

Research Article

Fabrication and Characterization of Nickel Chloride Doped PMMA Films

Wasan A. Al-Taa'y,¹ Saad F. Oboudi,² Emad Yousif,³ Mohammed Abdul Nabi,¹
Rahimi M. Yusop,⁴ and Darfizzi Derawi⁴

¹Department of Physics, College of Science, Al-Nahrain University, Baghdad, Iraq

²Department of Physics, College of Science, Baghdad University, Baghdad, Iraq

³Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq

⁴School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

Correspondence should be addressed to Rahimi M. Yusop; rahimi@ukm.my

Received 19 August 2014; Revised 29 November 2014; Accepted 30 November 2014

Academic Editor: Weihua Tang

Copyright © 2015 Wasan A. Al-Taa'y et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Films of PMMA and PMMA doped with NiCl₂ with different contents were prepared using the casting technique. The optical properties of all films were investigated using spectrophotometric measurements of absorbance and transmittance in the wavelength range 200–800 nm. The change of the calculated values of the optical energy gaps with increasing NiCl₂ content has been interpreted in terms of the structural modifications of the PMMA matrix. The optical energy gap decreased from 3.6 to 3.05 eV with increasing the NiCl₂ concentration to 0.4%. The effect of doping on the optical constants of films such as refractive index, extinction coefficient, real and imaginary parts of dielectric constant, optical conductivity, and skin depth has been reported. All these constants were increased with increasing NiCl₂ concentration with the exception of skin depth which is different result.

1. Introduction

Optical properties of polymer films are very important for many technological applications [1], ranging from protective coatings to paintings, microelectronic, semiconductors, and optoelectronic devices depending on the reflectance and transmittance properties of the films during their preparation [2, 3]. PMMA as a polymeric waveguide has attracted much attention for use as optical components and in optoelectronics devices due to their low cost and volume productivity. Recently, some researchers reported optical components such as an optical switch, a coupler, a splitter, and a transceiver [4, 5].

PMMA is considered as an excellent host material for doping due to their good transparency (the transmission for visible light is very high), resistivity, mechanical strength, and optical homogeneity which can play an important role in building up advanced optical materials [6]. It is one of

the earliest and best known polymers. PMMA was seen as a replacement for glass in a variety of applications and is currently used extensively in glazing applications. The material is one of the hardest polymers and is rigid, glass-clear with glossy finish and good weather resistance [7].

Owing to the influence of doping on the properties of polymeric materials, the controlled preparation of PMMA of different doping materials and concentrations is always the researcher's purpose; these doping processes cause a remarkable change in their properties [8, 9]. The present work is a part of a systematic study of the effect of doping of NiCl₂ on PMMA on improving their physical properties. Therefore, we study the effect of the doping level (W) using both the optical absorption measurements and the determination of the optical constants and energy gap. The accurate determination of the optical constants of these materials is important, in order not only to know the basic mechanisms underlying these

phenomena but also to exploit and develop their interesting technological applications.

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, and 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 was measured using indicating micrometer $0.25 \mu\text{m}$; all layers were found to be in the range of $20 \pm 1 \mu\text{m}$; these layers were clear, transparent, and free from any noticeable defect showing light bluish color.

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

3. Results and Discussion

The optical properties of films by means of optical absorption in the UV-VIS region of 200–800 nm have been investigated. Figure 1 shows the dependence of absorbance (A) on wavelength (λ) of all films before and after being doped by NiCl_2 salt with different concentrations (0.1, 0.2, 0.3, and 0.4%). It is observed that in the visible region all films have very low transparent; then absorbance is rapidly decreased with increasing wavelength. This behavior may be attributed to perfection and stoichiometry of the films. Also it can be observed from the figure that the absorbance increased with increasing the doping concentration of NiCl_2 to 0.4%; this result agrees with the previous work [10]. It has been observed that the absorption peaks appear at wavelengths 240, 242, 248, 249, and 251 nm as the concentration of dopant varies from 0 to 0.4 mol/L in PMMA matrix, respectively. The shifting occurring in the spectra may be due to the polarity of solvent used in the synthesis or may be due to the dispersion of rare earth oxide particles in the PMMA matrix [11].

From the transmittance (T) data and according to Tauc [12] relation, the most satisfactory representation is obtained by plotting the quantity $(\alpha h\nu)^2$ as a function of $(h\nu)$. The plot of $(\alpha h\nu)^2$ versus $h\nu$ for different dopant percentage in polymer samples is shown in Figure 2. The observed behavior suggests allowed direct transition for amorphous material [13]. The values of optical energy gap E_{opt} obtained from the extrapolation of the linear region are found to be decrease for all samples 3.6, 3.5, 3.29, 3.19, and 3.05 eV with increasing the doping percentage of NiCl_2 0.1, 0.2, 0.3, and 0.4%, respectively. The decrease in E_{opt} with increasing NiCl_2 concentration can be understood by considering the mobility gap variation in the doped polymer [14]. The figure shows a linear dependence for pure PMMA in one region representing one optical absorption edge as mentioned before in previous work

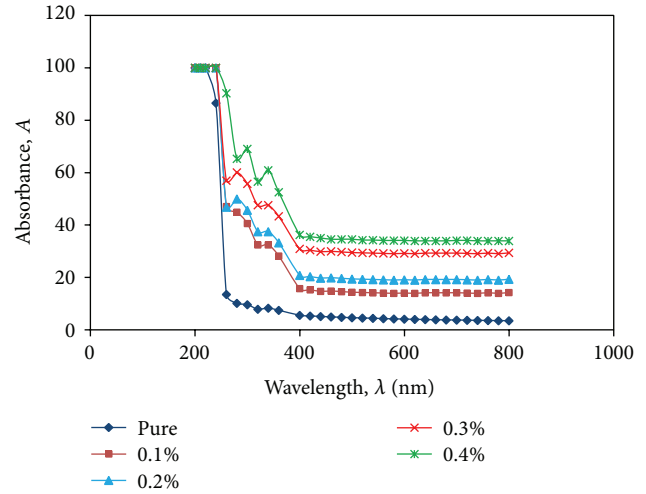


FIGURE 1: The variation of absorbance with wavelength for pure and doped PMMA films.

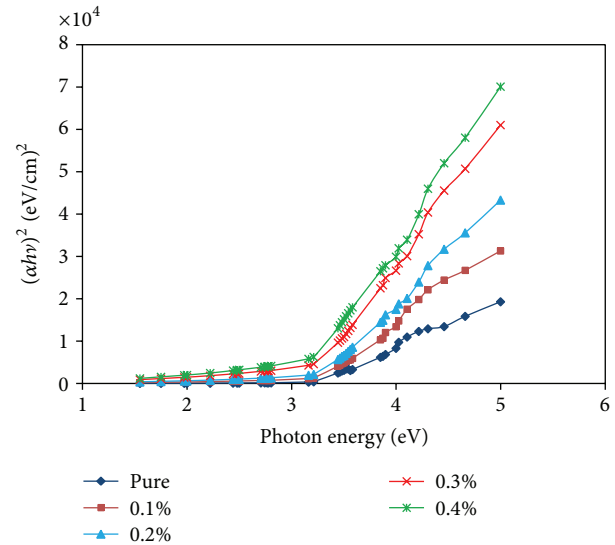


FIGURE 2: The $(\alpha h\nu)^2$ versus photon energy for pure and doped PMMA films.

[9, 15–17]. The value obtained in this work is close to others previously reported for the allowed direct transition.

The refractive index (n) is an important parameter for optical materials and applications. Thus, it is important to determine optical constants of the films. The refractive index of the films was determined from the following relation [18]:

$$n = \left(\frac{1 + R}{1 - R} \right) + \sqrt{\frac{4R}{(1 - R)^2} - K^2}, \quad (1)$$

where R represent the reflectance and k is the extinction coefficient ($k = \alpha\lambda/4\pi$) where α is the absorption coefficient. The n and k values of dependence of wavelength are shown in Figures 3 and 4, respectively, for all samples before and after being doped. As seen in these figures, the n and k values increase with increasing the doping concentration of

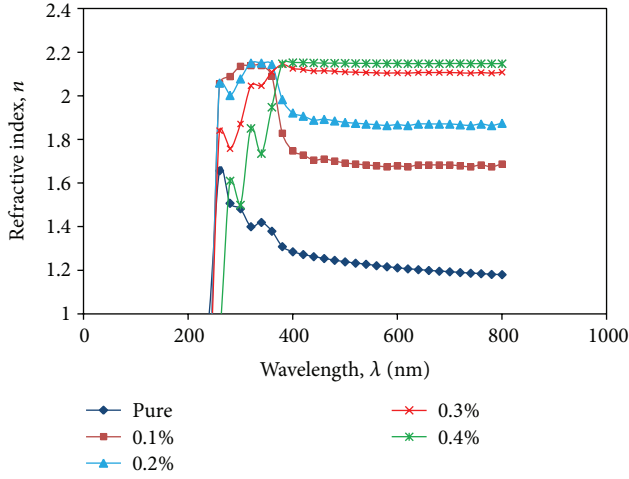


FIGURE 3: The variation of refractive index with wavelength for pure and doped PMMA films.

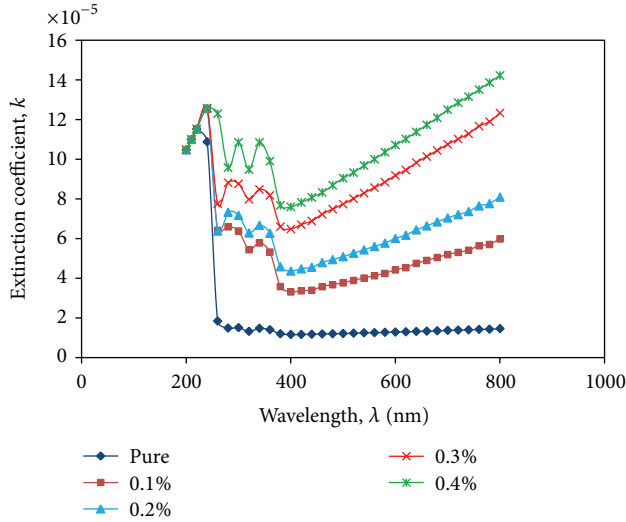


FIGURE 4: The extinction coefficient versus wavelength for pure and doped PMMA films.

NiCl₂; this result agrees with the previous work [19]. Such behavior corresponds to the density of absorbing centers such as impurities absorption, excitation transition, and other defects in the crystal lattice dependent on the conditions of sample preparation.

The dielectric constant is defined as $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$; real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant are related to the n and k values. The ϵ_1 and ϵ_2 values were calculated using the following formulas [20]

$$\begin{aligned} \epsilon_1 &= n^2 - k^2, \\ \epsilon_2 &= 2nk. \end{aligned} \quad (2)$$

The ϵ_1 and ϵ_2 values of dependence of wavelength are, respectively, shown in Figures 5 and 6 for pure and doped films. The ϵ_1 values are higher than ϵ_2 values. It is seen that the ϵ_1 and ϵ_2 values increase with increasing wavelength and with

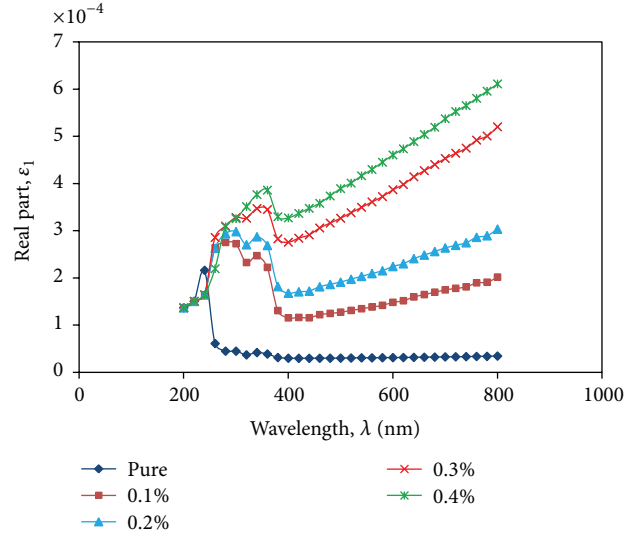


FIGURE 5: The variation of real part of dielectric constant with wavelength for pure and doped PMMA films.

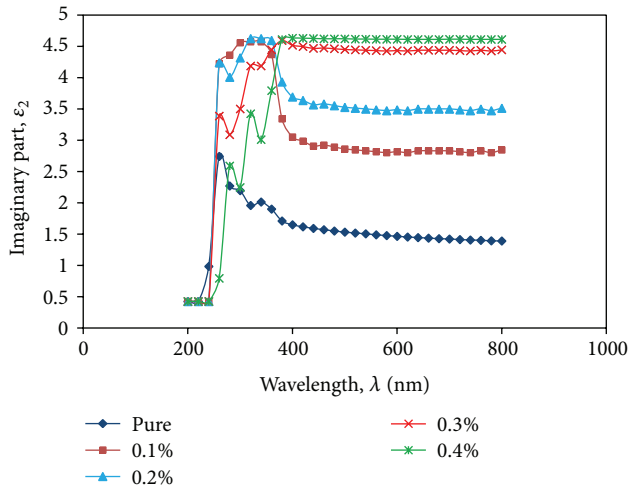


FIGURE 6: The variation of imaginary part of dielectric constant with wavelength for pure and doped PMMA films.

the doping concentration of NiCl₂. The values of dielectric constant at 400 nm for 0, 0.1, 0.2, 0.3, and 0.4% NiCl₂ content were 1.75, 3.08, 3.71, 4.45, and 4.60, respectively, for real part and 0.000035, 0.000123, 0.000177, 0.000285, and 0.000342, respectively, for imaginary part. Moreover, this increase by the variation of ϵ_1 mainly depends on n^2 because of small values of k^2 while ϵ_2 mainly depends on k value which is related to the variation of absorption coefficients [21].

The optical conductivity (σ) was calculated using the following relation [22]:

$$\sigma = \frac{\alpha n c}{4\pi}, \quad (3)$$

where c is the velocity of light.

Figure 7 shows the variation of optical conductivity with the wavelength. It was observed that the optical conductivity

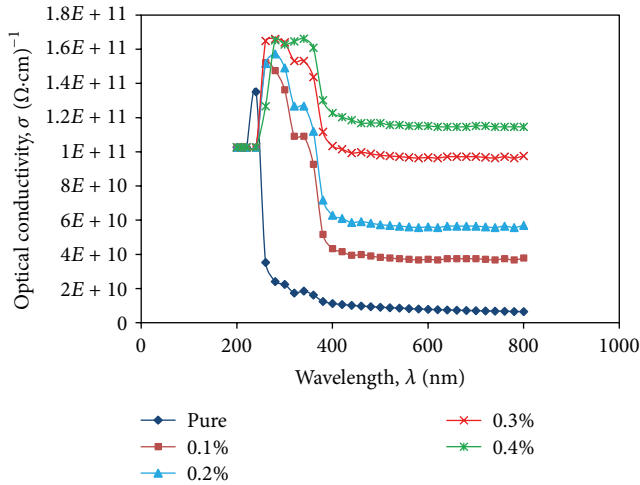


FIGURE 7: The optical conductivity versus wavelength for pure and doped PMMA films.

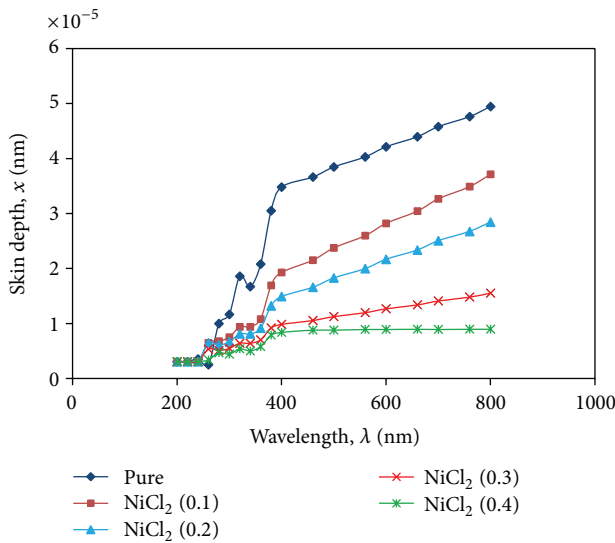


FIGURE 8: The skin depth versus wavelength for pure and doped PMMA films.

increases as the doping percentage of NiCl_2 in the PMMA increases to 0.4%. It can be noticed from the figure that the optical conductivity for all films increased in the low wavelengths region and decreased in the high wavelength region; this decrease is due to the low absorbance of the films in that region.

The skin depth (x) could be calculated using the following relation [23]:

$$x = \frac{\lambda}{2\pi k}. \quad (4)$$

Figure 8 shows the variation of skin depth as a function of wavelength for all films. It is clear from the figure that the skin depth increases as the wavelength increases; this behavior could be seen for all samples, but the skin depth decreases

as the doping concentration increases, so the skin depth is a transmittance related.

4. Conclusion

PMMA and NiCl_2 doped PMMA films were prepared by using casting technique. Both pure and doped samples were characterized. Results indicate that the optical band gap and the optical parameters are strongly dependent on doping with NiCl_2 . The optical band gap decreased from 3.6 to 3.05 eV with increasing the doping concentration to 0.4%. The refractive index, extinction coefficient, the real and imaginary parts of dielectric constant, and the optical conductivity were calculated and they are tending to increase with increasing the doping concentration of NiCl_2 ; on the other hand, the skin depth decreases with increasing the doping concentration. These present observations can help improve the understanding of the optical parameters of NiCl_2 films.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors thank the Al-Nahrain University and Universiti Kebangsaan Malaysia for the funding (Codes AP-2011 17, DPP-2013-054, UKM-MI-OUP-2011, AP-2012-017, and DLP 2013-002).

References

- [1] A. Tawansi, H. M. Zidan, Y. M. Moustafa, and A. H. Eldumiaty, "Optical and electrical properties of NiCl_2 filled PVC films," *Physica Scripta*, vol. 55, no. 2, pp. 243–246, 1997.
- [2] R. Oslanec, A. C. Costa, R. J. Composto, and P. Vlcek, "Effect of block copolymer adsorption on thin film dewetting kinetics," *Macromolecules*, vol. 33, no. 15, pp. 5505–5512, 2000.
- [3] G. Reiter, "Dewetting as a probe of polymer mobility in thin films," *Macromolecules*, vol. 27, no. 11, pp. 3046–3052, 1994.
- [4] Y. S. Heo, S. Chung, K. Cho, C. Chung, D.-C. Han, and J. K. Chang, "Effects of peak anomalies with the hydrophilic or hydrophobic properties of reservoirs during serial injection on a capillary electrophoresis microchip," *Journal of Chromatography A*, vol. 1013, no. 1-2, pp. 111–122, 2003.
- [5] Z. Chen, Y. Gao, J. Lin, R. Su, and Y. Xie, "Vacuum-assisted thermal bonding of plastic capillary electrophoresis microchip imprinted with stainless steel template," *Journal of Chromatography A*, vol. 1038, no. 1-2, pp. 239–245, 2004.
- [6] A. Tawansi, A. El-khodary, H. M. Zidan, and S. I. Badr, "The effect of MnCl_2 filler on the optical window and the physical properties of PMMA films," *Polymer Testing*, vol. 21, no. 4, pp. 381–387, 2002.
- [7] T.-L. Tsai, C.-C. Lin, G.-L. Guo, and T.-C. Chu, "Effects of microwave-assisted digestion on decomposition behavior of polymethyl methacrylate (PMMA)," *Materials Chemistry and Physics*, vol. 108, no. 2-3, pp. 382–390, 2008.
- [8] B. Zhang and F. D. Blum, "Thermogravimetric studies of adsorbed PMMA," *Polymer Preprints*, vol. 43, no. 1, pp. 484–485, 2002.

- [9] A. Kurt, "Influence of $AlCl_3$ on the optical properties of new synthesized 3-Armed poly(methyl methacrylate) films," *Turkish Journal of Chemistry*, vol. 34, no. 1, pp. 67–79, 2010.
- [10] M. H. Mohmmad, "Study of optical constants of (PMMA) doped with (C₁₄H₁₄N₃O₆S)," *Ibn Al-Haitham Journal for Pure and Applied Science*, vol. 23, pp. 1–14, 2010.
- [11] M. Chahar, V. Ali, and S. Kumar, "Preparation and spectral investigations of neodymium oxide doped polymethylmethacrylate based laser material," *International Journal of Scientific and Research Publications*, vol. 2, pp. 2250–3153, 2012.
- [12] J. Tauc, *Amorphous and Liquid Semiconductors*, Plenum Press, New York, NY, USA, 1974.
- [13] A. N. Alias, Z. M. Zabidi, A. M. M. Ali, M. K. Harun, and M. Z. A. Yahya, "Optical characterization and properties of polymeric materials for optoelectronic and photonic applications," *International Journal of Applied Science and Technology*, vol. 3, no. 5, pp. 11–38, 2013.
- [14] H. Zahr El-Deen and A. I. Hafez, "Physics-chemical stability of PVA films doped with Mn^{+2} ions against weathering conditions," *The Arabian Journal for Science and Engineering*, vol. 34, no. 1A, pp. 13–26, 2009.
- [15] H. M. Zidan, A. Tawansi, and M. Abu-Elnader, "Miscibility, optical and dielectric properties of UV-irradiated poly(vinyl acetate)/poly(methylmethacrylate) blends," *Physica B: Condensed Matter*, vol. 339, no. 2-3, pp. 78–86, 2003.
- [16] H. M. Zidan and M. Abu-Elnader, "Structural and optical properties of pure PMMA and metal chloride-doped PMMA films," *Physica B*, vol. 355, no. 1–4, pp. 308–317, 2005.
- [17] S. H. Deshmukh, D. K. Burghate, S. N. Shilaskar, G. N. Chaudhari, and P. T. Deshmukh, "Optical properties of polyaniline doped PVC-PMMA thin films," *Indian Journal of Pure and Applied Physics*, vol. 46, no. 5, pp. 344–348, 2008.
- [18] T. K. Hamad, R. M. Yusop, W. A. Al-Taa'y, B. Abdullah, and E. Yousif, "Laser induced modification of the optical properties of nano-ZnO doped PVC films," *International Journal of Polymer Science*, vol. 2014, Article ID 787595, 8 pages, 2014.
- [19] H. A. Muhammed, S. C. Sami, and F. H. Nadir, "The effect of Iro chromate on the optical properties of PMMA films," *Diyala Journal for Pure Science*, vol. 6, pp. 161–169, 2010.
- [20] W. Al-Taa'Y, M. Abdul Nabi, R. M. Yusop et al., "Effect of nano ZnO on the optical properties of poly(vinyl chloride) films," *International Journal of Polymer Science*, vol. 2014, Article ID 697809, 6 pages, 2014.
- [21] A. H. Ahmad, A. M. Awatif, and N. Zeid Abdul-Majied, "Doppin effect on optical constants of polymethylmethacrylate (PMMA)," *Engineering & Technology*, vol. 25, no. 4, pp. 558–568, 2007.
- [22] J. I. Pankove, *Optical Processes in Semiconductors*, Dover, New York, NY, USA, 1975.
- [23] J. F. Eloy, *Power Lasers*, National School of Physics, John Wiley & Sons, Grenoble, France, 1984.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

