

Optical properties of NaI doped polyvinyl alcohol films

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ABSTRACT

The optical characteristics of polyvinyl alcohol (PVA) doped with different concentrations (0, 1, 2, 3 and 4 wt%) of NaI nanocrystalline powders were studied. The films are prepared using solution casting technique, in order to investigate the effect of NaI additions on the optical properties of PVA host. The optical properties of samples are investigated by measuring optical absorption spectra in the wavelength range from 190 to 850 nm at 300 K using UV-Vis spectroscopy. The influence can be explained by the PVA matrix. The results show that $E_{g_{opt}}$ of the films decreases with increasing NaI contents. The absorbance, absorption coefficient, extinction coefficient, finesse coefficient, refraction index and reflectance of PVA doped with NaI increase with increasing of doping percentages except the transmittance. The real and imaginary parts of the dielectric constant and optical conductivity increases with increase sodium iodine concentration. The indirect optical band gaps for these undoped and doped PVA films were estimated to be about 5.05, 4.91, 4.79, 4.70 and 4.55 eV for indirect allowed transitions, whereas the indirect forbidden band gaps were determined as 4.91, 4.82, 4.75, 4.65 and 4.54 eV with increase sodium iodine contents, respectively. Absorption spectra peaks of the pure and doped films have shown an absorption band at 284.5 nm assigned to the monovalent state of sodium and iodine ions. The spectra peak points are between 204 and 259 nm for the calculated variables.

Keywords: Polyvinyl-alcohol, doping, optical properties, sodium iodine, optical energy gap, concentration.

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INTRODUCTION

Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer, its molecular formula is $(C_2H_4O)_x$, and density is between 1.19 and 1.31 g/cm³. PVA has excellent film forming and adhesive properties. With higher humidity more water is absorbed, which acts as a plasticizer, and will then reduce its tensile strength. PVA is fully degradable and dissolves quickly. PVA has a melting point of 230°C. It decomposes rapidly above 200°C, as it can undergo pyrolysis at high temperatures (Fromageau et al., 2003). PVA is used as an emulsion polymerization aid, to make polyvinyl acetate dispersions (SRI Consulting CEH Report, 2012). Some uses of PVA include: thickener, modifier, textile sizing agent paper coatings and release liner. When doped with iodine, PVA can be used to polarize light, and is not prepared by polymerization of the corresponding monomer (Agabekov et al., 2012). Shao et al. (2012) studied optical properties of PVA coated In_2O_3 nanoparticles which was performed

with photoluminescence (Mahendia et al., 2011). Mahendia et al. (2011) studied optical and structural properties of PVA films embedded with citrate-stabilized gold nanoparticles. Yovcheva et al. (2012) found the refractive index of PVA films with TiO_2 nanoparticle inclusions with low concentration up to 1.2 wt%. Suo et al. (2012) observed a transparent PVA nanocomposite thin film (30 to 50 nm) reinforced with core/shell [(CdSe)/(ZnS)] quantum dots. Juan et al. (2012) studied electrospun nanofibrous mats as efficient scaffold materials. Jorkaala and Stenonen (2002) observed photoinduced second-order nonlinear optical effects in ZnSe nanocrystallites incorporated within photo-polymer PVA matrices. Mircea et al. (2004) carried out the electronic mechanisms induced by the UV exposure of thin films of PVA doped with pairs of mixed valence metal ions. Uma Devi et al. (2011) studied the effect of PVA films doped with NaI up to additions on the electrical

properties. Uma Devi et al. (2002) studied optical absorption in the wavelength range of 190 to 600 nm. Khanna et al. (2005) found that yellow and orange light emission from nanoparticles of CdS embedded PVA has been observed as thin films. Thi et al. (2010) carried out the Cu doping and PVA capping induced optical property changes in ZnS. Abdullah and Saber. (2011) prepared films of pure and doped PVA with different concentrations of NiCl₂ using the casting technique. Varishetty et al. (2010) prepared Li⁺ ion conducting polymer composite electrolyte films based on PVA, LiAsF₆ and ceramic filler TiO₂ using solution cast technique. Ahad et al. (2012) prepared the polymer electrolytes at different weight percent ratios by solution casting technique. This work focuses on the absorption spectrum, optical energy gap using in electronic components (device types such as bipolar, capacitors, etc), and the localized peak of energy photon of PVA doped with NaI.

EXPERIMENTAL

Materials

PVA doped with sodium iodine was prepared with weight percent (0, 1, 2, 3 and 4 wt%). It was dissolved in glass beaker (30 ml) by distilled water using magnetic stirrer and placed in British (5 cm diameter) using casting technique to prepare the films. Each sample was poured in 25 cm² glass basin after being cleaned with water using ultrasonic device. The samples were put in dried oven at 50°C for 2 h. The thickness of the dried samples is 0.04 cm. The spectrum of absorption and transmittance were recorded for wavelengths (190 to 850 nm) by using double beam spectrophotometer (UV-Vis – CECIL 2700, provided by optima 300 plus company) at room temperature.

Theoretical

The relationship between incident intensity and penetrating light intensity is given by Equation 1 (Neama, 2012):

$$I = I_0 e^{-\alpha t} \quad (1)$$

Where t is the thickness of matter (cm) and α is the absorption coefficient (cm⁻¹),

$$\alpha t = 2.303 \log I/I_0 \quad (2)$$

where the amount of $\log I/I_0$ represents the absorbance (A).

The absorption coefficient can be calculated by:

$$\alpha = 2.303 (A/t) \quad (3)$$

If the amount of absorption is $\alpha \geq 10^4 \text{ cm}^{-1}$, the electronic transitions are direct. The amount of optical energy gap from this region can be evaluated by the relation (Neama, 2012):

$$\alpha hu = A(hu - E_g)^m \quad (4)$$

Where hu is the photon energy, A is the proportional constant, E_g is the allowed or forbidden energy gap of direct transition and m is a constant.

The refraction index consists of real and imaginary parts ($N = n -$

ik), the relation between reflectivity and refractive index is given by Equation 5 (Neama, 2012):

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

Where k is the extinction coefficient.

The absorbance and transmittance can be calculated by the following equation:

$$R + A + T = 1 \quad (6)$$

The refractive index can be expressed by Equation 7 (Neama, 2012):

$$n = \sqrt{\frac{4R - k^2}{(R-1)^2} - \frac{(R+1)}{(R-1)}} \quad (7)$$

The extinction coefficient can be calculated by using Equation 8:

$$k = \frac{\alpha \lambda}{4\pi} \quad (8)$$

Where λ is the wavelength of the incident ray.

The relation between the complex dielectric constant and the complex refractive index N is expressed by:

$$\epsilon = N^2 \quad (9)$$

It can be concluded that (Neama, 2012):

$$(n-ik)^2 = \epsilon_1 - i\epsilon_2 \quad (10)$$

The real and imaginary complex dielectric constant can be expressed by Equations 11 and 12, respectively:

$$\epsilon_1 = n^2 - k^2, \quad \epsilon_2 = 2nk \quad (11)$$

Also, the finesse coefficient is given by:

$$F = \frac{4R}{(1-R)^2} \quad (12)$$

The optical conductivity is related to light speed and can be expressed by the following equation:

$$\sigma_{opt.} = \frac{nc\alpha}{4\pi} \quad (13)$$

RESULTS AND DISCUSSION

The obtained optical parameters were found to be strongly affected by NaI dopant. Figure 1 shows the optical absorbance as a function of the wavelength of PVA doped with NaI at different concentrations. It is shown that there is a simple shifting in the intensity of the peak. The absorbance increases with increasing doping

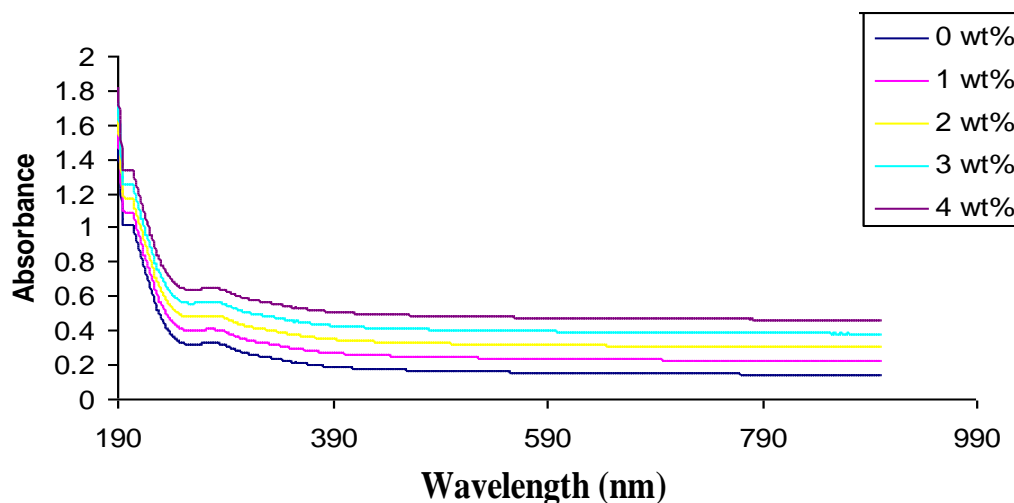


Figure 1. The absorbance as a function of wavelength of NaI doped PVA films at different concentrations.

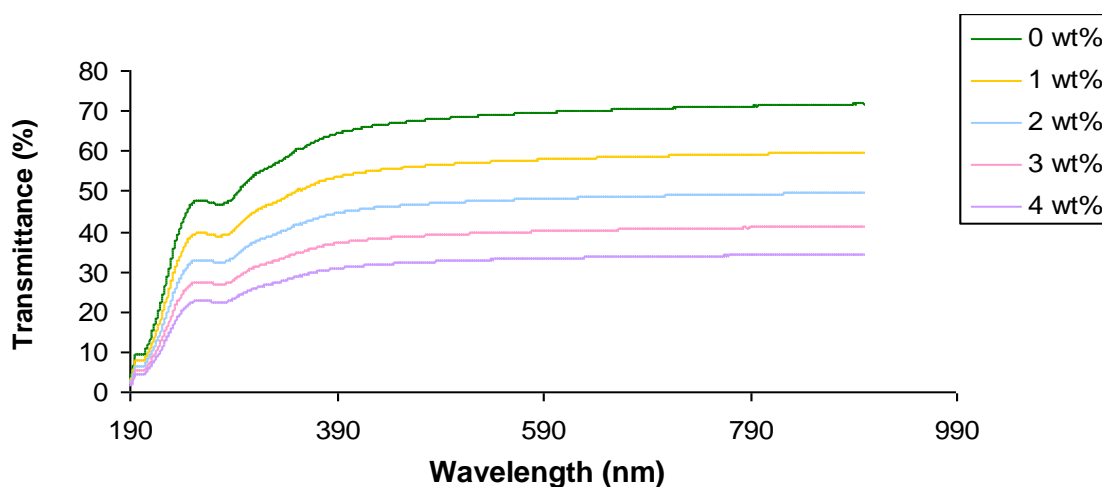


Figure 2. The transmittance for NaI doped PVA films as a function of wavelength at different concentrations.

concentration. This is because the filling of sodium and iodine ions combined with the polymer chains which absorb the incident radiation at the shortest wavelengths greater than 190 nm by the free electrons. So chemically, a simple change in the structure of polymer has occurred (Abudul Munaim and Hashim, 2010; Dahshan, 2002).

Figure 2 shows an optical transmittance spectrum as a function of incident wavelength on NaI doped PVA films. The transmittance percent decreases with increasing ions concentration; this is because of layer form of covalent bonds between polymer chains and additives that decrease the transmitting of the incident light especially at the shortest wavelengths. The electrons in the outer orbits have travelled to the higher energy levels and have occupied vacant positions of energy bands. Thus, part of incident light does not penetrate through it. However, the

undoped PVA have no free electron and the conduction band needs photon with high energy, after which it has high transmittance (Dahshan, 2002).

The relationship between the reflectance and wavelength is described in Figure 3. There is a simple change in the position of peak for all samples. The reflectance increases with increasing the additives of sodium and iodine ions in the film, but the lowering of the curves is slightly decreased as wavelength increase. This result means that there is no clear change in the structure of the polymer.

The gradient of the absorption coefficient is from high photon energy to low photon energy. This means that the possibility of electron transition is little, because the energy is not sufficient to move the electron from the valence band to the conduction band ($h\nu < E_g$). These

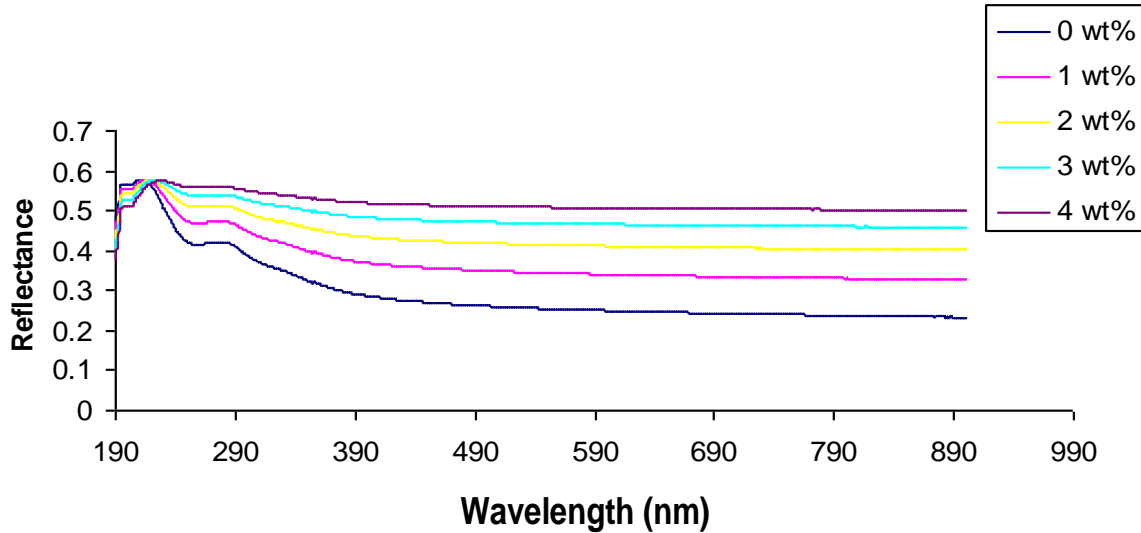


Figure 3. The reflectance as a function of wavelength of NaI doped PVA films at different concentrations.

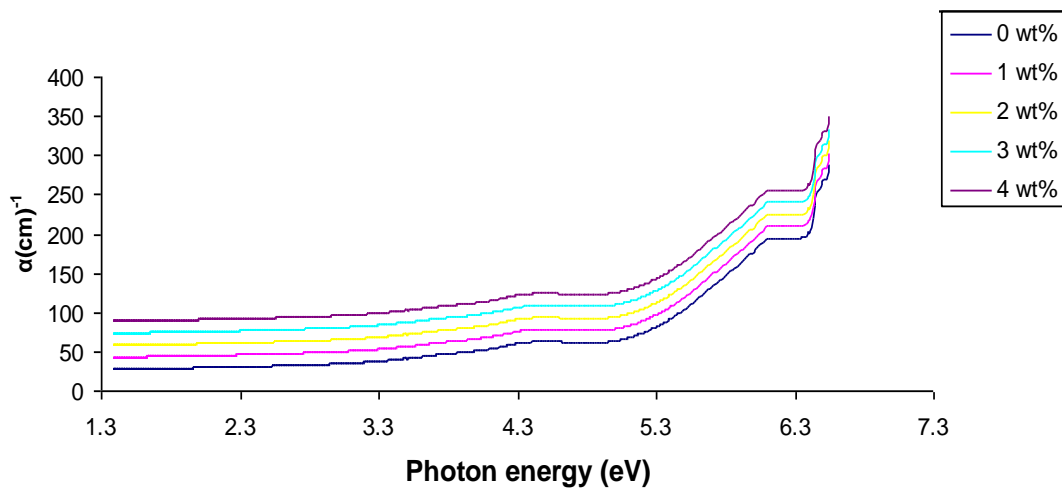


Figure 4. The absorption coefficient of NaI doped PVA films as a function of photon energy.

variations are shown in Figure 4. It was observed that at high energy, absorption is great and the forbidden energy gap is less (Abdul Munaim and Hashim, 2010). It is expected that indirect transition of electron occur at low absorption coefficient and the electronic momentum is maintained with assistance of photon. The energy of incident photon is greater than the forbidden energy gap (Neama, 2012).

Figure 5 shows the relationship between absorption edge $(\alpha h\nu)^{1/2}$ for casting material as a function of photon energy. At extension of the curve to the values of $(\alpha h\nu)^{1/2} = 0$, we get indirect allowed gap transition.

From Figure 6, we see that the values of energy gap decrease with increase of the weight percentage of added salt. These attributes to the creation of the site levels in forbidden indirect energy gap lead to facilitate

the crossing of electron from the valence band to the local levels to conduction band (Gabur, 2010; Abdul Munaim and Hashim, 2010). In other meaning, the electronic conduction depends on added impurities.

Figure 7 shows the values of energy gap for the allowed indirect transition that is greater than the forbidden indirect transition. The different generation of site levels between valence and conduction bands depends on $m = 2$ or 3. The energy gap is inversely proportional to weight percentage, because the increasing of doping generates a new energy level between the valence band and the conduction band. These two types of energy gaps are close to each other at higher doping concentrations.

Figure 8 describes the change in refractive index for PVA-NaI as a function of wavelength that has occurred due to an increase in n with increasing the doping

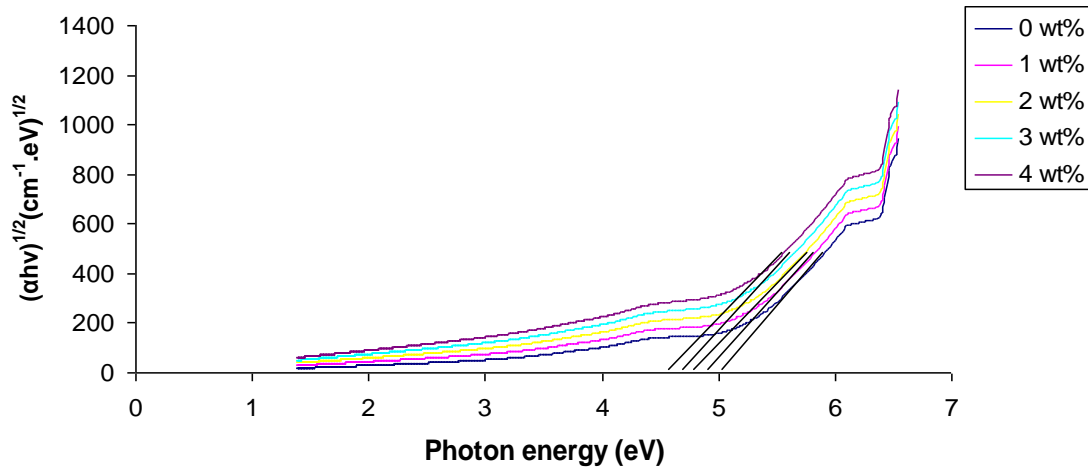


Figure 5. $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plots of NaI doped PVA films for different dopant concentrations with energy gap of allowed indirect transitions.

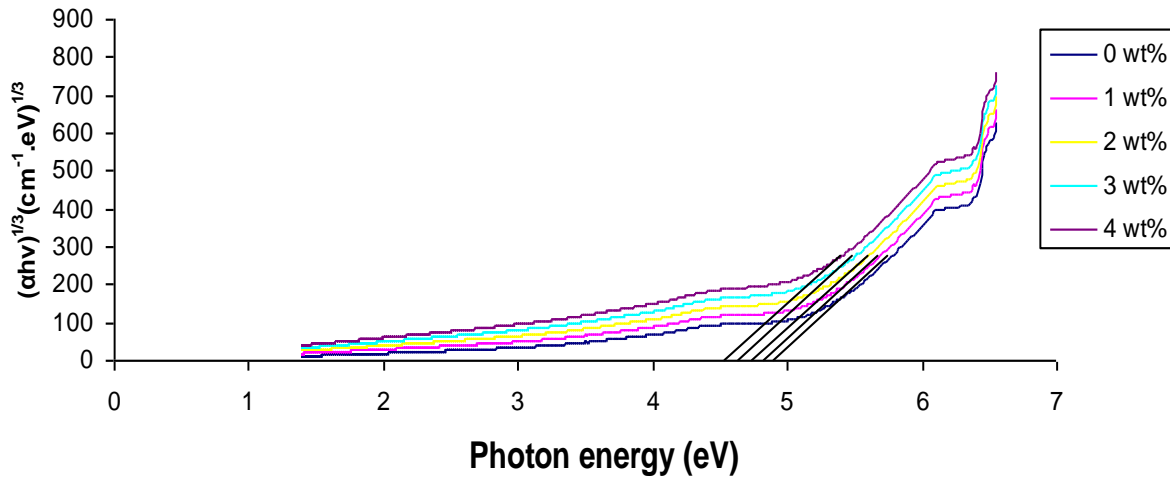


Figure 6. $(\alpha h\nu)^{1/3}$ vs. $h\nu$ plots of NaI doped PVA films for different dopant concentrations with energy gap of forbidden indirect transitions.

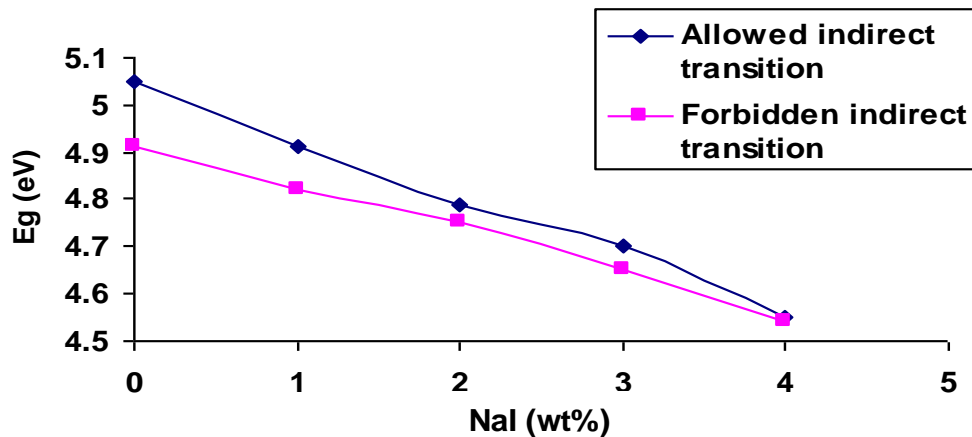


Figure 7. The dependence of E_g on doping levels for allowed and forbidden indirect transitions.

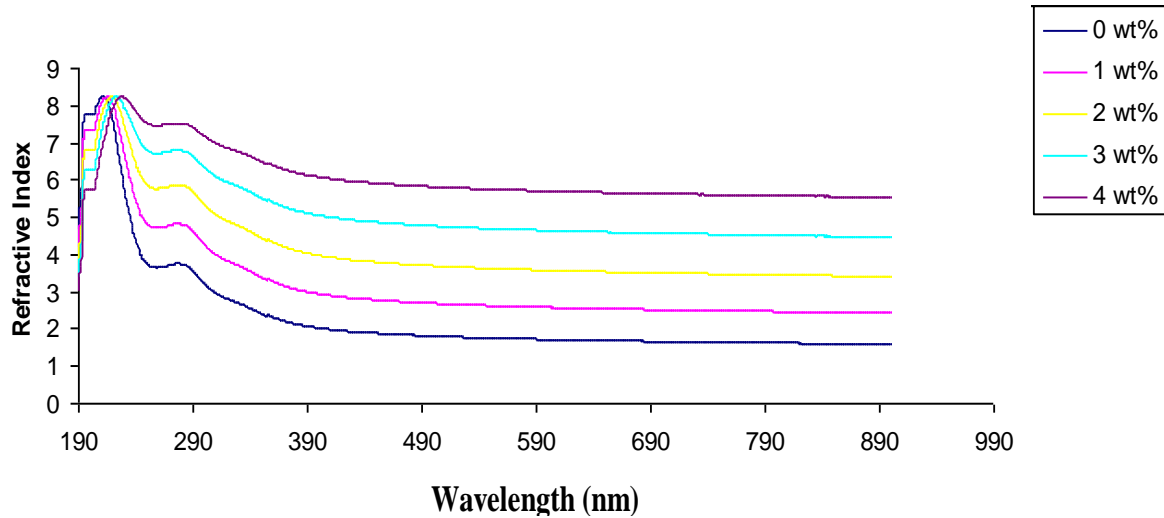


Figure 8. The refraction index of NaI doped PVA films as a function wavelength at different concentrations.

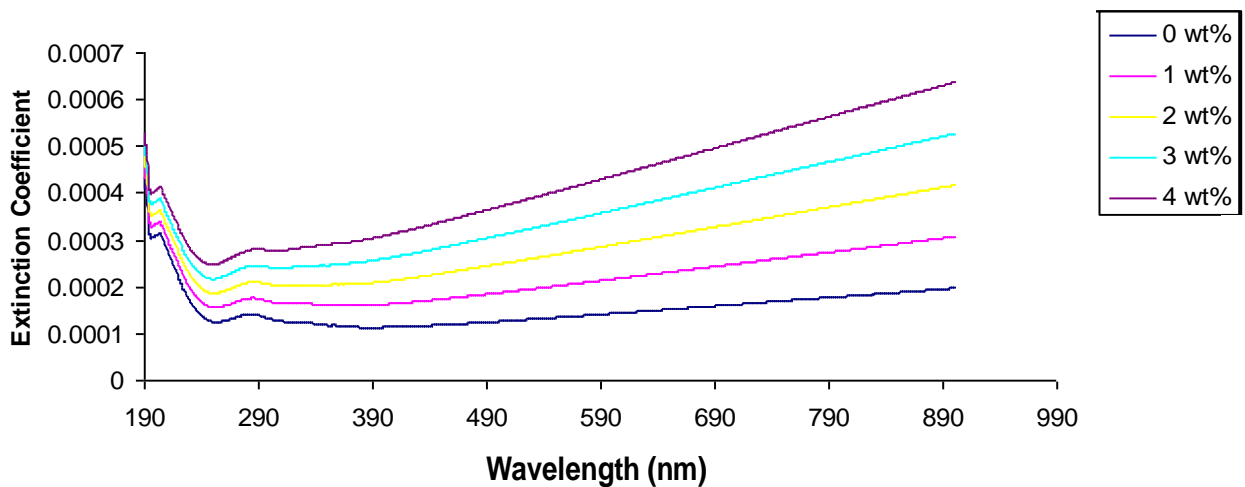


Figure 9. The extinction coefficient for NaI doped PVA films as a function of wavelength.

percentages. This is because pure polyvinyl alcohol is an amorphous crystalline substance with low density that increases with added NaI. The refraction index decreases at the greatest wavelengths and increases at the greatest doping concentration, because the transmission of the longest wavelength is more.

The change of extinction coefficient as a function of wavelength is shown in Figure 9. It was noted that k has lower value at low concentration, and this is attributed to increase in the absorption coefficient with increased doping percentages of added salt ions. The extinction coefficient is high at the longest wavelengths and high concentration.

The real dielectric depends on n^2 and k^2 , but the imaginary dielectric depends on k and n . The real and imaginary dielectric constant (ϵ_1 and ϵ_2) for PVA-NaI have

been calculated from Equation 11, Figures 10 and 11 show the change of these constants with wave lengths. The values of the real dielectric constant are high with respect to the imaginary dielectric constant, because they are dependent on n and k values.

Figure 12 shows the values of finesse coefficient against wavelengths at different concentrations of NaI doped PVA. It was observed that F values decrease at 211 to 276 nm wavelengths. The position of the peaks spectrum is slightly shifted especially at the greatest concentration of doping. This means that there is a little change in polymer structure as a result of doping. Also, the finesse coefficient increases with increasing doping percentage because of doped additives that lead to changing in reflectance which F is dependent on R , as described in Equation 12.

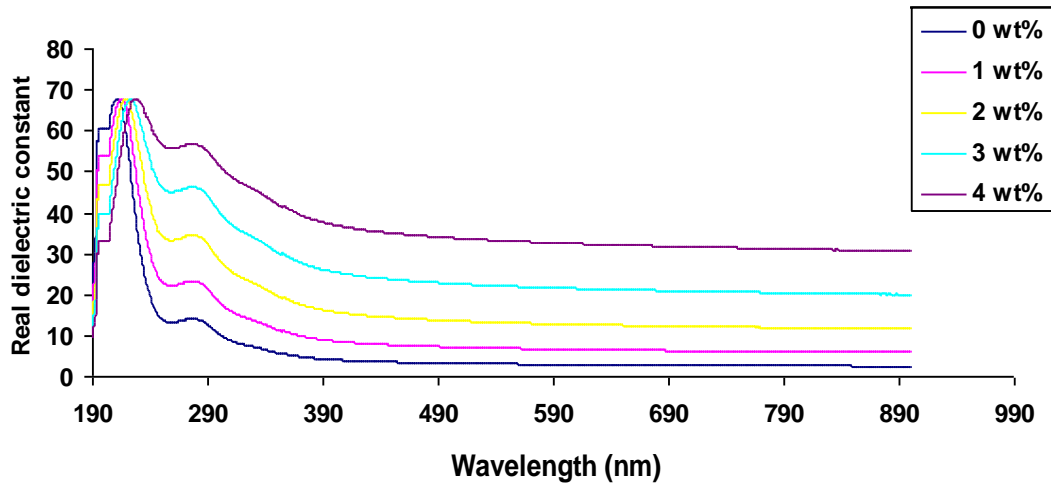


Figure 10. The real dielectric constant for PVA-Nal films as a function of incident wavelength.

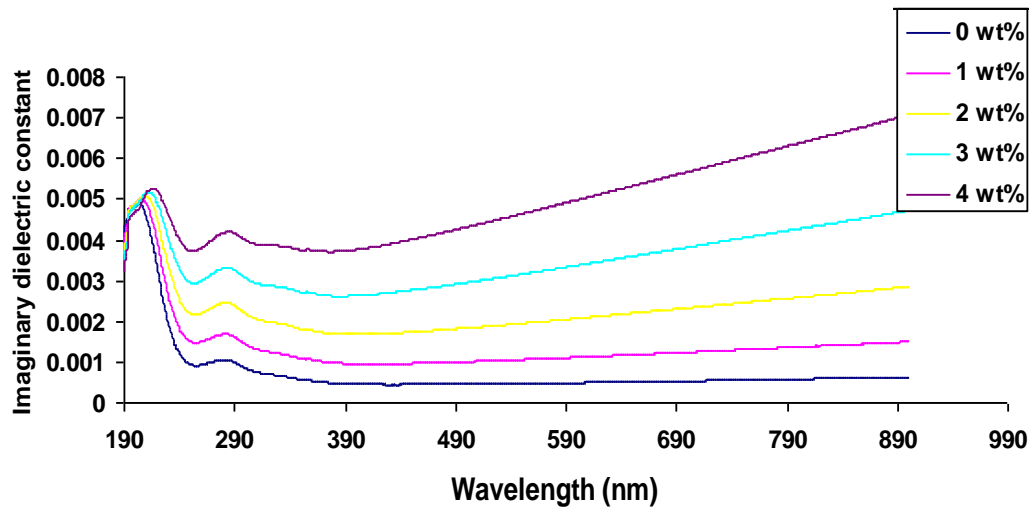


Figure 11. The imaginary dielectric constant for PVA-Nal films as a function of incident wavelength.

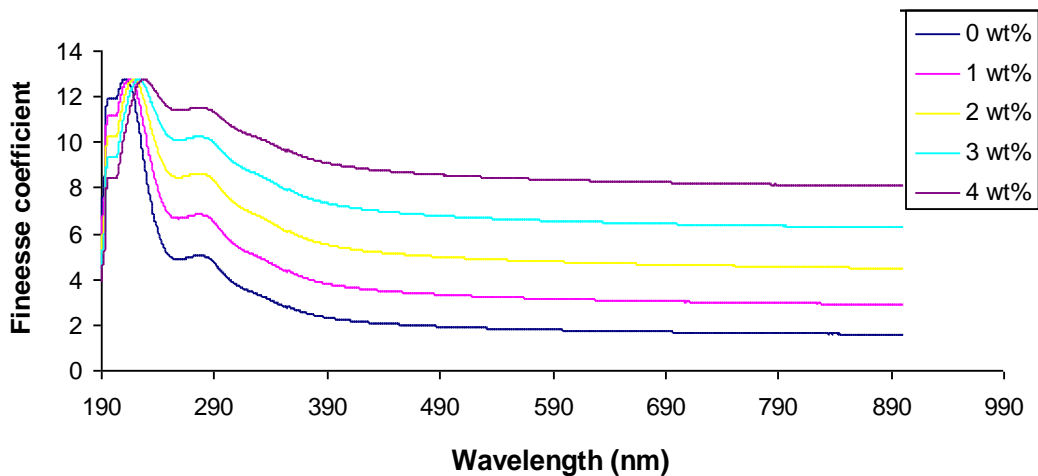


Figure 12. The Finesse coefficient as a function of wavelength for NaI doped PVA films.

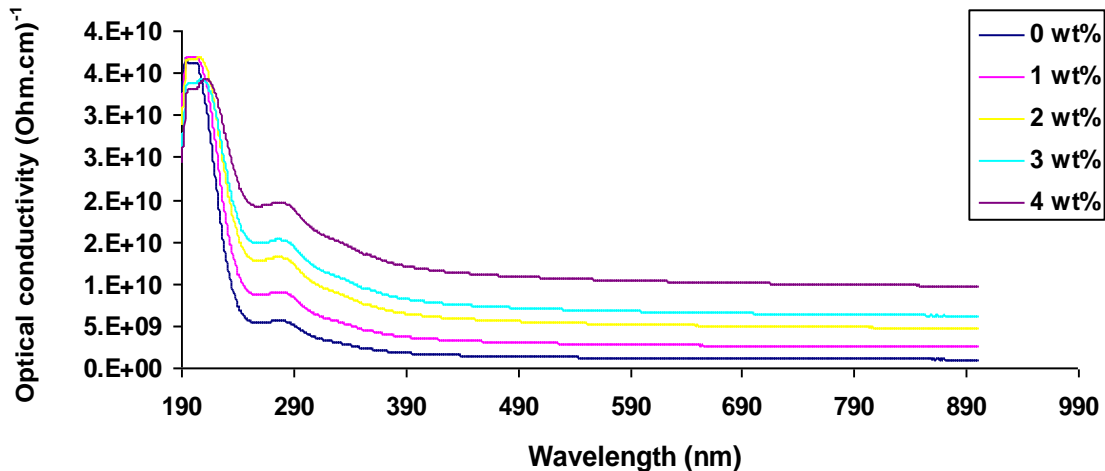


Figure 13. The optical conductivity as a function of wavelength for NaI doped PVA films.

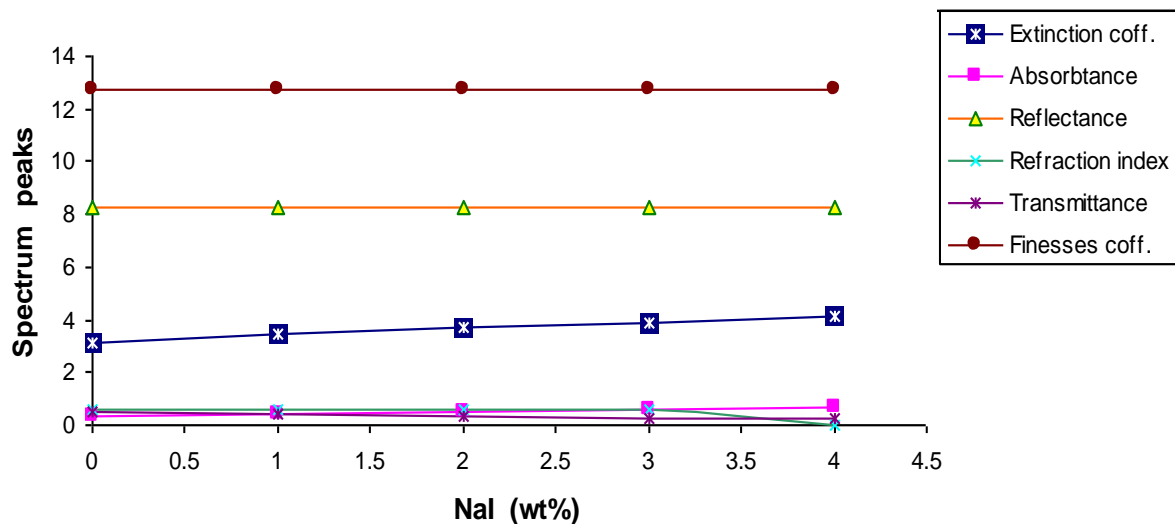


Figure 14. The spectrum peaks as a function of weight concentration of NaI doped PVA films.

The optical conductivity decreases suddenly after 200 nm wavelength as shown in Figure 13. It was observed an increase in optical conductivity as increasing in doping percentages. This means that the generation of sodium and iodine ions percentages increases the contribution of electron transitions between the valence and conduction bands, which lead to reduction of energy gap as a result of site level generation. This optical conductivity becomes constant after 500 nm.

To combine the peak points, Figure 14 describes the variations between the values of spectra peak and the optical parameters. It was observed that the peak values of finesse coefficient, refraction index and reflectance are constant, while the peak values of extinction coefficient and absorbance are increased, but the transmittance decreases as doping percentages of NaI increases.

Conclusion

The absorbance, absorption coefficient, extinction coefficient, finesse coefficient, refraction index and reflectance of NaI doped PVA films increase with increasing of doping percentages, except the transmittance. The energy gap of indirect transition decreases with increasing of doping. The dielectric constant (real and imaginary), increases with increasing doping content. The allowed indirect transition optical energy gap is greater than the forbidden indirect transition.

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