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Dispersion Characterization of conductive polymer

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Pure and doped PMMA films with $NiCl_2$ have been deposited by using casting method. Optical measurements were studied by UV- VIS technique in the wavelength ranges (200-800)nm. The optical properties and dispersion parameters of films have been studied as a function of doping concentration of $NiCl_2$. Changes in direct optical energy band gap of films were confirmed after doping, the optical energy gap decreased from 3.29eV for the pure PMMA to 1.90eV after increasing the doping concentration of $NiCl_2$ to 0.4%, These result were inversely with the Urbach tails where increased from 278 to 702 meV. The changes in optical properties and dispersion parameters were investigated. An increase in the doping concentration causes an increase in the reflectance, absorption coefficient and in the average oscillator strength from 1.73 to 4.29 eV. The transmittance, single-oscillator energy, static refractive index, static dielectric constant, moments of the imaginary part of the optical spectrum, average oscillator position and average oscillator strength were decreases with increasing $NiCl_2$ content.

Keywords: PMMA, $NiCl_2$, Conductive polymer, Optical Properties, Dispersion parameters.

1. INTRODUCTION

As a polymeric material, Poly(methyl methacrylate) PMMA, has attracted particular interest for its high chemical resistance, advantageous optical properties, simple synthesis, and low cost. These characteristics make it suitable as a host material for multiple valance metal ions and showed a strong dependence of donor–acceptor mechanism between the metal ion and the polymer matrix [1]. PMMA has attracted great attention due to its unique properties such as, excellent mechanical properties [2], thermal capability and electrical performance [3], low optical absorption, simple synthesis and low cost [4], high transparency in the visible region, low refractive index [5], possible to use in nonlinear optics [6].

These characteristics create many potentially commercial applications, like, photonic of nanotechnology [7], as an optical diffuser in a liquid crystal display backlighting unit (BLU) [8], humidity sensing after surface modification of PMMA by argon/oxygen plasma processing [9], as a gas sensors [10], optical device such as optical lenses and polymer optical fiber [11], PMMA is also widely used in consumer products [12].

Many attempts have studied the optical, structural and other properties of PMMA films doped with multiple valance metal ions such as methylene blue and methyl red, Al_2O_3, $MnCl_2$, I/KI, CuCl, ZnSe, CdS, $MnCl_2$, $MgBr_2$, CrF_3, $FeCl_3$, etc [13-18]. These researches showed a strong dependence of donor–acceptor mechanism between the metal ion and the polymer matrix. Also, these studies showed changes in the properties like crystallinity, structural and optical behavior of the polymer due to doping. The nickel chloride $NiCl_2$ was synthesized and chosen as a dopant for its excellent solubility in PMMA. In this paper, the effect of $NiCl_2$ on the optical properties and dispersion parameters of PMMA was studied as a function of $NiCl_2$ concentration in order to be use in the optical devices, for this purpose.

2. EXPERIMENTAL DETAILS

Films of poly (methyl methacrylate) PMMA doped with different weight concentration of nickel chloride ($NiCl_2$) salt (0.1, 0.2, 0.3, 0.4)% have been prepared by the dispersed polymer and $NiCl_2$ dissolve in 100 ml chloroform with stirring the solution, using a magnetic stirrer for about (30 min) at room temperature for complete dissolving. Different polymer solutions (volumetric solutions) were casted as a layer, dried at room temperature for 24 hours. Layer thickness were measured using (indicating micrometer 0.25 μm), all layers found to be in the range of (20 $\pm$ 1)μm, these layers were clear, transparent, free from any noticeable defect and showing light bluish color.

Optical Transmittance, Reflectance and Absorbance were recorded in the wavelength range (200-800)nm using computerized UV-visible spectrophotometer (Shimadzu UV-1601 PC). Optical transmittance, reflectance and absorbance were reported in order to study the effect of doping on the parameters under investigation.

3. RESULTS AND DISCUSSION

The optical absorption measurements were carried out in the UV/VIS region (200-800)nm for pure and doped PMMA films with different concentrations of $NiCl_2$. The transmittance (T) of all films recorded in the applied wavelength (λ) range is shown in Figure (1). It is clear from this figure that transmittance spectra for all films increased with increasing wavelength. Increasing the $NiCl_2$ content of the films decreases transmittance for all wavelength range. This means that there is some absorption in that wavelength range.

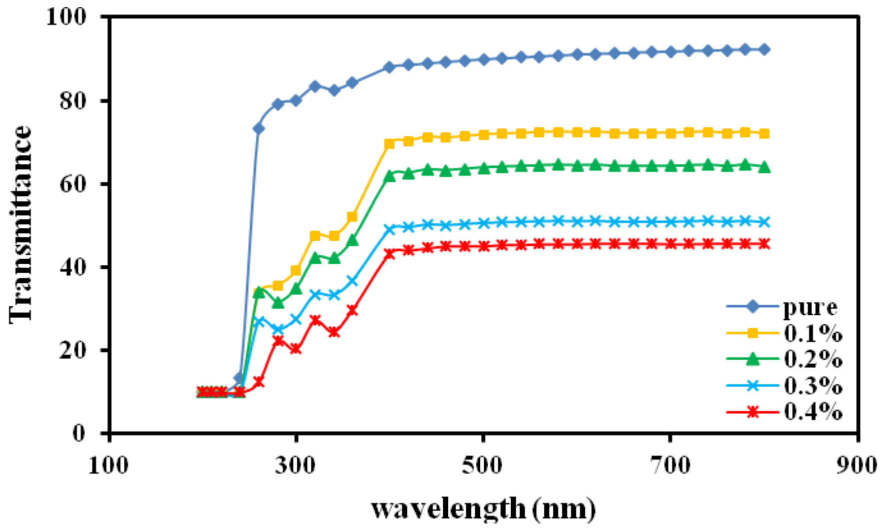

Figure 1. The variation of transmittance with wavelength for pure and doped PMMA films.

Figure (2) shows the optical reflectance (R) spectra for pure and doped PMMA films. The reflectance has been found by using the relationship:

$R + T + A = 1$ …………….. (1)

Where A represent the absorbance. The overall reflectance of the films increases as the doping concentration with $NiCl_2$ increases. Also, it is seen that the reflectance for the doped films is limited only by the surface reflectance of about 20% in the visible region.

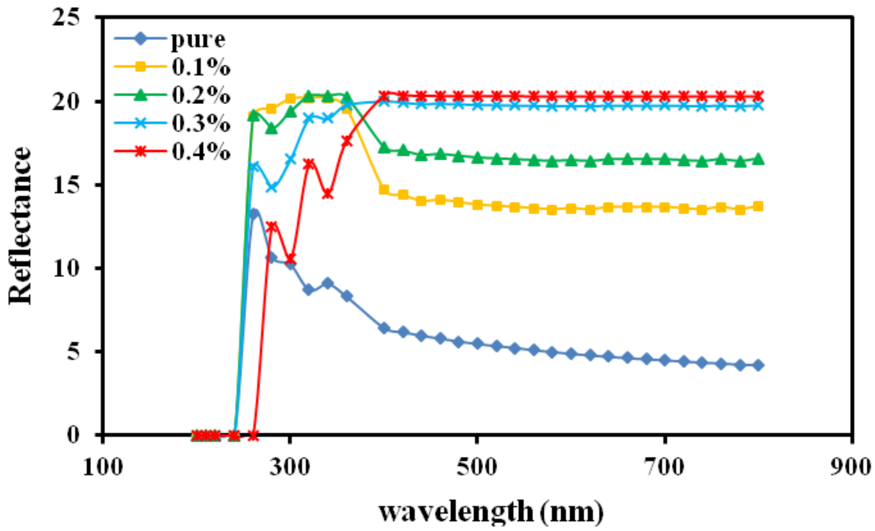

Figure 2. The variation of reflectance with wavelength for pure and doped PMMA films.

The optical properties of films by means of optical absorption in the UV-Vis region of (200–800)nm have been investigated. The absorption coefficient (α) could be calculated by using the following relation [19]:

$\alpha = 2.303\ A / t$ ……………….. (2)

Where t is the film thickness. Figure (3) Shows the dependence of the absorption coefficient (α) on the wavelength. The absorption coefficient decreases with increasing the wavelength. Also it can be observed from the figure that the absorption coefficient increases with increasing the doping contents of $NiCl_2$ to 0.4%, this increasing can be attributed to the existence of more electronic transitions from higher vibration levels of the ground state to higher sublevels of the first excited singlet state [20].

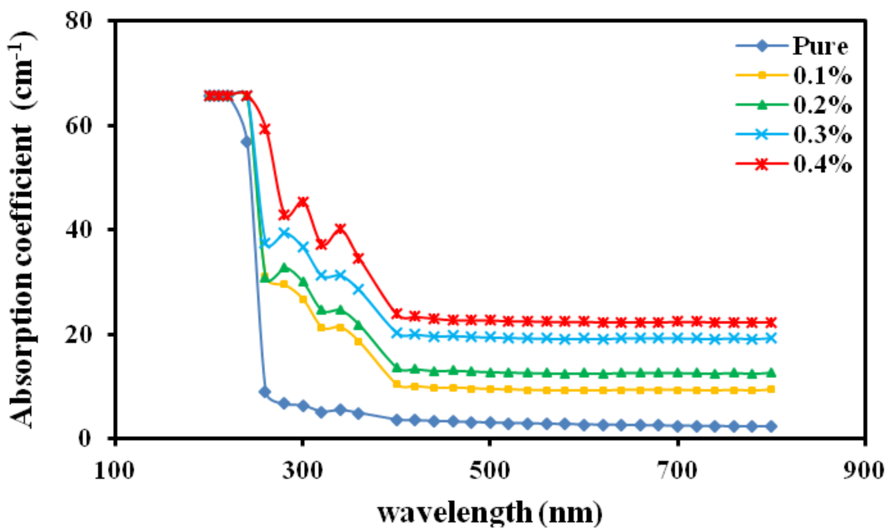

Figure 3. Variation of Absorption coefficient with wavelength for pure and doped PMMA films.

The incorporation of dopants into polymeric materials often reveals the formation of band tailing in the band gap. The tail of the absorption edge is exponential, indicating the presence of localized states in the energy band gap (E_g). The amount of tailing can be predicted to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach [21]. The absorption edge gives a measure of the energy band gap and the exponential dependence of the absorption coefficient, in the exponential edge region Urbach rule is expressed as [22,23]:

$\alpha = \alpha^{\circ} \exp (h\upsilon / E_U)$ ………………… (3)

Where α° is a constant, hυ is a photon energy, E_U is the Urbach energy, which characterizes the slope of the exponential edge. Figure (4) shows Urbach plots of the films. The value of E_U was obtained from the inverse of the slope of lnα with hυ and is given in Table (1). The dopants change the width of the localized states in the optical band. E_U values change inversely with the optical band gap. The Urbach energy values of PMMA, PMMA:$NiCl_2$ 0.1%, PMMA:$NiCl_2$ 0.2% PMMA:$NiCl_2$ 0.3%

and PMMA:$NiCl_2$ 0.4% films were calculated to be 278, , 323, 421, 565 and 702 meV respectively. The increase of E_U suggests that the atomic structural disorder of PMMA films increase by $NiCl_2$ doping. So, this increase leads to a redistribution of states, from band to tail. As a result, both a decrease in the optical gap and a widening of the Urbach tail are taken place.

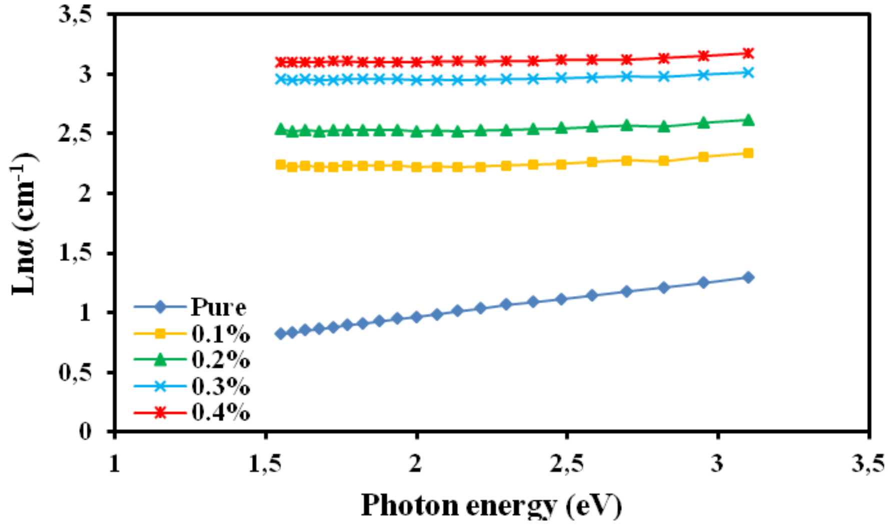

Figure 4. lnα versus photon energy for pure and doped PMMA films.

The refractive index (n) dispersion plays an important role in optical communication and designing of the optical devices. Therefore, it is important to determine dispersion parameters of the films. The dispersion parameters of the films were evaluated according to the single-effective-oscillator model using the following relation [24, 25]:

$$n^2 -1 = [E_d\, E_o / E_o^2 - (h\upsilon)^2] \quad \ldots\ldots\ldots\ldots\ldots (4)$$

The physical meaning of the single-oscillator energy E_o is that it simulates all the electronic excitation involved and E_d is the dispersion energy related to the average strength of the optical transitions [26], which is a measure of the intensity of the inter band optical. This model describes the dielectric response for transitions below the optical gap. $(n^2-1)^{-1}$ vs. $(h\upsilon)^2$ plots for the films was plotted as shown in Figure (5). E_o and E_d values were determined from the slope, $(E_oE_d)^{-1}$ and intercept (E_o/E_d), on the vertical axis and are given in Table (1). E_o values decreased with the dopants as the optical band gap decrease because the depending on it where the energy band gap is calculated from E_o. According to the single-oscillator model, the single oscillator parameters E_o and E_d are related to the imaginary part of the complex dielectric constant, The static refractive index n(o) evaluated from equation (4) then the value of static dielectric constant ε_∞ was calculated. The dielectric constant were observe a decrease with increasing $NiCl_2$ content. The dielectric constant relates to the permittivity of the material. The permittivity expresses the ability of a material to polarise in response to an applied field. It is the ratio of the permittivity of the dielectric to the permittivity of a vacuum [27].

The moments of the imaginary part of the optical spectrum M_{-1} and M_{-3} moments can be derived from the following relations [28]:

$E_o^2 = M_{-1} / M_{-3}$ …………….. (5)

$E_d^2 = M^3_{-1} / M_{-3}$ ………..……. (6)

The values obtained for the dispersion parameters E_o, E_d, E_g, n(o), ε_∞, M_{-1} and M_{-3} are listed in Table (1). All these parameters changes with the dopants.

For the definition of the dependence of the refractive index on the light wavelength, the single-term Sellmeier relation can be used [24]:

$n^2(\lambda) - 1 = S_o.\lambda_o^2 / 1 - (\lambda_o/\lambda)^2$ ……………. (7)

Where λ_o is the average oscillator position and S_o is the average oscillator strength. The parameters S_o and λ_o in equation (7) can be obtained experimentally by plotting $(n^2 - 1)^{-1}$ against λ^{-2} as shown in Figure (6), the slope of the resulting straight line gives 1/ S_o, and the infinite-wavelength intercept gives 1/ S_o λ_o^2. The results shows a decrease in the band gap which may be attributed to the presence of unstructured defects, that increase the density of localized states and cause a widening in the Urbach tail and consequently decrease the energy gap.

Table 1. The optical parameters

Samples	E_u meV	E_o (eV)	E_g (eV)	E_d (eV)	M_{-1} eV^{-2}	M_{-3} eV^{-2}	ε_∞	n(o)	$S_o x10^{13}$ m^{-2}	λ_o nm
Pure	278	6.58	3.29	1.73	1.128	0.0779	2.12	1.45	8.35	106.04
PMMA/$NiCl_2$ (0.1%)	323	5.22	2.61	1.88	0.777	0.0381	1.77	1.33	1.71	751.79
PMMA/$NiCl_2$ (0.2%)	421	5.17	2.58	2.69	0.515	0.0189	1.51	1.23	3.43	563.55
PMMA/$NiCl_2$ (0.3%)	565	4.52	2.26	3.51	0.363	0.136	1.36	1.16	4.79	572.84
PMMA/$NiCl_2$ (0.4%)	702	3.80	1.90	4.29	0.264	0.0061	1.26	1.12	1.06	353.92

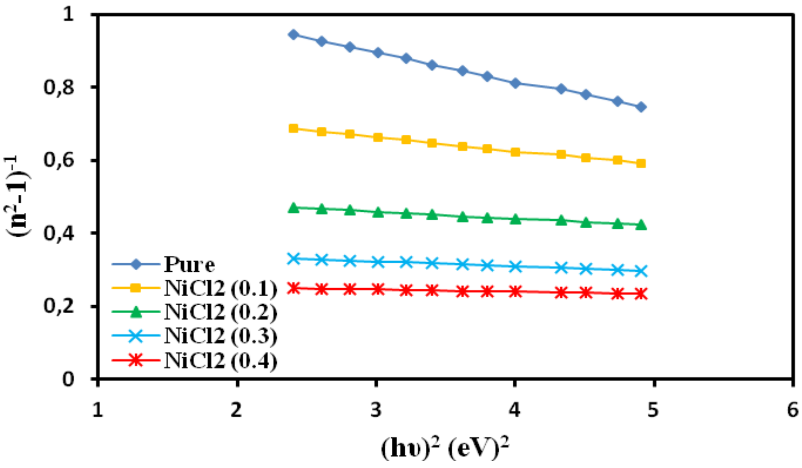

Figure 5. Variation in $(n^2 - 1)^{-1}$ as a function of $(h\upsilon)^2$ for pure and doped PMMA films.

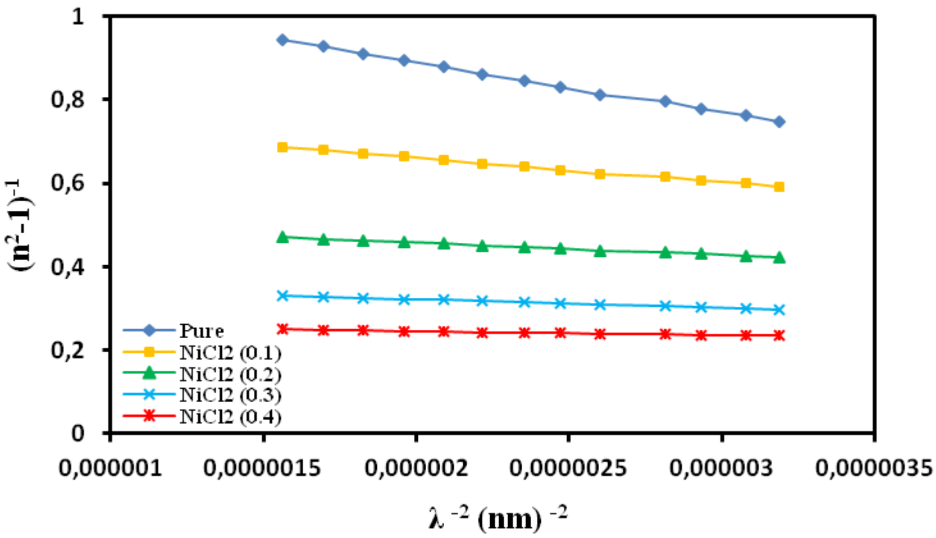

Figure 6. Variation in $(n^2 - 1)^{-1}$ as a function of $(\lambda)^{-2}$ for pure and doped PMMA films.

4. CONCLUSION

The aim of this studying to get of the conductive polymer by adding $NiCl_2$ salt to PMMA polymer, films where prepared by using casting method. Both pure and doped samples were optically characterized by using UV-VIS technique and the results were systematically presented. The optical properties reflection and absorption coefficient were increases with increasing $NiCl_2$ concentration but the transmission is decreased. Optical band gap was calculated and found to be decreases with the increasing of the doping concentration from 3.29 to 1.90 eV of 0.1 to 0.4 wt% respectively, these result were inversely values with the Urbach tails where increase from 278, to 702 meV. The optical dispersion parameters were characterized. single–oscillator parameters, static refractive index, static dielectric constant, moments of the imaginary part of the optical spectrum, average oscillator position and average oscillator strength were determined where decreases with increasing the doping contents of $NiCl_2$ to 0.4%. It was shown that the average oscillator strength value increase from 1.73 to 4.29 eV with increasing of doping concentration.

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