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RESEARCH ARTICLE

Effect of $MnCl_2$ Additive on Optical and Dispersion Parameters of Poly methyl Methacrylate Films

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Abstract

PMMA films with various content of $MnCl_2$ additive (1, 3%) are prepared by casting method. Amorphous films of PMMA-Mn are examined using X-ray diffraction (XRD). UV-Visible spectrophotometer is used to record the transmittance spectra, which decreased with the increasing of $MnCl_2$. Energy gap value decreased from 3.91 eV for PMMA to 3.39 eV for film with 3% additive of $MnCl_2$, while the Urbach energy are increased from 555 meV to 741 meV for the same additives. Dispersion parameters are determined using Wemple and DiDomenico model. The E_d, E_o, and So increased with the increasing of $MnCl_2$ additive, while n (0), λ_o, and M_{-1}, M_{-3} are decreased.

Keywords: *PMMA, Dispersion parameters, Composite, Optical properties.*

Introduction

Composite materials have got much importance for various applications [1]. One of the most polymeric materials used in application is poly methyl methacrylate PMMA, which have unique properties like transparent in visible light, high strength, thermal stability, good toughness and stiffness [2, 5]. This work was focus to study effect of $MnCl_2$ additive on structural and dispersion Parameters of PMMA composite.

Materials and Methods

Films of poly methyl methacrylate polymer doped by $MnCl_2$ were deposited using casting technique. PMMA with purity of 98%, were used as a matrix polymer dissolved by chloroform solvent .Doped with material with volumetric content of 1% and 3%.

These films were left to dry in an oven kept at 40 °C for 6 hours in order to obtain clear and homogenous films free from cracks. The films were cut as 1 cm^2 .Thickness of the films was measured by digital micrometer and they were in the range of 20 micron. Double beam spectrophotometers supplied from Schimadzu Company Japan were used to get transmittance and absorbance spectra in wavelength range of (300-900) nm.

Results and Discussion

Casting method was used to prepare PMMA-Mn films with various content of $MnCl_2$. XRD pattern of the films are presented in the Figure 1 that refer to the amorphous of the prepared films.

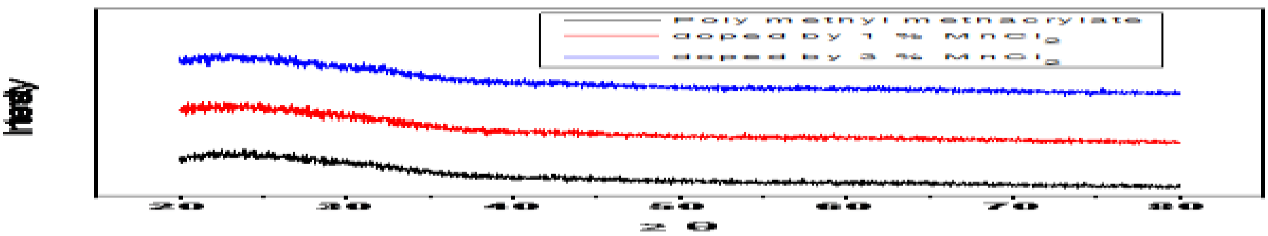

Figure 1: XRD pattern of pure and $MnCl_2$ dopant

Transmittance spectra versus wavelength for PMMA-$MnCl_2$ composites as shown in Figure 2. It can be noticed from this figure that transmittance decreased with increasing of $MnCl_2$ content.

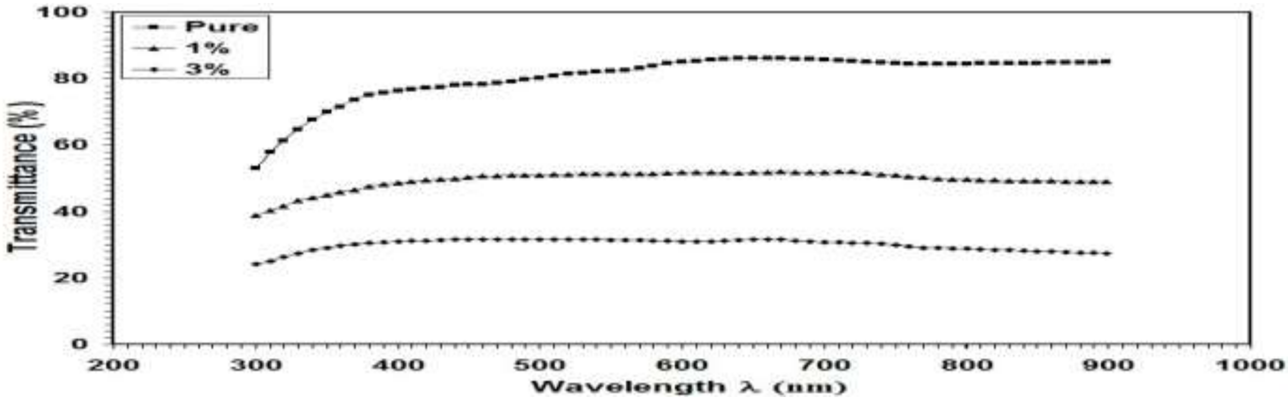

Figure 2: Transmittance versus wavelength for (PMMA-$MnCl_2$) composites

Absorption coefficient (α) of (PMMA-$MnCl_2$) composites is defined by following equation [6]:

$$\alpha = 2.303A/t \quad (1)$$

Fig. 3 shows relation between absorption coefficient of (PMMA-$MnCl_2$) composites and wavelength. From this Fig., absorption coefficient of (PMMA-$MnCl_2$) composites decreased with increasing of $MnCl_2$ percentage.

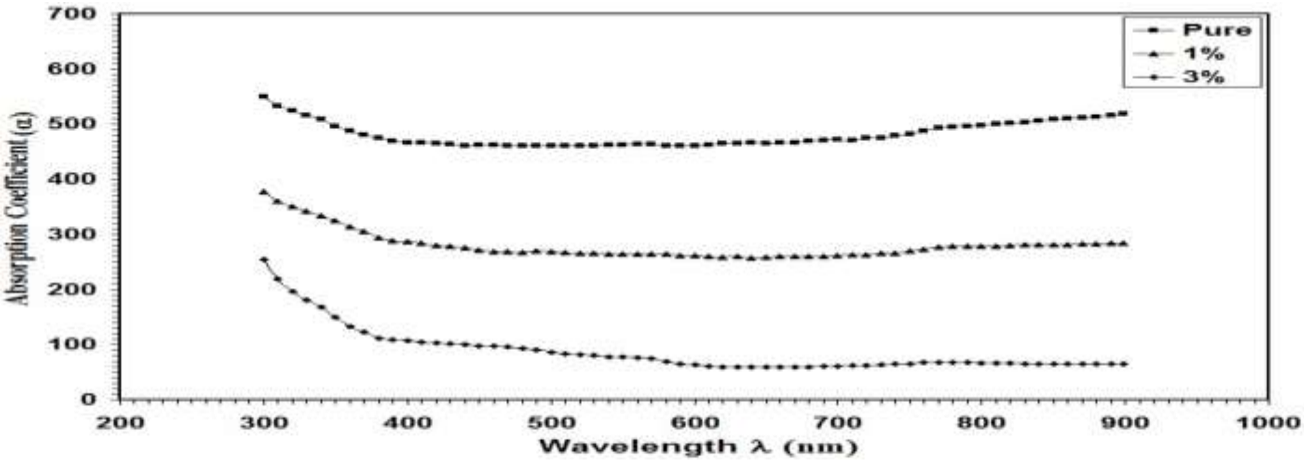

Figure 3: α of PMMA- $MnCl_2$ composites with wavelength

From the above figure we note that the absorption coefficients of PMMA-MnCl2composites are less than 10^4 cm^{-1}, so transition is indirect. The extinction coefficient (k_o) for PMMA- $MnCl_2$ composites can be calculated by the equation [7, 8]:

$$k_o = \frac{\alpha\lambda}{4\pi} \quad (2)$$

Where λ: wavelength of incident photon.

From Figure 4 it can be noticed effect of $MnCl_2$ concentration on extinction coefficient of PMMA with different wavelength for incident light. As shown in figure, the extinction coefficient of PMMA is increased with increase of the Manganese oxide NPs, which was due to increase of α [9].

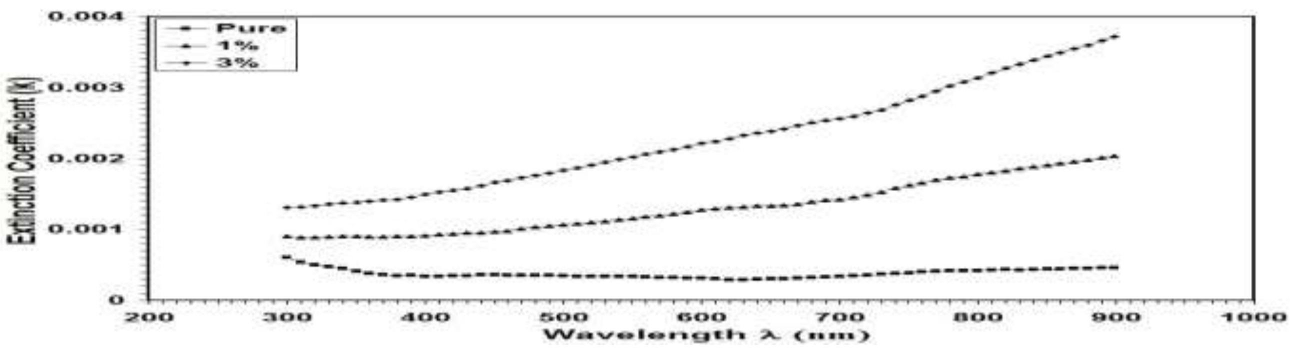

Figure 4: k_o versus of wavelength for PMMA- $MnCl_2$ composites

Dielectric constant is defined is divided into two parts: real (ε_r) and imaginary (ε_2) parts of dielectric constant. ε_1 and ε_2 values were calculated using following equations [10, 11]:

$$\varepsilon_r = n^2 - k^2 \quad (3)$$

$$\varepsilon_i = 2nk(4) \quad (4)$$

The ε_1 and ε_2 values of dependence of wavelength are shown in Figures (5, 6) for PMMA- $MnCl_2$ composites. It is seen that ε_{r1} and ε_i values increased with increasing of $MnCl_2$ concentration. This increase could be attributed to increase of light absorption and density of PMMA- $MnCl_2$ composites with the increase of MnCl2 concentrations [12].

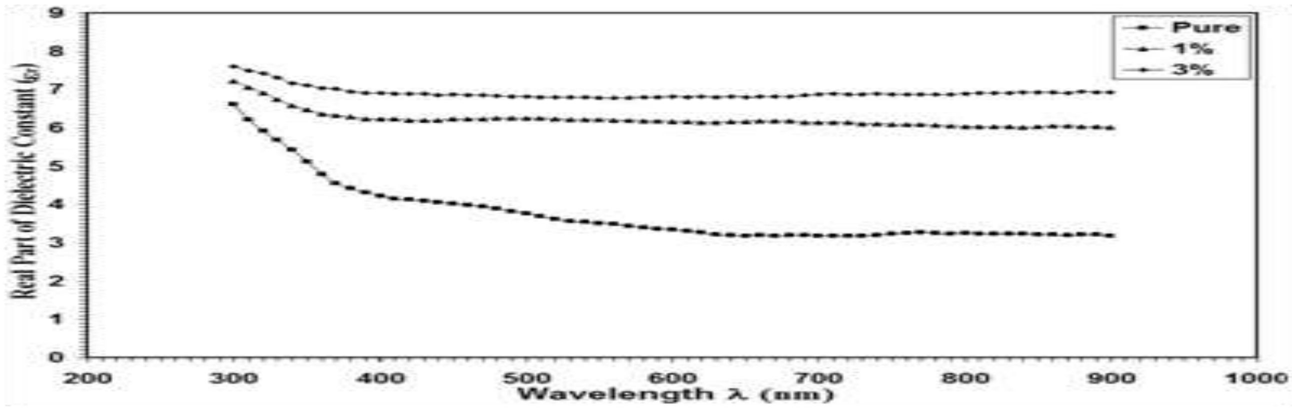

Figure 5: ε_r versus wavelength for PMMA- $MnCl_2$composite

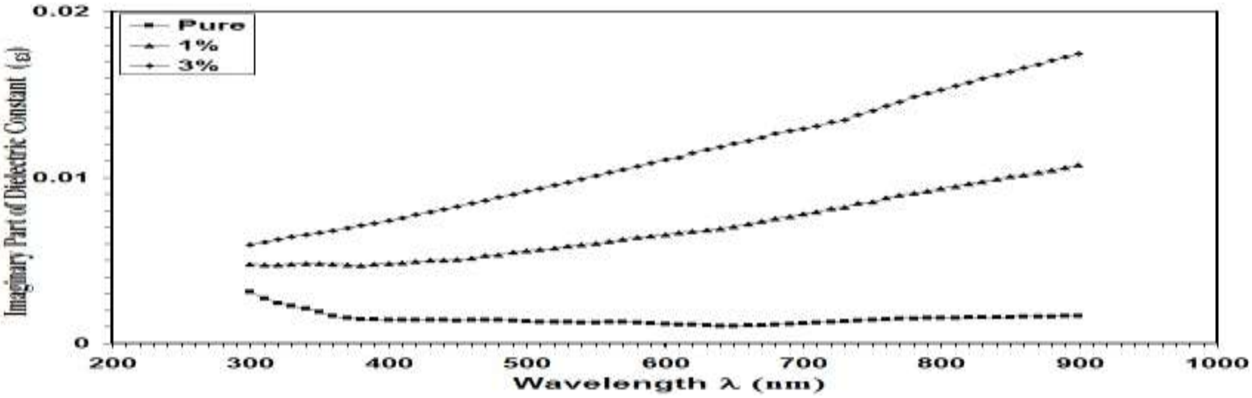

Figure 6: ε_I versus wavelength for PMMA- $MnCl_2$ composite

Urbach tail is considered as the width of localized state, which is exists in optical band gap, which can be related to the exponential tails for the density of states determined by the relation [13]:

$$\alpha = \alpha_o \exp\left(\frac{E}{E_U}\right) \quad (5)$$

Where E_U is Urbach energy and α_o is a constant. Urbach energy can estimated from plotting lnα on y-axis with photon energy (hυ) on the x-axis (as in Figure 7), the inverse slope represent the Urbach energy. The values of Urbach energy decrease with increasing of $MnCl_2$ additive, these values are listed in Table (1).

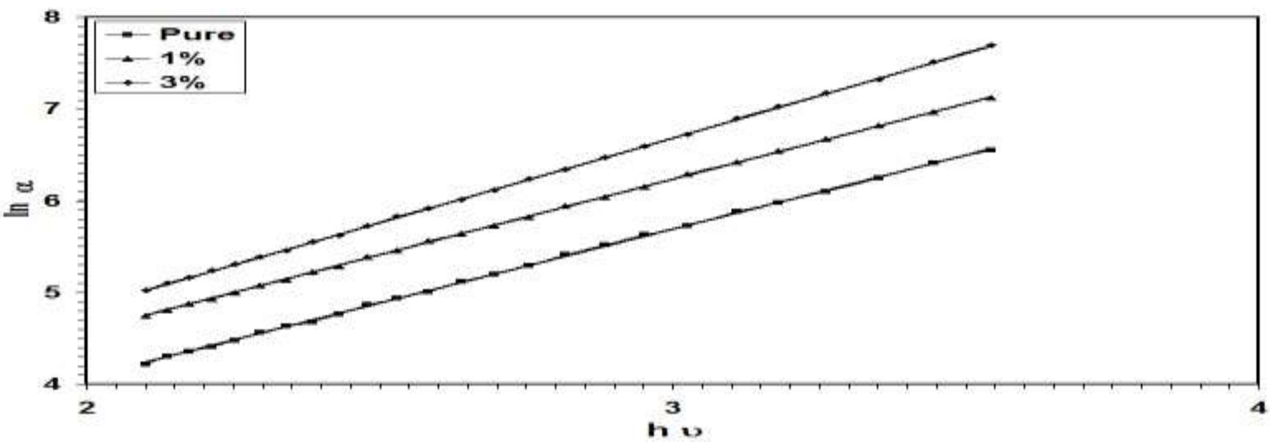

Figure 7: lnα with photon energy for PMMA- $MnCl_2$ composite

Single-oscillator model Wemple and Didomenico dispersion relationship was used to calculate dispersion parameters [14]:

$$n^2(E) = 1+\frac{E_o E_d}{E_o^2 - E} \quad (6)$$

Where E_o is single-oscillator energy, E_d is dispersion energy, and E is photon energy. Figure 8 represent relationship between $(n^2-1)^{-1}$ and $(h\upsilon)^2$ was plotted to determine dispersion parameters (E_o and E_d) from slope $(E_oE_d)^{-1}$ and intercept (E_o/E_d) [15]. Values of E_o and E_d increase with increasing of $MnCl_2$ additive in the PMMA-Mn films. The values are listed in Table (1).

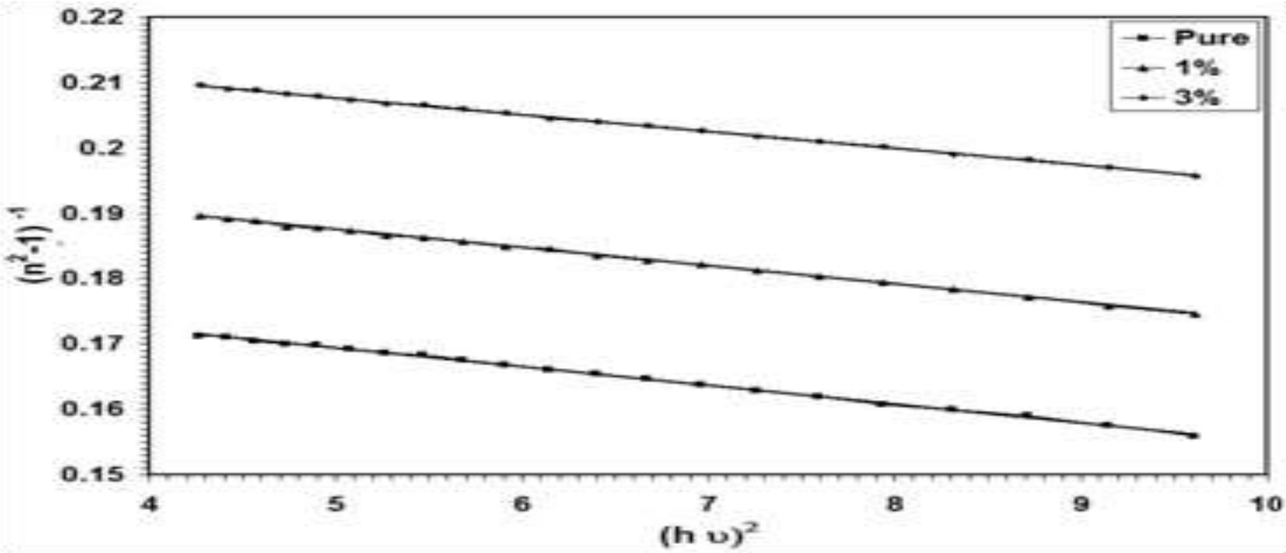

Figure 8: $(n^2-1)^{-1}$ via $(h\upsilon)^2$ of PMMA- $MnCl_2$composite

Moments of imaginary part of optical spectrum M_{-1} and M_{-3} can be derived from the following relations [16]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad (7)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad (8)$$

The values of moments (M_{-1} and M_{-3}) decrease with increasing of $MnCl_2$ additive, these values are listed in Table (1). Long wavelength refractive index (n_∞) of PMMA-Mn films were determined from the interception of vertical axis in Figure 8, and also represent ($\varepsilon_\infty = n^2_\infty$) [17]. The single-term Sellmeier relation can be used to determine refractive index (n) [18]:

$$n^2(\lambda)-1 = \frac{S_o\lambda_o^2}{1-(\frac{\lambda_o}{\lambda})^2} \quad (9)$$

Where λ_o is average oscillator position and S_o is average oscillator strength. These parameters can be determine from plotting $(n^2-1)^{-1}$ on y-axis with $1/\lambda^2$ on x-axis as shown in Figure 9. These values are shown in Table (1).

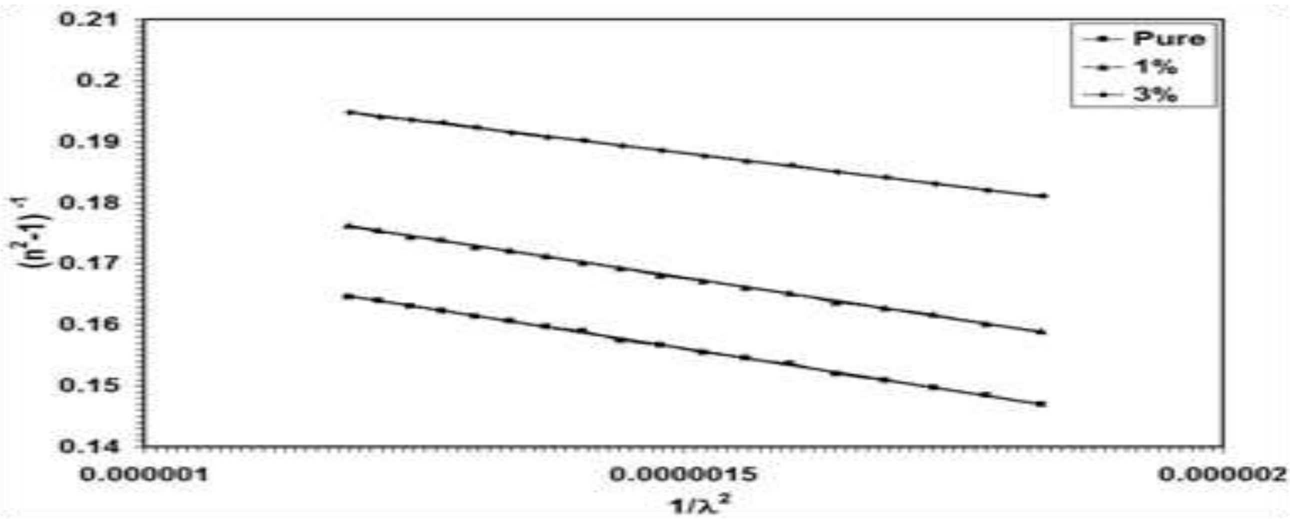

Fig.9: $(n^2-1)^{-1}$ via $1/\lambda^2$ for PMMA- $MnCl_2$films

Table 1: Urbach energy and optical parameters of PMMA $MnCl_2$films

Sample	E_d (eV)	E_o (eV)	E_g (eV)	ε_∞	n(o)	M_{-1}	M_{-3} eV^{-2}	S_o x10^{13} m^{-2}	□o □nm	U_E meV
Pure	42.60	8.08	4.00	6.26	2.5	5.2630	0.080	3.70	358	625
1 %	43.35	8.23	4.11	6.26	2.5	5.2600	0.075	3.72	336	600
3 %	44.52	8.50	4.25	5.76	2.4	4.250	0.060	4.67	322	540

Conclusions

PMMA films with various content of $MnCl_2$ additive that prepared by casting method. These films were examined by XRD .All the films were amorphous. Transmittance spectra, was decreased with the increasing of $MnCl_2$. Energy gap value decreased from 3.91 eV for pure PMMA to 3.39 eV for film with 3% additive of $MnCl_2$, while the Urbach energy are increased from 555 meV to 741 meV for the same additives. Dispersion parameters are determined using Wemple and DiDomenco model.

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