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Effect of annealing temperature on the optical properties of DCM-PS doped with TiO_2 nanoparticles thin films

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IJSER **Abstract**— Polystyrene (PS) blended with DCM laser dye co-doped with TiO_2 nanoparticles thin films were prepared using cast method. The TiO_2 nanoparticles was synthesized using sol-gel technique and the characteristics of these nanoparticles were investigated using XRD to estimate the phase of TiO_2, while the scanning electron microscope (SEM) was used to estimate the particle size. The optical properties of final samples such as absorbance, absorption coefficient, refractive index and the optical conductivity of the prepared thin films were studied under effect of annealing temperature.

Index Terms— Polystyrene, TiO_2 nanoparticles, sol-gel teghnique, Cast Method, Thin Films, energy gap, optical properties

1 Introduction

Polymers have several advantages, such as easy processing, low cost, flexibility, high strength, and good mechanical properties. In the microelectronic fabrication industry, polymers are used in the photolithography process. Polymer blending is the simplest technique in polymer engineering for creating new solid materials with more enhanced properties. Polymer blending with other polymer materials or small molecules such asanthracene, pyrene, or pyridine has been performed [1]. Polymer materials have also been mixed with other salts or hybridized with other inorganic/nanoparticle materials to modify the optical properties of the polymer system. All these techniques affect the optical properties of polymers. This work is aimed to understand the fundamental optical properties of PS polymer blended with TiO_2 nanoparticles as inorganic material and DCM laser dye as organic molecule.

Last years the hybrid composites based on nanodispersed semiconducting, ferroelectric or ferromagnetic fillers and polymer hosts have drawn considerable theoretical and practical interest because of their potential of combining properties of individual components and emergence of new and unique qualities connected with nanosized filler particles and features of their formation [2].

Transparent polymeric materials have found one of their most promising applications in lasers, in which they can be used as active elements with lasing dyes, antireflective filters for Q-modulation, laser optics etc. [3, 4]. The solid matrix-dye lasers make possible the combination of the advantages of solid state lasers with the possibility of tuning the radiation over a broad spectral range, which overlaps almost completely the visible region. Polymers like Polystyrene (PS), polyurethane, sol gels and silica gels etc. can be employed as matrices for impregnating laser dyes [5, 6].

Nanoparticle-filled polymers provide advantages over micron-filled polymers because they provide resistance to degradation [7] and improvement in thermo-mechanical properties without causing a reduction in dielectric strength [8].

It is believed that with the development of material science, nanocomposites of TiO_2 and polymershave found further applications in many fields [9]. And due to versatile and the exotic properties, 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. [10].

Two effects of TiO_2 are commonly known; first the high refracting index and the associated effect of light scattering [11]. And second the degradation effect on polymer matrices [12].

The formation of charge transfer complexes between the polymer host matrix and the dopant are observed. In the form of thin films they have many potential applications in batteries [13] and sensors [14]. A fundamental understanding of the properties of polymer thin films is critical for the successful use of soft materials in current and future technologies particularly at the nano scale. Using the copolymers, composites, polymer blends and by doping them, the thermal, electrical, dielectric, mechanical and optical properties can be better achieved. The attention of researchers has drawn to study effect of doping because the optical properties of polymers can be tailored to a specific requirement by the addition of suitable dopant materials.

In this paper, the synthesis of DCM/PS doped with titanium dioxide nanoparticles thin films using casting method was reported and an investigation is undertaken on the optical properties of these films, with a focus on thermal effects on the values of energy gap and refractive index of the films without changing its structure.

2 Experimental part

Laser dye solutions were prepared by dissolving the required amount of the DCM dye in alcohol 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 with 10 ml titanium alkoxide), as the raw material, mixed with 40 ml 2-propanol in a dry atmosphere. This mixture was then added dropwise into another mixture consisting of 10 ml water and 10 ml 2-propanol, in order to inves-

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tigate 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, the obtained gel then dried at 105oC for several hours until it turned into a yellow block crystal. Calcinations of the synthesized materials were carried out at 500ºC for six hours in a furnace.

The nanopowder structure were analyzed with a Shimadzu 6000 X-ray diffractometer using Cu Kα radiation (λ=1.5406Å) in reflection geometry. A proportional counter with an operating voltage of 40 kV and a current of 30 mA was used. XRD patterns were recorded at a scanning rate of 0.08333° s-1 in the 2θ range (20° - 60°). While scanning electron microscopy (SEM) was used to achieve the morphology of TiO_2 samples, and to determine the sizes of nanoparticles. SEM measurements of type (IMA, Germany), which a focused beam of electrons to generate an image or to analyses the surface of specimen.

To prepare PS doped with DCM thin films, firstly dissolving 0.015gm from DCM in 10ml THF solvent and stirrer about 30 minutes to obtain homogenous solution, then 2gm PS dissolve in 30ml THF with 2 hours vigorous stirring to get the polymer solution. To synthesis the final thin films, 1ml DCM solution mixed with 5ml PS solution and stirrer about 10 minutes to get homogenies solution. Then 2.648×1020 particle densities of obtained TiO_2 nanoparticles was suspended in THF solvent and added to the mixture of DCM-PS after that by use then cast method can be casting on glass substrate at room temperature. To study the temperature effect on the optical properties of the films, different temperatures applied on the final samples as 30, 40, 50, 60, 70 oC.

Thin films thickness was measured using the optical interferometer method employing He-Ne laser 0.632μm, and found to 0. 457μm for all samples.

The optical absorption and transmission spectra of DCM doped with PS thin films were recorded using UV-VIS double beam spectrometer in the wave length range from 190 to 1100nm. The absorption coefficient (α) was calculated using the equation [15]

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

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 this transitions type given by [16]

$$\alpha h\upsilon=B(h\upsilon-E_g)^r \qquad (2)$$

Where: E_g: energy gap between direct transition

B: constant depended on type of material

υ: frequency of incident photon.

r: exponential constant, its value depended on type of transition,

r =1/2 for the allowed direct transition.

r =3/2 for the forbidden direct transition.

While in case of indirect allowed and forbidden transitions, the bottom of (C.B.) is not over the top of (V.B.), the electron transits from (V.B.) to (C.B.) not perpendicularly where the value of the wave vector of electron is not equally before and after transition of electron. This transition type happens with helpful of a like particle is called "Phonon", for conservation of the energy and momentum law. The absorption coefficient for transition with phonon absorption is given by [17]

$$\alpha h\upsilon=B(h\upsilon-E_g\pm E_{ph})^r \qquad (3)$$

Where E_g: energy gap for indirect transitions

E_{ph}: energy of phonon, is (+) when phonon absorption and (-) when phonon emission

(r = 2) for the allowed indirect transition

(r = 3) for the forbidden indirect transition

The reflective index (n) of the thin films calculated from the equation [18]

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

The extinction coefficient can be calculated in terms of the absorption coefficient using the equation [19]

$$K=\frac{\alpha\lambda}{4\pi} \qquad (5)$$

The real and imaginary complex dielectric constant can be expressed by equations (6, 7) respectively [20] [21]

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

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

The optical conductivity of thin films can be calculated using the equation [22]

$$\sigma=\frac{\alpha nc}{4\pi} \qquad (8)$$

3 Result and Discussion

XRD spectrum of the TiO_2 nanoparticles which synthesized via sol-gel technique at pH3 and calcination of the synthesized material was carried out at temperature of 500°C for 6 hours in furnace shown in figure (1).

The anatase phase was identified at 2θ of 25.40°, 38.10°, 48.20°, 53.90° and 55.10° degrees, and the characteristic peak of anatase is sharper and clear to observe, in particular at 25.40° degree.

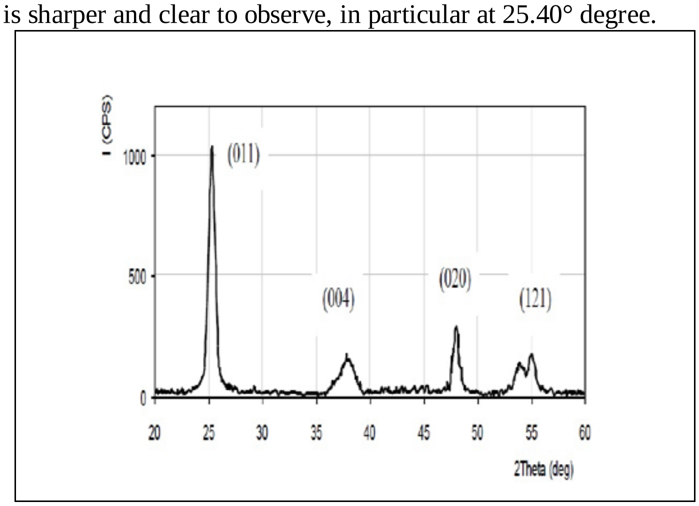

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Figure (1) XRD spectrum of TiO_2 nanoparticles

The scanning electron microscope (SEM) image of TiO_2 nanoparticles is presented in figure (2). Titania particle size determination was carried out with (SEM) after preparing TiO_2 at pH3 and 500oC calcination temperature, the nanoparticles then suspend as film using spin coating process. The corresponding value of the TiO_2 nanoparticles size is about (55nm).

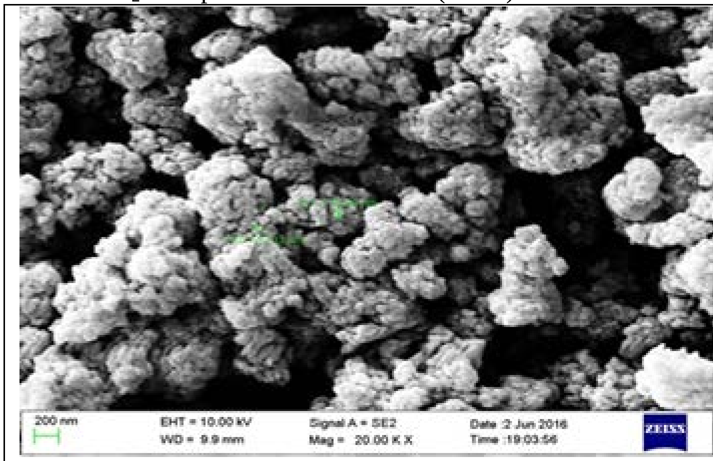

Figure (2) Scanning electron microscope of the TiO_2 nanoparticles

Figure (3) shows the absorption spectra of samples at different annealing temperatures (30, 40, 50, 60 and 70)^{o}C respectively under investigation the range 300-800nm which is the convenient spectral region. In the UV-region, the absorption increases as the wavelength increases for all samples, and there are absorption bands in the visible region since the sample is semitransparent. Also one can see that the absorption edge has been slightly changed (decreasing) with increasing annealing temperature.

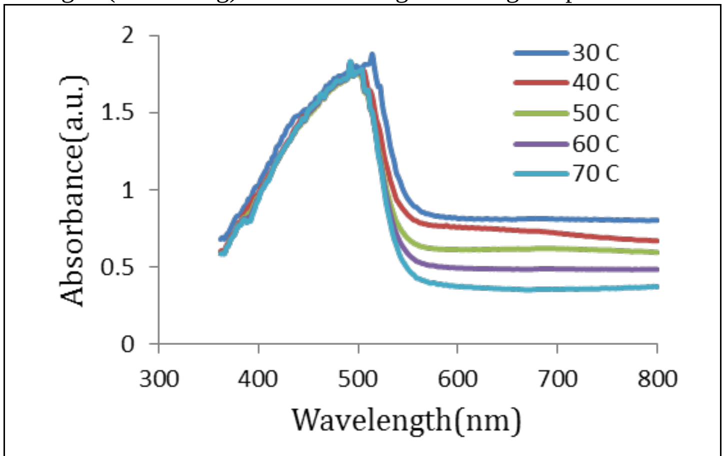

Figure (3) Absorbance for DCM-PS doped with TiO_2 nanoparticles thin films at different annealing temperatures

Figure (4) shows the dependence of the reflectance for all thin films on the wavelength at different annealing temperatures. It is clear that the reflectance decreases with increasing the photon energy (low wavelengths; UV-region), but the middle of visible region it will increase as the photon energy increases. Also it can be seen from figure (4) that the reflectance affected with change the annealing temperature, as the annealing temperature increase the reflectance decreases slightly.

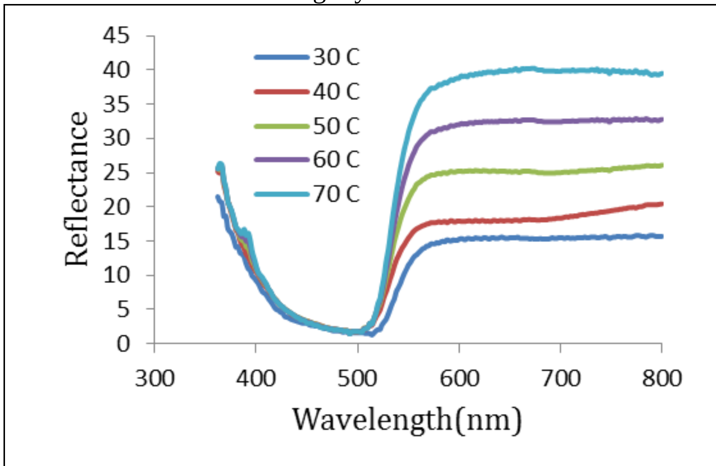

Figure (4) Reflectance for DCM-PS doped with TiO_2 nanoparticles thin films at different annealing temperatures

The absorption coefficient was calculated using equation (1) and the result shown in figure(5) which shows the variation of absorption coefficients for DCM-PS doped with TiO_2 nanoparticles thin films at different annealing temperatures, the absorption coefficient ($\alpha > 10^4 cm^{-1}$) is related to direct band transitions. The energy gaps of thin films were estimated using equation (2).

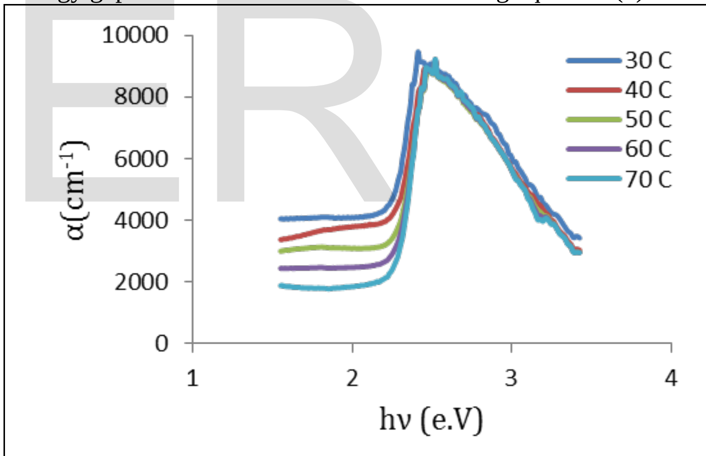

Figure (5) Absorption coefficient for DCM-PS doped with TiO_2 nanoparticles thin films at different annealing temperatures

The variation of $(\alpha h\nu)^2$ as the incident photon energy ($h\nu$) of DCM-PS doped with TiO_2 nanoparticles thin films at different annealing temperatures was shown in figure (6). The optical band gap was determined by extrapolating the linear portion of this plot at $(\alpha h\nu)^2=0$ which indicates that the direct allowed transition dominates in the DCM-PS doped with TiO_2 nanoparticles thin films.

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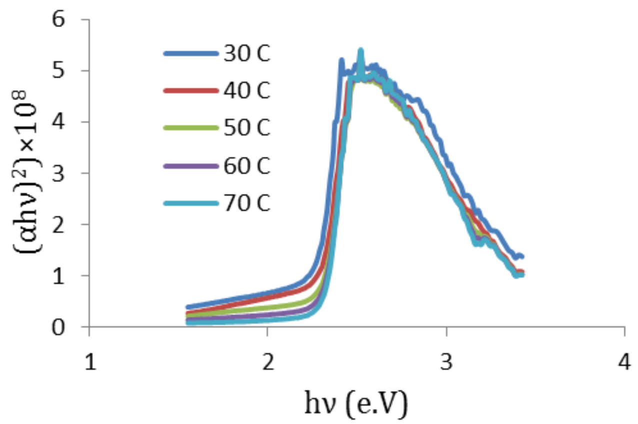

Figure (6) Relationship between (αhv)2 and photon energy (e.V)

Figure (7) shows the variation of $(\alpha h\nu)^{1/2}$ with photon energy , which used to estimate the indirect energy gap and the phonon energy with helping of equation (3).

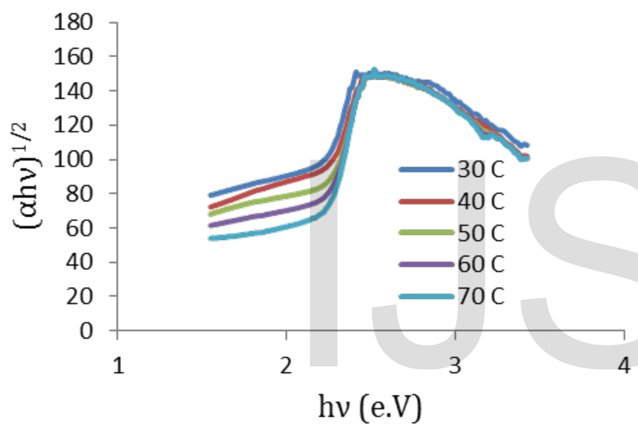

Figure (7) Relationship between $(\alpha h\nu)^{1/2}$ and photon energy (e.V)

The energy gap values for direct and indirect for all thin films at different annealing temperatures are summarized in table (1).

TABLE (1) ELECTRONIC TRANSITIONS ENERGY GAP (E.V) AND PHONON ENERGY (E.V) FOR PS/ DCM DOPED WITH TiO_2 NANO-PARTICLES THIN FILMS.

Temperature (°C)	Allowed direct band gap (e.V)	Allowed indirect band gap (e.V)	Allowed indirect phonon energy (e.V)
30	2.28	0.13	1.89
40	2.24	0.15	1.77
50	2.22	0.21	1.65
60	2.18	0.22	1.6
70	2.14	0.22	1.52

From table (1), it observed that allowed direct band gap will decrease from (2.28-2.14eV) with increasing the annealing temperatures from (30-70 °C). This decreasing may be attributed to increasing in the density of local energy levels with increasing the annealing temperature between the covalent and valance bands. While in indirect electronic transition, one can see that the allowed indirect band gap was increasing with increasing the annealing temperature for all samples and the phonon energy values will decreasing with increasing annealing temperature.

Figure (7) shows the variation of refractive index as a function of wavelength the values of the refractive index decreases slightly with increasing the wavelength in the UV and the beginning of visible regions, but at wavelength more than 500nm it will increasing up to 560nm, then any increasing in wavelength unaffected on the value of refractive index for all samples. Also one can observed from figure (7) there is a slightly change in the refractive index (increasing) with increasing annealing temperature this due to the crystal quality and the grain size [23].

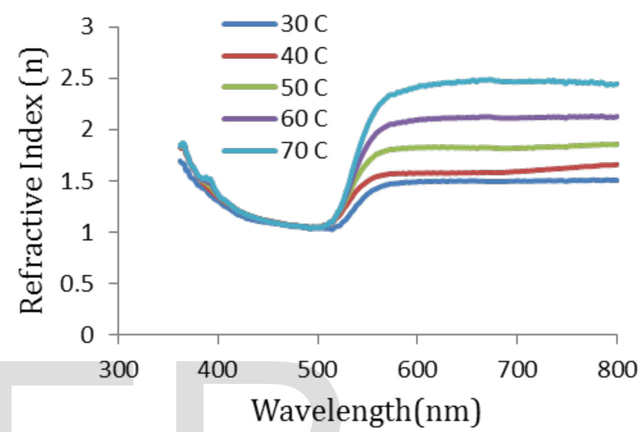

Figure (8) Refractive Index against the Wavelength(nm)

The spectral dependence of the extinction coefficient (K) was obtained using equation (5). Figure (9) shows the relation between (K) and wavelength for DCM-PS doped with TiO_2 nanoparticles thin films at different annealing temperatures. It is clear that the extinction coefficients increase rapidly as the wavelength increase up to (500nm) and then slightly decrease up to (550nm), more than this wavelength any increasing in wavelength unaffected on the value of the extinction coefficient, all the curves have the some behavior but the extinction coefficient decrease as the annealing temperature increase. This might be due to the change in surface morphology during annealing.

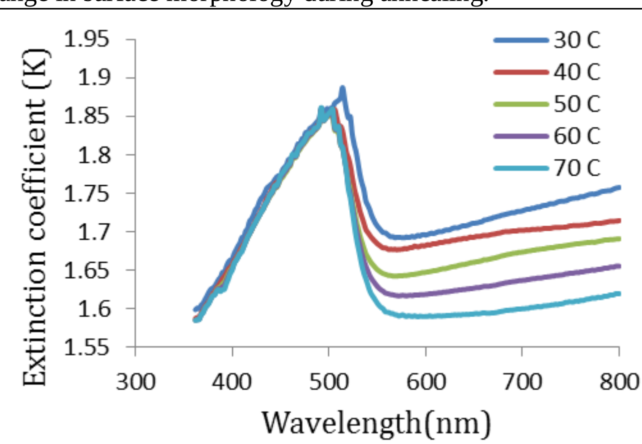

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Figure (9) Extinction coefficient against the Wavelength(nm)

Real (ε_r) and imaginary (ε_i) parts were calculated using equations (6 and 7), and figures (10 and 11) indicate the plot of both (ε_r) and (ε_i) versus wavelength.

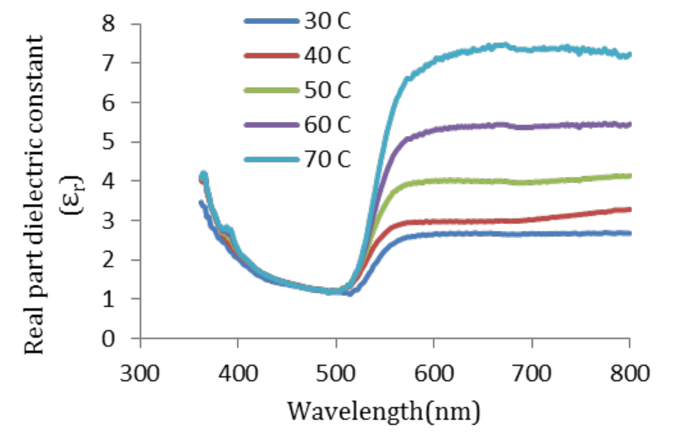

Figure (10) Real part dielectric constant versus the wavelength(nm)

The real and imaginary parts of dielectric constant follow the same pattern as the refractive index and extinction coefficient resplendence of (ε_r) on refractive index and (ε_i) on the value of extinction coefficient and the value of real part are higher than the imaginary parts.

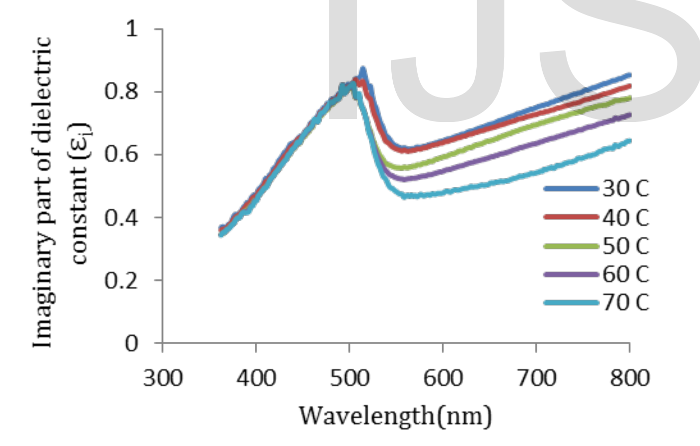

Figure (11) Imaginary part of dielectric constant versus wavelength(nm)

Figure (12) shows the dependence of the optical conductivity for DCM-PS doped with TiO_2 nanoparticles thin films at different annealing temperatures, which calculated using equation (8). It is clear that the optical conductivity increase with increase annealing temperature for all samples.

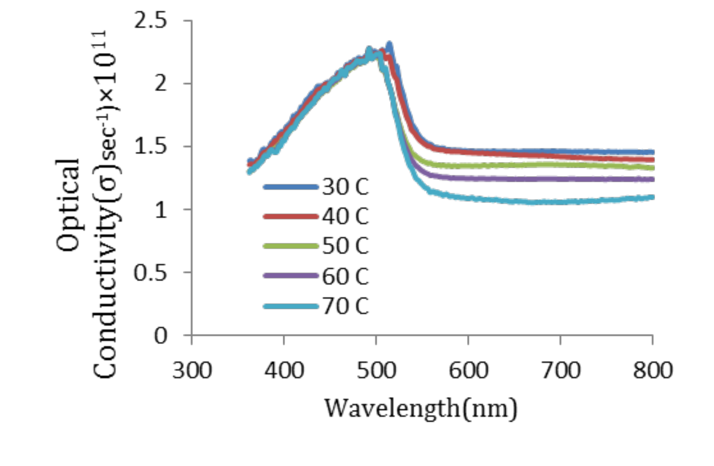

Figure (12) Optical conductivity as a function of the wavelength

4 Conclusion

The effect of annealing temperature on the optical properties of DCM-PS doped with TiO_2 nanoparticles thin films synthesized using cast method was studied. The band gap and the energy of these films in case of direct electronic transitions are decreasing as the annealing temperature increases, but in case of in direct electronic transitions its vice versa. The increasing in annealing temperature causes different effects on the optical properties of the prepared samples, such that the absorption, absorption coefficient, reflectance, extinction coefficient, and the real part of dielectric constant are decrease as the annealing temperature increasing. While the refractive index, imaginary part of dielectric constant, and the optical conductivity of prepared thin films are increase as the annealing temperature increasing

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