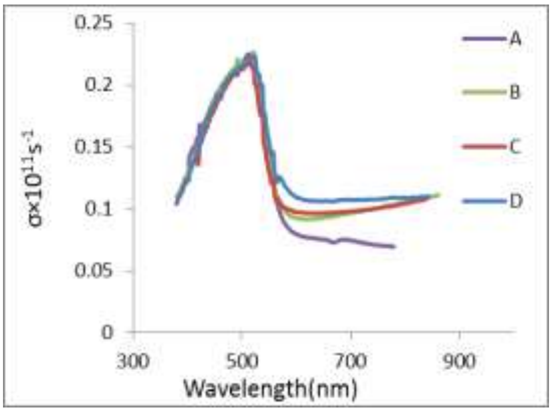

Fig.(6):Optical conductivity as a function of wavelength.

Both real (ε_r) and imaginary (ε_i) dielectric constant are measured for prepared films by using relations [22]

$$\varepsilon_r = n^2 - K^2 \quad (5)$$

$$\varepsilon_i = 2nK \quad (6)$$

Figures (7) and (8) illustrate variation of (ε_r) and (ε_i) as a function of wavelength. The figures show that in all samples the real part behaves like the refractive index because of the smaller value of (K^2) compared to (n^2), while (ε_i) depends mainly on the (K).

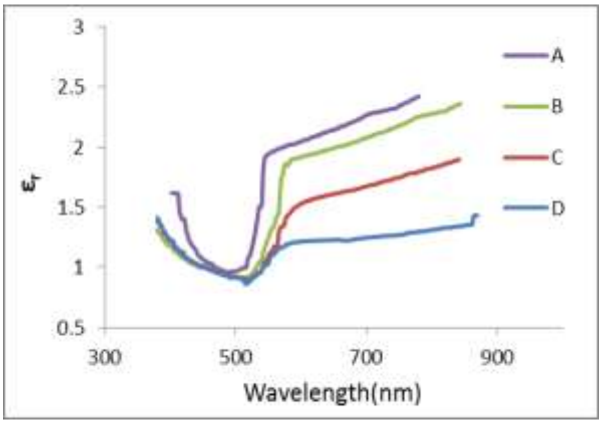

Fig.(7):Real part dielectric constant against the wavelength

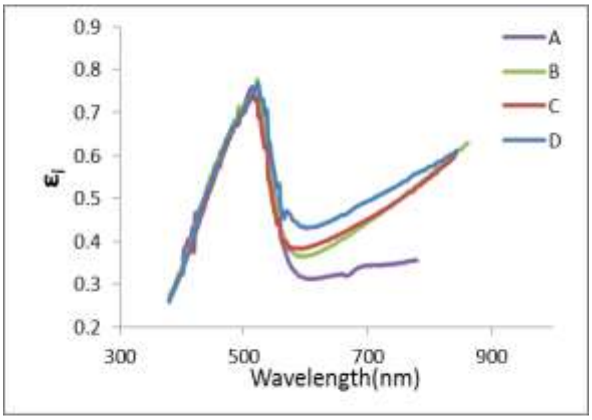

Fig.(8): Imaginary part dielectric constant against the wavelength

The direct allowed and forbidden transitions happen between near top points of valance band (V.B.) and bottom points of covalent band (C.B.), the absorption coefficient for these transitions type is given by [23]

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

Where υ is frequency of incident photon, B: constant depended on type of material E_g: energy gap between direct transition , and r: exponential constant and its value depends on type of transition, where

r =1/2 for the allowed indirect transition.

r = 2 for the allowed direct transition.

The relations between $(\alpha h\upsilon)^2$, $(\alpha h\upsilon)^{1/2}$ and photon energy (hυ) were drawn as depicted in figure (9) and figure (10) respectively and are use to calculate both allowed direct and indirect energy gaps.

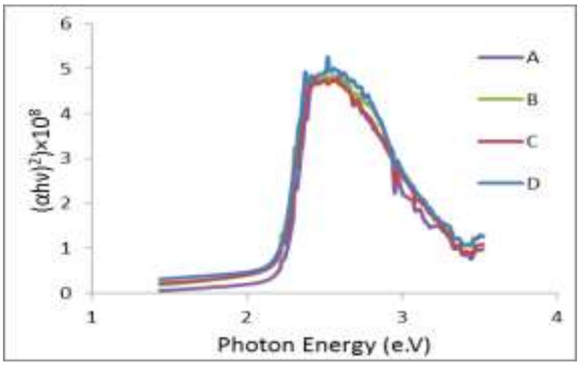

Fig.(9): Relationship between $(\alpha h\nu)^2$ and photon energy (e.V)

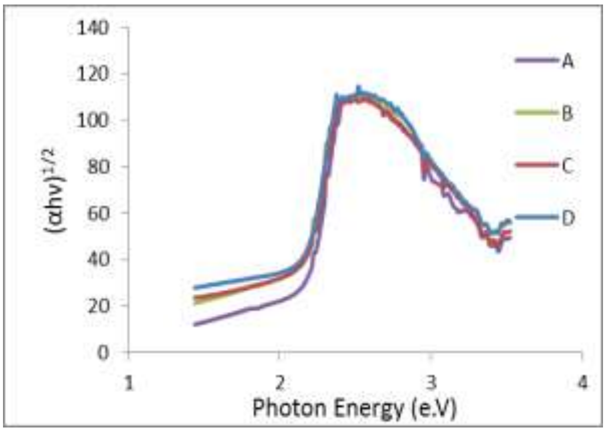

Fig.(10): Relationship between $(\alpha h\nu)^{1/2}$ and photon energy (e.V)

The energy gap value depends on the films deposition conditions. The energy gap values for direct and indirect for all thin films are summarized in table (1).

Table (1) the energy gap values for direct and indirect for all thin films

Sample	Particle density of TiO_2(cm^{-3})	Allowed direct band gap (e.V)	Allowed indirect band gap (e.V)
A	0.882×10^{20}	2.22	2.19
B	1.765×10^{20}	2.19	2.17
C	2.648×10^{20}	2.183	2.16
D	3.530×10^{20}	2.175	2.13

From table (1) and the figures (9 and 10), it can be observed that (E_g) in direct transitions is decreasing with the increasing of titania nanoparticles density for all films This results was in a good agreement with [24].Particle density led to increased levels of localized near valence band and conduction band and these levels ready to receive electrons and generate tails in the optical energy gap and tails is working toward reducing the energy gap.

Conclusion

Nanostructured titanium dioxide is prepared using sol gel method and doping in the DCM-PVC matrix, was directly affected on the optical properties of the PVC thin films. The optical absorption coefficient (α) of PVC doped with DCM thin films mixed with different particle density of titania nanoparticles is about ($\alpha > 10^3 cm^{-1}$). This converts to a large probability that direct electronic transition will happen. Also these films have allowed direct transition and allowed indirect transition. Increasing of the particle density for all films cause a decrease in the optical band gap value and intensity reflection and an increase in the optical constants extinction coefficient, imaginary part of the dielectric constant and optical conductivity.

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