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Characterizations of DCM/PS Co-Doped Anatas Particulates Thin Film Underwent the Annealing Treatments

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Abstract

In this research, the thin films of DCM/PS mixed Titanium dioxide (TiO_2) nanopowder were prepared using the casting procedure. Titanium dioxide nanopowder was synthesized via the sol-gel method. Nanoparticulates depicts was analyses with X-Ray Diffraction. 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. The optical absorption edge characterized using Tauc formula and the energy band gaps that of allowed electronic transitions for the designed specimens have calculated. The dispersion of the refractive index is debated in expressing of the single-oscillator Wemple DiDomenico model. Fineness coefficient, critical (climacteric) angle and Brewster angle determined through refractives indices and reflectance.

Keywords: Polystyrene; Particulates Titanium Dioxide; Casting Route; XRD

INTRODUCTION

Optical polymer properties built on the interaction through the electromagnetic radiation and charge contained in the material such as charges ionic or electronic addition to kinds of the allocation of these charges [1]. Knowledge of the optical polymers properties gives to obtain acquaintances interested with the internal-structure and physical of the materials bonds. Consideration of the visible spectrum awards a conception of the scope to using materials in several applications. Therefore, the study for ranges of ultraviolet spectrum helps a thought of the energy package and the quality of transitions [2]. Changes of heat treatments have a significant and direct influence on physical properties of polymers because the local movement of polymer chains depends on the temperature [3]. Polystyrene is very little pricing as well wide the use for many applications. It's the main characteristics take in solidity, transparency, high refractive index, good electrical isolation characteristics, weak water absorption, and easiness of coloring and treatment as mention [4].

A more paramount restriction of polystyrene in many applications is its brittleness. This limitation led up to examination a mixture of polystyrenes with material having rubber properties [5]. Polymers were also blended with other salts or interbreed with other inorganic nanoparticle materials to modulate the optical polymer properties. Most of used techniques have affected the optical polymers properties. In this investigation, predominantly to understanding the essential optical properties of PS-polymer mixture with Titanium dioxide (TiO_2) Nano particulates as inorganic material and DCM laser dye as organic molecule. Solid-state dye lasers, involving of an organic laser dye dissolved in a solid matrix, have been the topic of nearly four decades ago. The dyes, most commonly dissolved in sol gels or polymers. Solid-state dye lasers exhibit functional advantages such as compactness as well as lessening some disadvantages related with the fiery and volatile organic solvents used in liquid dye lasers [6]. (TiO_2) is the most extensively studied photo-catalytic material, with outstanding chemical and physical properties.

On excitement, electrons are advanced to the conduction band and holes are then consequently created in its valence band. Such charge carriers are able to reduce and oxidize many species adsorbed on the semiconductor particles and motivate the oxidative annihilation of organics up to their mineralization [7]. One of the important organic materials that used in the current study is the fluorescent dyes, which are organics moleculas with aromatic ring structures, which possess delocalized by electrons that could be excitead by photons with ease [8]. The organic laser dye used in during research is DCM, [2-[2-[4- (dimethylamino) phenyl]ethenyl]-6-methyl-4H- pyran-4-ylidene]-propanedinitrile and the chemical formula is $C_{19}H_{17}N_3O$, which mixed with TiO_2 nanoparticulates synthesized via sol-gel way and co-doped with PS polymer of the chemical formula (C8H8)n to prepare thin films. The fashioning of charge transfer combinations between the matrix polymer host and dopant are observed. In the style of thin films they have many potential usages in batteries and sensors [9-10].

A main understanding of the polymer properties of thin films is definitive for the effective use of fine materials at current and futures techniques especially with Nano-scale. Using co-polymers, composites, polymer blends and by doping. The mechanical, optical, electrical and di-electrical properties in addition to the thermal properties can be better achieved. The interest of researchers have drawn to study effects the doping because of optical polymer properties' adding can be needed to particular by the addition of appropriate dopant materials.

In this study, installation of DCM/PS co-doped mixture with TiO2 nanoparticulates thin films via casting route have done. Additionally, the optical films properties, as well the thermal effects on the values of electronic energy band gap and refractive index of the thin films, were achieved

EXPERIMENTAL PROCEEDING

Titanium dioxide nanoparticulates were predestined by the sol-gel procedure. The nanoparticles structure has been described with X-Ray Diffraction(XRD). The other words the morphology of TiO_2 detected using the scanning electron microscopy(SEM). SEM was focused beam of electrons to generate an image or to analyses the surface of specimen, and to determining nanoparticles size. For more details about the microstructural of nanoparticulates TiO_2 refer to [8].

To prepare final solution firstly dissolving 2gm from PS in 30ml, THF with 120 min., vigorous stirring to obtaining solution of polymer, then after 0.015gm DCM dissolve in 10ml, THF solvent and stirring for half hour to getting the homogenous solution. However, to synthesis the final thin films, 5ml-PS solution mixture with 1-ml DCM solution and stirrer for 10 minutes to get homogeneous solution. Then 2.648×10^{20} particle densities of acquired TiO_2 nanoparticulates has suspending within THF solvent and adding to DCM/PS-mixture then using casting method can be poured in the substrate-glass at room temperature. To study the influences temperatures on the optical films properties. There are several temperatures (30, 40, 50, 60, 70 C°) conducted on the samples in final stage as annealing treatment. Thin films thickness has been measured by the optical interferometer procedure employing He-Ne laser 0.632µm, and found to 0.457 µm for all samples. Absorbance (A) were measured using Spectrophotometer, which range of wavelengths where (190-1100) nm. The optical-absorption-coefficient (α) was computed using the equation [11]:

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

Where: x is the film thickness.

The optical absorption coefficient is very important because it supplies information about the electronic transition via use eq. as mention [12]:

$$\alpha = B\,\frac{(h\upsilon - E_g)^{\frac{1}{2}}}{h\upsilon} \qquad (2)$$

Where B is constant , υ is frequency

The optical-absorption and especially the absorption band edge is useful way for studying optically prompted transition and provides information about the configuration and optical-energy gap in thin films. The absorption edge in many materials follows the Urbach rule [13]:

$$\alpha = \alpha_o Exp\left(\frac{h\upsilon}{E_u}\right) \qquad (3)$$

The extinction coefficient (K) is obtained in terms of the absorption coefficient is given by eq. [14]:

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

The refractive index (n) can be calculated by using eq. [15]:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \qquad (5)$$

In order to analyze the refractive index dispersion of DCM-PS doped with TiO_2 nanoparticles thin films at various annealing temperatures used the single-oscillator model developed by DiDomenico and Wemple. The refractive index can be expressed in terms of the dispersion energy E_d and single-oscillator energy E_o.

The single-oscillator model for the refractive index dispersion is expressed in equation [16]:

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\upsilon)^2} \qquad (6)$$

Fineness Coefficient (F) was investigated by calculating the reflectance, the equation of Fineness coefficient is given by [17]:

$$F = \frac{4R}{(1-R)^2} \qquad (7)$$

As for the critical angle (θ_c) was calculated by measuring the refractive index which is given by the equation [18]:

$$\theta_c = \sin^{-1}\left(\frac{1}{n}\right) \qquad (8)$$

Brewster angle (θ_B) was calculated by measuring the refractive index which is resulted of eq. [19]:

$$\theta_B = \tan^{-1}(n) \qquad (9)$$

RESULTS AND DISCUSSIONS

Optical absorbance measurements were taken for DCM/PS doped with TiO_2 nanoparticulates samples to compare influence several annealing temperatures on optical properties of composites as shown in figure 1. However the absorbance and reflectance measurements are limited to wavelengths at which the sample has an all measuring parameters.

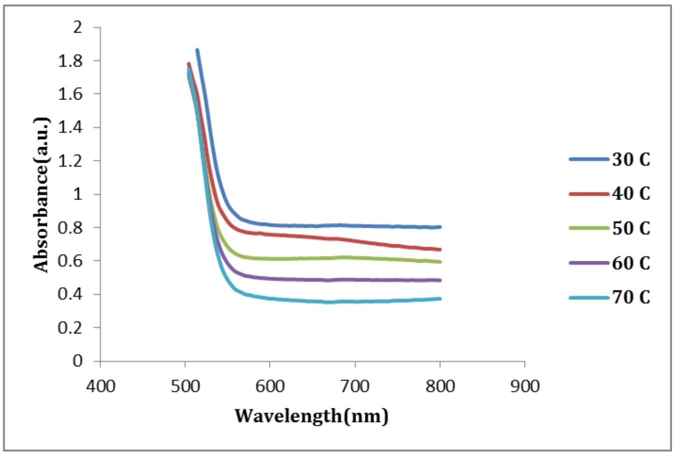


Figure 1: Shows compare the effect temperatures on the optical properties of the composites.

The absorption increases as the wavelength increases for all samples, and there are absorption bands in the visible region spectrum since the sample is semitransparent. Also it can see that the absorption edge has been slightly changed (decreasing) with increasing annealing temperature. The shift in the absorption edge obtain from the heat treatment is explained by a change in the defect structure of the films [20]. The absorption coefficient was computed using equation (1) and the result shown in figure 2 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 band gaps for prepared thin films were estimated using equation (2).

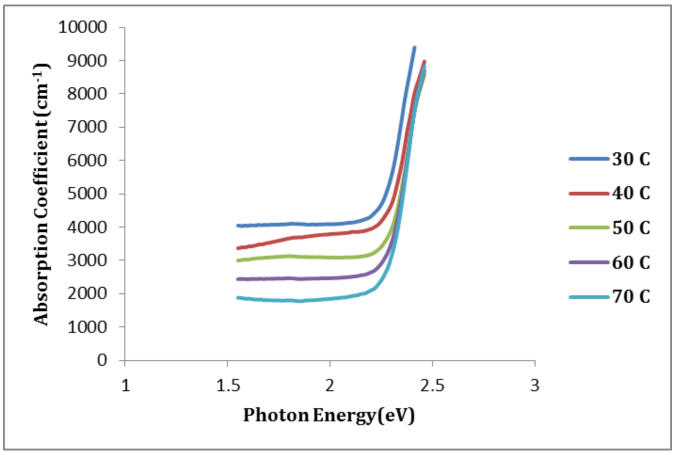


Figure 2: The absorption coefficient was computed using equation (1).

The variation of $(\alpha h\nu)^2$ as the incident photon energy (eV) of DCM-PS doped with TiO_2 nanoparticles thin films at various annealing temperatures was displayed in figure 3. The optical band energy gap was resulted by estimating the linear piece 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.

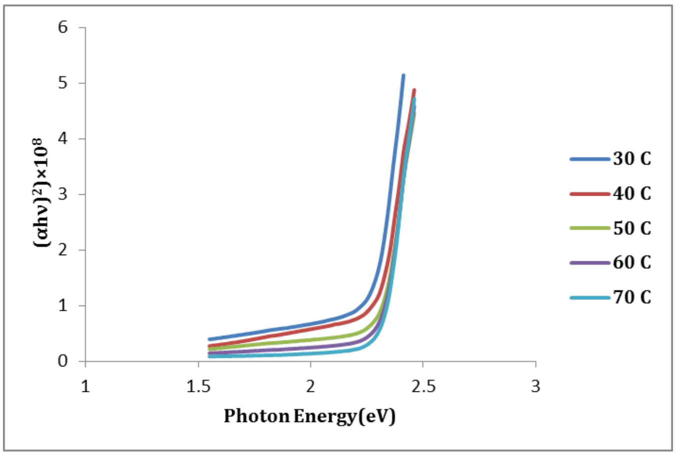
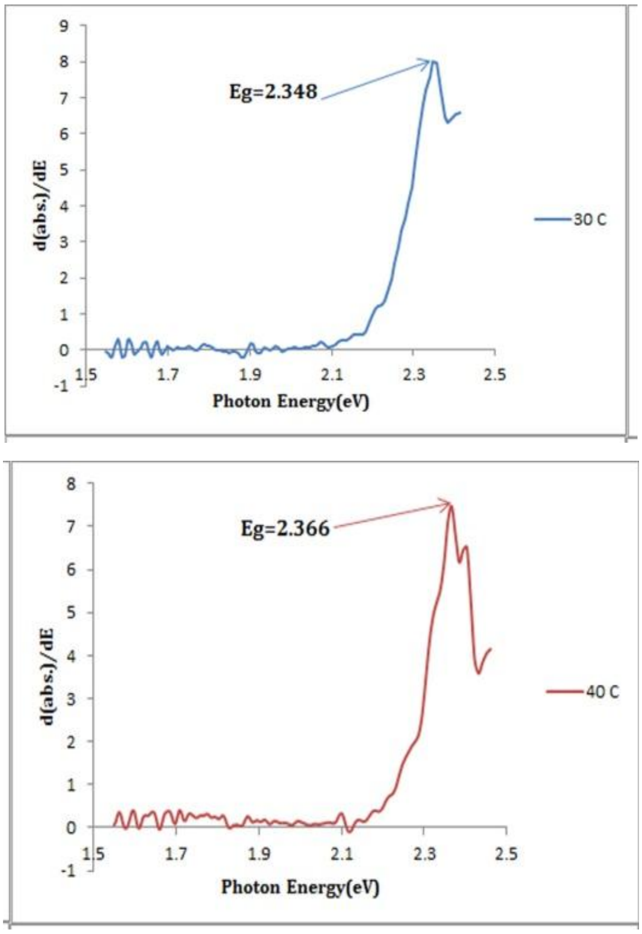


Figure 3: Display variation of $(\alpha h\nu)^2$ as the incident photon energy (eV) of DCM-PS doped with TiO_2 nanoparticles thin films at various annealing temperatures.

The direct electronics transitions energy gaps for prepared thin films at different annealing temperatures are summarized in table 1. Figure 4 shows the dependence of the first derivative of the absorption on the photon energy for prepared thin films at different annealing temperatures.



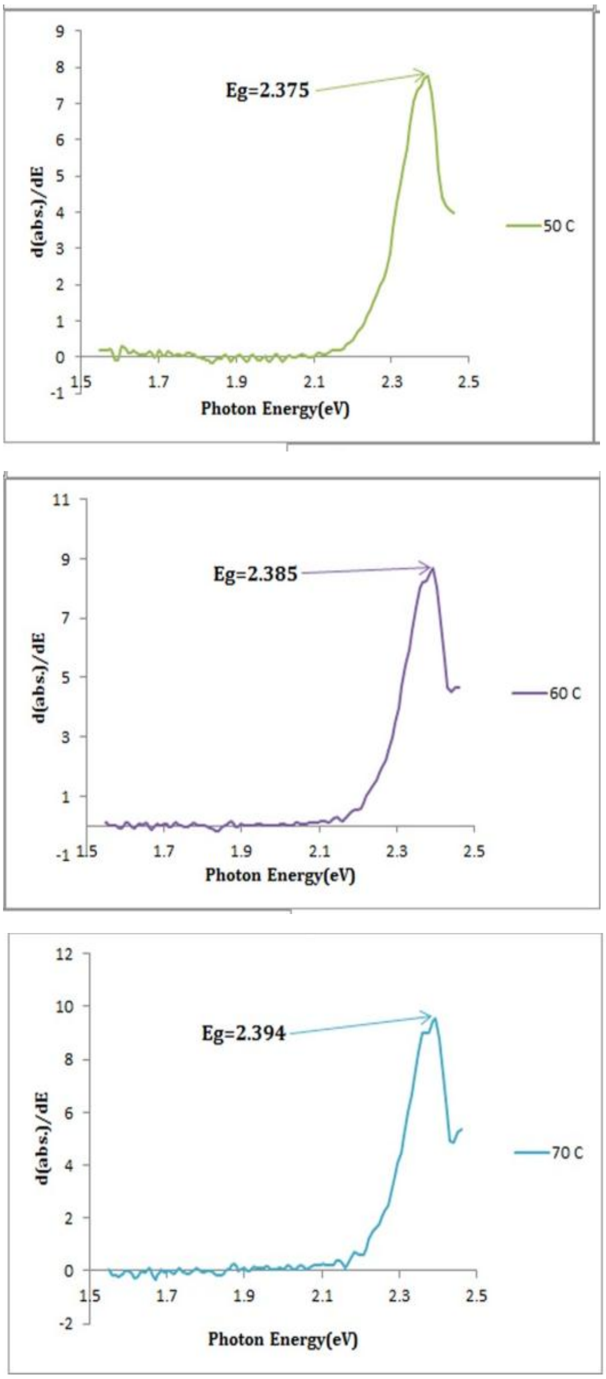


Figure 4: Shows the dependence of the first derivative of the absorption on the photon energy for prepared thin films at different annealing temperatures.

When taking the first derivative of the absorption as a function of the photon energy, it was observed that the increase in annealing temperature has led to an increase in the values of the energy gap represented by the curve for all samples as in figure 4, the energy gap values which obtained from the first derivative are recorded in the table 1, this is coexistent with the results of Tauc's model of the energy band gap values.

The values of Urbach energy were calculated as the reflexive incline of the linear portion of the plot. Moreover, Figure 5 shows the plot of (lnα) versus photon energy (eV) for DCM-PS doped with TiO_2 nanoparticles thin films at different annealing temperatures and the values of Urbach energy are summarized in table 1.

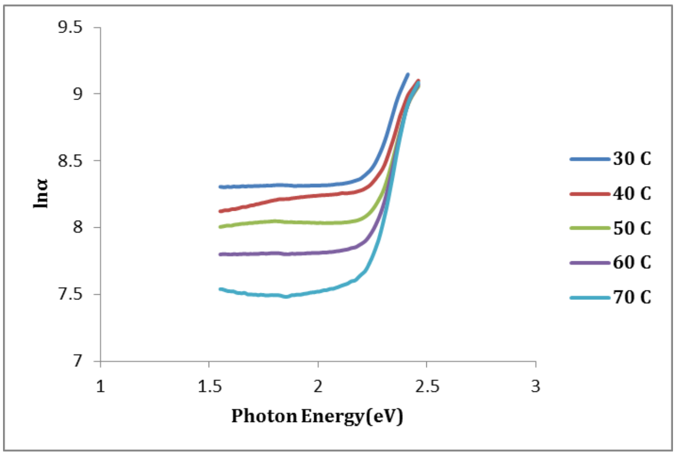


Figure 5: Urbach energy values were decreased with increasing the energy gap and change of annealing temperatures.

One can observe of figure 5 that Urbach energy values were decreased with the increasing the energy gap and with the increasing of annealing temperatures, this behavior due to the decreasing of defect levels in the allowed band gap by increasing annealing temperatures this results agree with [21].

The spectral dependence of the extinction coefficient (K) on the wavelength variation for DCM-PS doped with TiO_2 nanoparticles thin films at different annealing temperatures was obtained using equation (4) this dependence is shown in figure 6.

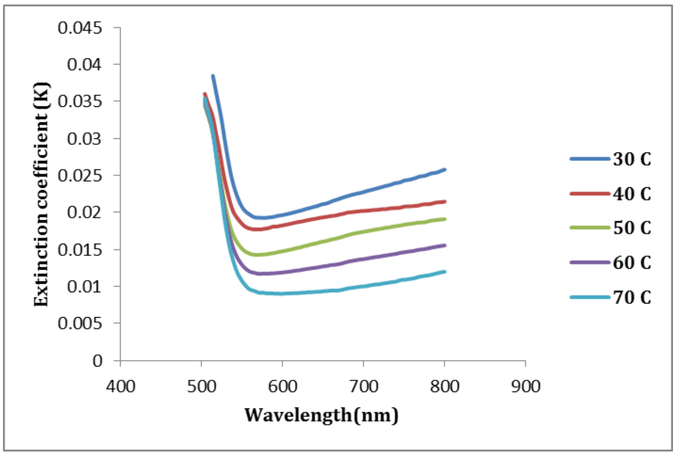


Figure 6: Spectral dependence of the extinction coefficient (K) on the wavelength variation for DCM-PS doped with TiO_2 at different annealing temp. using equation (4).

It is clear that the extinction coefficients slightly decrease up to (550nm), more than this wavelength any increasing in wavelength unaffected on the value of the extinction coefficient; all curves have the same behavior but the extinction coefficient decrease as the annealing temperature increase. This might be due to the change in morphology of surface during annealing. Figure 7 display the varying of refractive index as a function of wavelength which computed using equation (5).

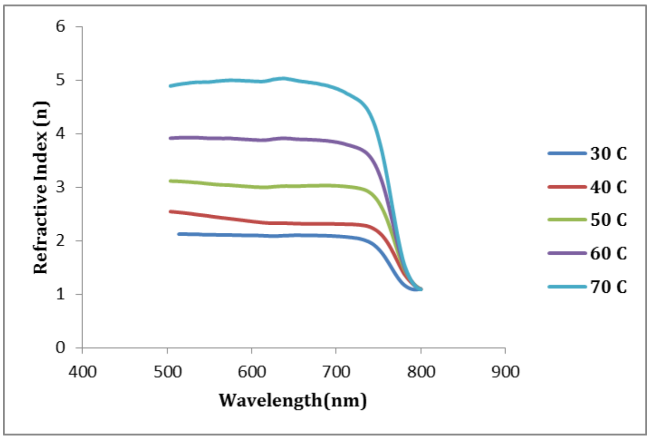


Figure 7: Show the varying of refractive index as a function of wavelength which computed using equation (5).

The values of the refractive index at wavelength increasing in wavelength unaffected on the value of refractive induces for all samples up to 720 nm, than it will decreasing with increasing in wavelength. Also one can observed from figure 7 there is a slightly alter in the refractive index (increasing) as annealing temperature increases this due to the crystal quality and the grain size [22].

Plotting 1/ (n^2 - 1) versus hv2 as shown in Figure 8, allows determining the oscillator parameters E_o and E_d values. E_o and E_d values were calculated from the slope and intercept on the vertical axis of 1/(n^2 - 1) versus hv^2 plot. The E_o and E_d values are short formed in table 1. E_o is an average energy gap and can be related to the band gap, E_g in close approximation $E_o \approx 2E_g$ [23].

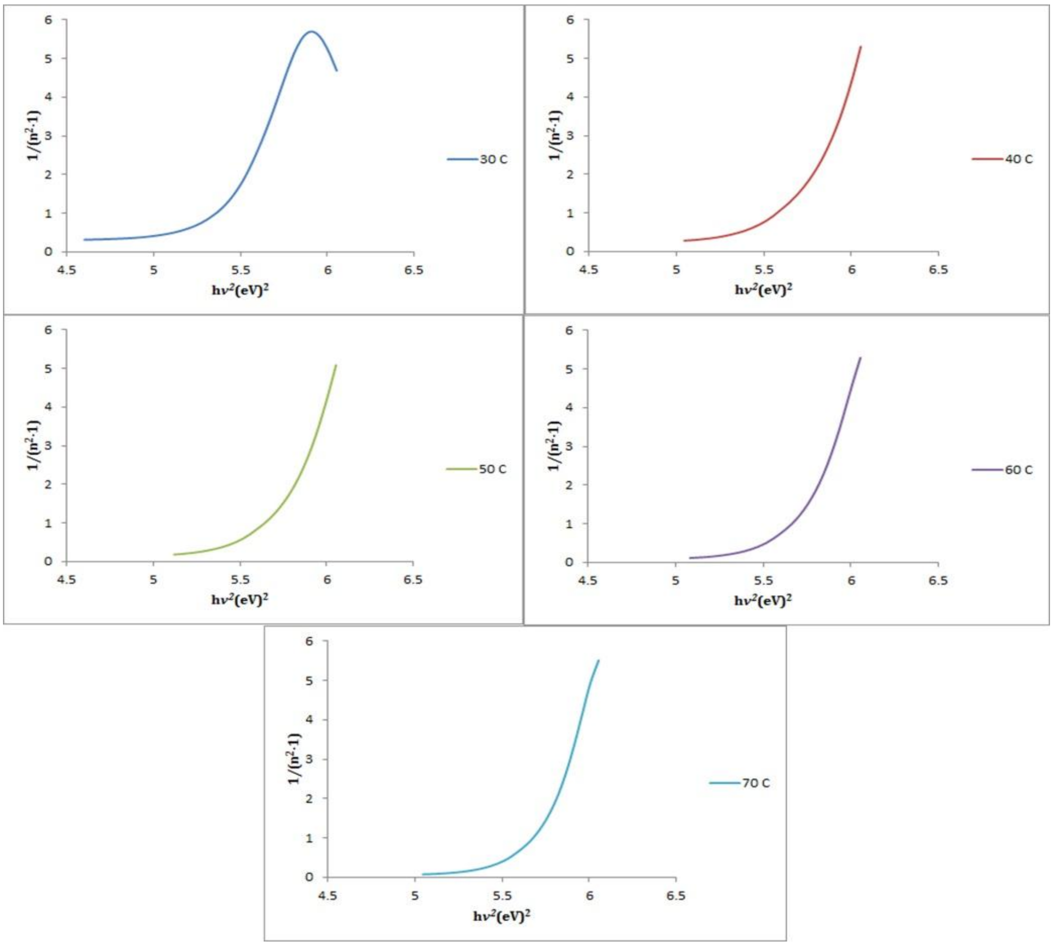


Figure 8: Show Plotting 1/(n^2 - 1) versus hv2.

Table 1: The calculated parameters for DCM-PS doped with TiO_2 nanoparticles thin films at different annealing temperatures.

Tempes.	single-oscillator energy E_o (eV)	Dispersion energy E_d(eV)	Urbach's energy E_u(eV)	E_g (eV), from Tauc model	E_g (eV), from derivative abs. spectra
30 °C	3.971	4.91	2.046	2.24	2.348
40 °C	4.143	5.248	1.514	2.27	2.366
50 °C	4.425	5.325	1.615	2.28	2.375
60 °C	4.499	5.326	1.231	2.29	2.385
70 °C	4.544	5.323	0.930	2.31	2.394

The coefficients of finesse of DCM-PS doped with TiO_2 nanoparticles thin films at various annealing temperatures were calculated using equation (7). Figure 9 is shown finesse coefficient maximum of all samples as the annealing temperature from 30 °C to 70 °C.

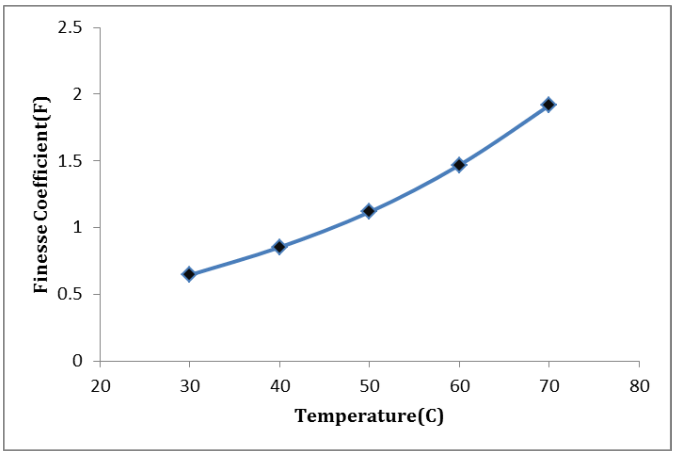


Figure 9: Finesse coefficient of DCM-PS doped -TiO_2 at several annealing temps.

Figure 9 shows that finesse coefficient of DCM-PS doped with TiO_2 nanoparticles thin films at different annealing temperatures have the same behavior to their reflectance, because this coefficient depends on reflectance, from another aspect the influences of increasing of annealing temperatures lead to increase the values of finesse coefficient, this is because the increasing of reflected light as a result of increasing the density after increasing of annealing temperatures, and this results agreement with reference [24]. Figure 10 shows that the critical angle of an inverse relationship with the refractive index, any increase in the refractive index causes a decrease in the critical angle, or it is a clear that as annealing temperatures increase, the density also increase therefore the incident rays will bend toward normal and causes critical angle to decrease and the result benefit with [24].

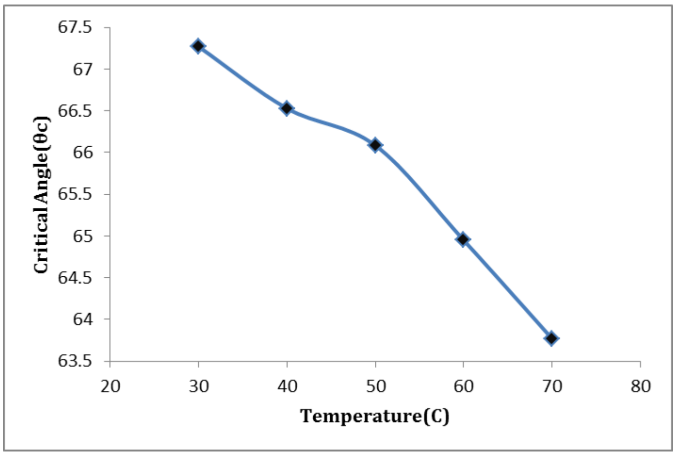


Figure. 10: shows the critical angle of an inverse relationship with the refractive index.

The values of Brewster depend mainly on the values of the refractive index positive relationship with the refractive index and figure 11 shows that the Brewster angle increases with increasing concentration and the reason for this is due to the increasing of refractive index with increased annealing temperatures.

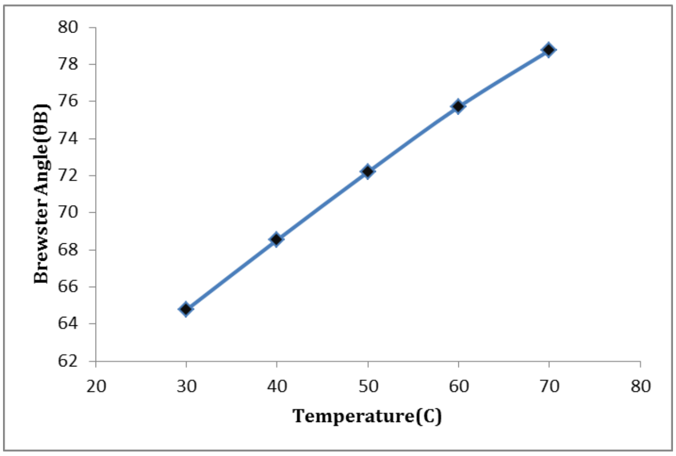


Figure 11: Brewster angle increases with increasing concentration.

CONCLUSION

In this study, it is found that optical properties change in there against rising the increasing annealing temperatures. Absorption and extinction coefficients of DCM-PS doped with TiO_2 nanoparticles thin films decrease with annealing temperatures. Urbach tail assures that the crosslink is decreased as the annealing temperatures increase (2.046-0.930)-eV. The optical energy gap was found to be direct from Tauc model (2.24-2.31)-eV. The energy gabs from derivative abs. spectra (2.348-2.394)-eV. All the values of the optical parameters were increase under increasing annealing temperatures.

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