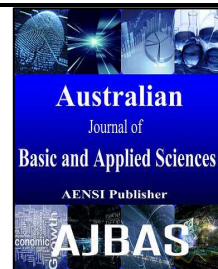




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Optical Properties of (PMMA-PVA)Blends doped with Sn, Ag and Fe

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ABSTRACT

The effect of doping with 2% Ag, Sn and Fe and blend ratio on the optical constants (refractive index n , extinction coefficient k and (real ϵ_r and imaginary part ϵ_i) of dielectric constants for Polymethylmethacrylate (PMMA) and polyvinyl acetate PVA blends using the transmittance and absorbance spectra were explained. The results showed that optical constants for undoped and doped blends exceeded those of neat PMMA but are lower than those of neat PVA. It was found that increasing of optical constant indicated the formation of miscible blends while decreasing of optical constant indicated to formation of immiscible blends. Some important parameters of optical absorption, such as the oscillator energy (E_0), dispersion energy (E_d), were evaluated.

The values obtained for the high frequency dielectric constant through Wemple – DiDomenico single oscillator procedure

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INTRODUCTION

The goal of the studying and development of new polymeric electrolytes is the possibility of their potential applications in various electrochemical devices, high performance solid-state batteries, energy conversion by fuel cells, chemical sensors, electrochromic windows, analog memory devices, etc., because of their safety performance, ease of handling, shelf life, cyclability and processibility (Vincent, C.A., 1987; MacCallum, J.A., C.A. Vincent, 1987; Bruce, P., 1995). Poly(vinyl alcohol) (PVA) is a polymer which has been investigated by many researchers for its applications as binder, blood prosthetic devices, electric double layer capacitors, electrochromic windows, sensors, bio-medical fields, fuel cells, etc., because of its excellent mechanical strength, bio-compatibility, electrochemical stability, high tensile strength and abrasion resistance, etc. (Masuda, K., *et al.*, 2000). It contains carbon chain backbone with hydroxyl groups attached to methane carbons. These OH groups can be a source of hydrogen bonding hence the assistance in the formation of polymer blends (Lee, J.H., *et al.*, 1995; Kanbara, T., *et al.*, 1991). PMMA is used in out-door electrical applications, high voltage applications, as transparent neutron stopper, standard broad cast television waves, radar bands, electrochemical windows, magnifiers, automotive tail lights (Plexiglas Design and Fabrication Data) because of

its good compatible nature with other polymers, high resistance, non-tracking characteristics, surface resistance, optical properties. The effect of different elements on the optical properties is explained. The optical constants were measured from transmittance spectrum. The static refractive index and dielectric constant were measured from the dispersion pattern.

Basic Relations:

The complex refractive index (N) is given by the equation (PANKOV, J.L., 1971):

$$N = n - ik \quad (1)$$

Where n is the real refractive index.

k is the imaginary part of (N) is obtained from the relation :

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

where α is the absorption coefficient.

λ is the wavelength.

The reflectance part (R) of incident electromagnetic plane wave can be obtained when the transmittance (T) and the absorbance (A) parts are known since:

$$A + T + R = 1 \quad (3)$$

Thus (R) can be calculated through applying the following equation :

$$R=1-(A+T) \quad (4)$$

For normal incident of plane electromagnetic wave the reflectance is given by the equation (PANKOV, J.L., 1971):

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

which leads to:

$$n = \sqrt{\frac{4R}{(R-1)^2} - k^2} - \frac{(R+1)}{(R-1)} \dots\dots\dots(6)$$

Thus (n) can be calculated when the reflectance (R) and (k) values are known .

The transmittance part of incident light (T) is depending on (α) through the following equation (KLOPFER, W., 1984):

$$T = \exp(-\alpha d) \quad (7)$$

Where (d) is thickness of sample, Thus the absorption coefficient (α) corresponding to any wavelength (λ) can be calculated by applying the relation:

$$\alpha = \frac{\ln\left(\frac{1}{T}\right)}{d} \dots\dots\dots(8)$$

or:

$$\alpha = 2.303 \log\left(\frac{1}{T}\right) \dots\dots\dots(9)$$

The dielectric constant ϵ which represents the responsiveness of electrons in matter to the incident electromagnetic field and depends on frequency (ALENSO, M., J. VENN, 1971). The real part of dielectric constant which represents the polarization term ϵ_r and imaginary part of dielectric constant ϵ_i can be calculated from the equations (PANKOV, J.L., 1971):

$$\epsilon_r = n^2 - k^2 \quad (11)$$

$$\epsilon_i = 2nk \quad (12)$$

The optical energy gap E_g can be obtained from extrapolation of the straight line portion of the plot of $(\alpha hv)^2$ versus (hv) to $\alpha = 0$ using Tauc (Tauc, J., 1974) empirical equation:

$$(\alpha hv) = A(hv - E_g)^r \quad (10)$$

where A is a constant, and $r = 1/2$ for direct allowed transition

Samples Preparation and Procedure:

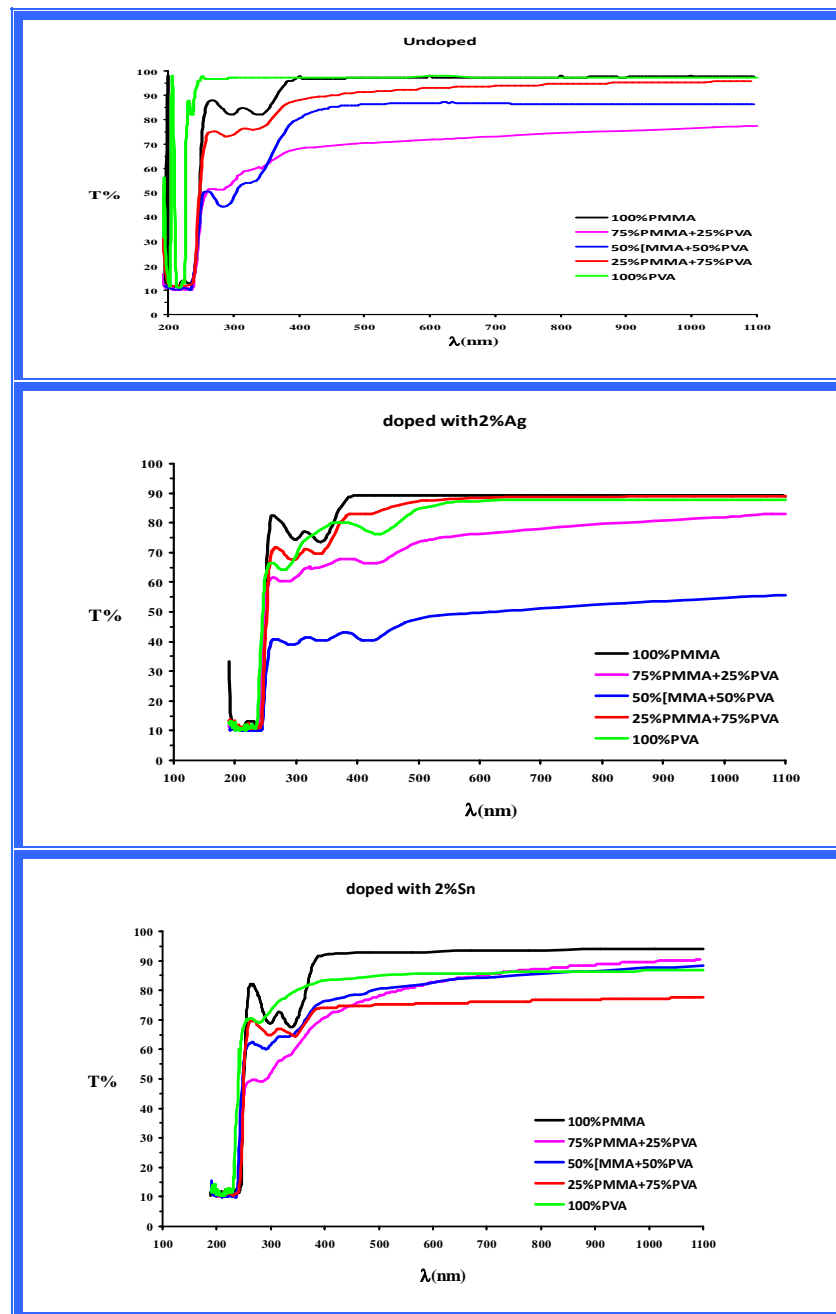
Polymethyl methacrylate (PMMA) and polyvinyl acetate PVA supplied by (HIMEDIA, India) as granules which were used as matrix and Tin(Sn), Silver Ag, and Fe as a micro powder is used as dopant in this work. N-N, Dimethyl Formamide (DMF)(CHEM Limited, India) was used as a solvent for PMMA and PVA. Appropriate weights of PMMA and PVA with the different weight blend ratios (100 PMMA, 75 PMMA + 25 PVA, 50 PMMA + 50 PVA, 25 PMMA + 75 PVA, 100 PVA) were dissolved separately in DMF. The two mixtures were stirred and heated up to 80 °C for two hours until PMMA and PVA solutions took a homogeneous viscous liquid appearance, then PVA solution was added to PMMA solution and mixture solution was left to cool down to laboratory temperature while the stirring of the mixture was carried out to ensure a homogeneous composition. The resulting solution was then poured into a casting glass plate with diameter 5cm and the DMF was allowed to evaporate in air at room temperature 20°C. This procedure provided mechanically stable, free standing and flexible films. The films were further dried in oven at 50°C for 24 hours to remove any trace of DMF. To prepare the doped blends, with 2% weight percentage (wt.%) of Sn, Ag, and Fe were added to the blend mixture solutions with the different blend ratios and stirred for 30 minutes and the same procedure above were repeated to get a blend films doped with 2% (wt.) of Sn, Ag, and Fe with thickness range of 0.3-0.4 mm. UV visible spectroscopy measurements were carried out using UV/160/Shimadzu spectrophotometer. The absorbance of the pure and doped PMMA with different elements and different concentration were measured in the range (200-1100) nm. The absorption coefficient was calculated using eq. (8). E_g was obtained by plotting the $(\alpha hv)^{1/r}$ versus (hv) . The linear portion was best fitted with $r=0.5$ indicating direct transition type. UV-VIS spectrophotometer was used to obtain the transmittance and absorbance spectrums in the wavelength range (200-1100)nm for (PMMA-PVA) undoped and doped blends. The reflectance (R) were obtained using eq.(5), (k) can be calculated using eq. (2), (n) can be obtained using eq.(6) while ϵ_r , ϵ_i is calculated using eqs. (11 and 12) respectively.

RESULTS AND DISCUSSION

The transmittance (PMMA-PVA) films prepared with different ratios, undoped and doped 1% Ag, Fe and Sn are shown in Fig.1. The transmittance pattern of all deposited thin films increases with the increase of (λ) . On the other hand the transmittance change in non systematic manner with PVA concentration, i.e. the transmittance decreases with PVA content in the

first stage and then increases, which means increases and decreases of the absorption. The shifts of transmittance toward longer wavelength (lower energies) accompanied the PVA addition attributed to formation of miscible blend which increases the density and consequently the samples because more

opaque to the incident light. It is obvious that doping lead to decreases the transmittance of all undoped blends.



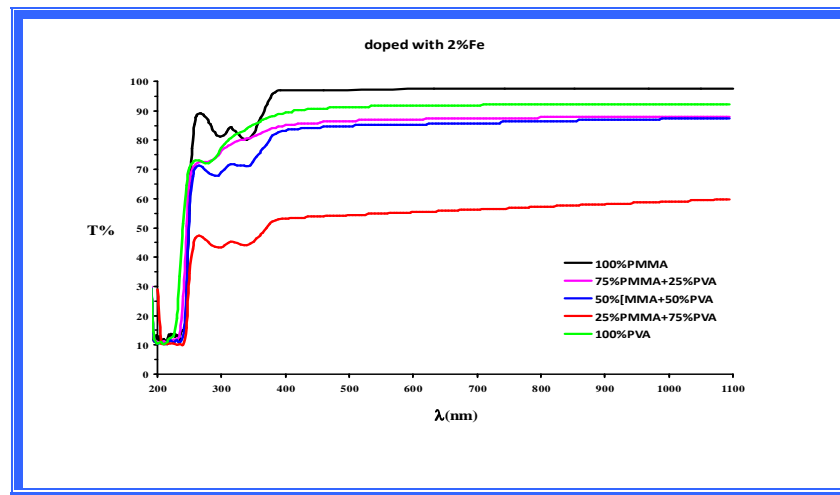
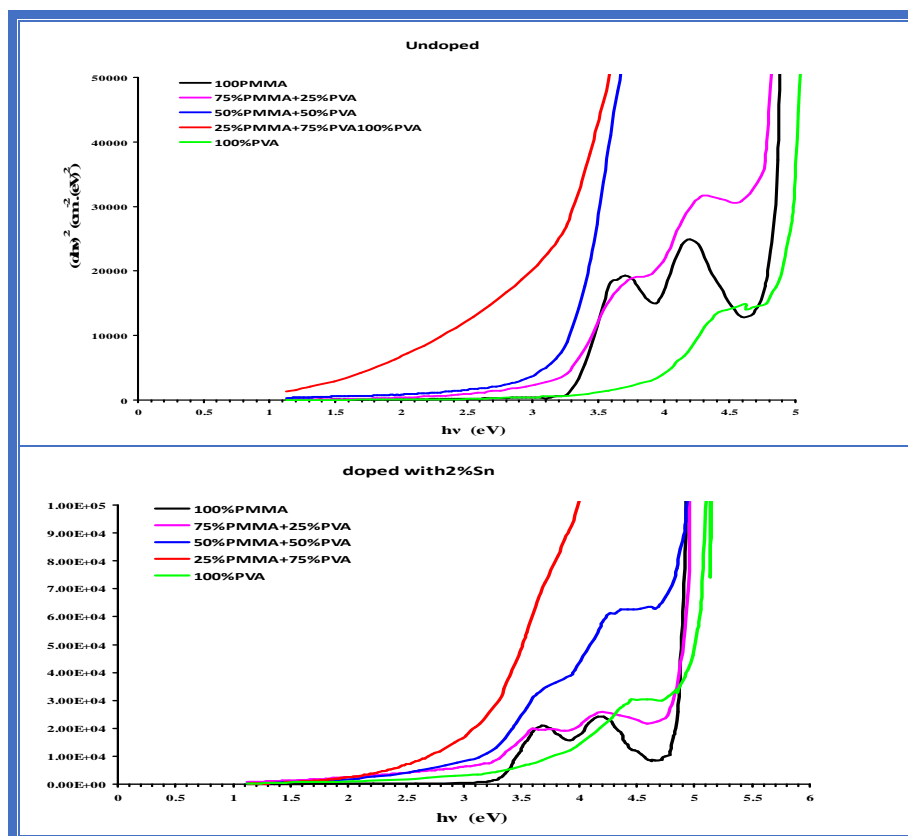


Fig. 1: Transmittance spectra of (PMMA-PVA) undoped and doped with Ag, Sn, and Fe.

The variation of $(\alpha h\nu)^2$ with photon energy ($h\nu$) for thin films and blends samples (100%PMMA, 75%PMMA+ 25 %PVA, 50%PMMA+50%PVA, and 100%PVA) undoped and doped with 1% Ag, Fe and Sn were plotted in Fig.1 and the optical energy gaps are determined and listed in tables (1 to 4). The results showed that the value of E_g of neat polymers PMMA and PVA are 4.7 and 4.85 eV which higher than E_g for residual blends, on the other hand it is clear that E_g decreases with the increase of PVA ratio in blend samples, moreover E_g decreases from 4.7 eV to 2.8 eV when PVA increase from 25% to 75%. This result is attributed to decrease in the

transmittance, which in turn to an additional shift of the optical absorption edge in the direction of lower energies. The determined value of (E_g) of PMMA and PVA sample agrees with the value reported by (Ahmad, H., S. Sabah, S. Hussien, 2012; Tagreed, K., *et al.*, 2011).

It obvious from Fig.2, that doping with the three elements has the same effect of the optical gap of the blends samples, i.e. E_g of the neat samples exceeded those of residual blends, however minimum value of E_g (2.2, 3, and 2.4 eV) take place at 50/50, 25/75, and 75/25 PMMA/PVA blend samples for doping with Ag, Sn and Fe respectively.



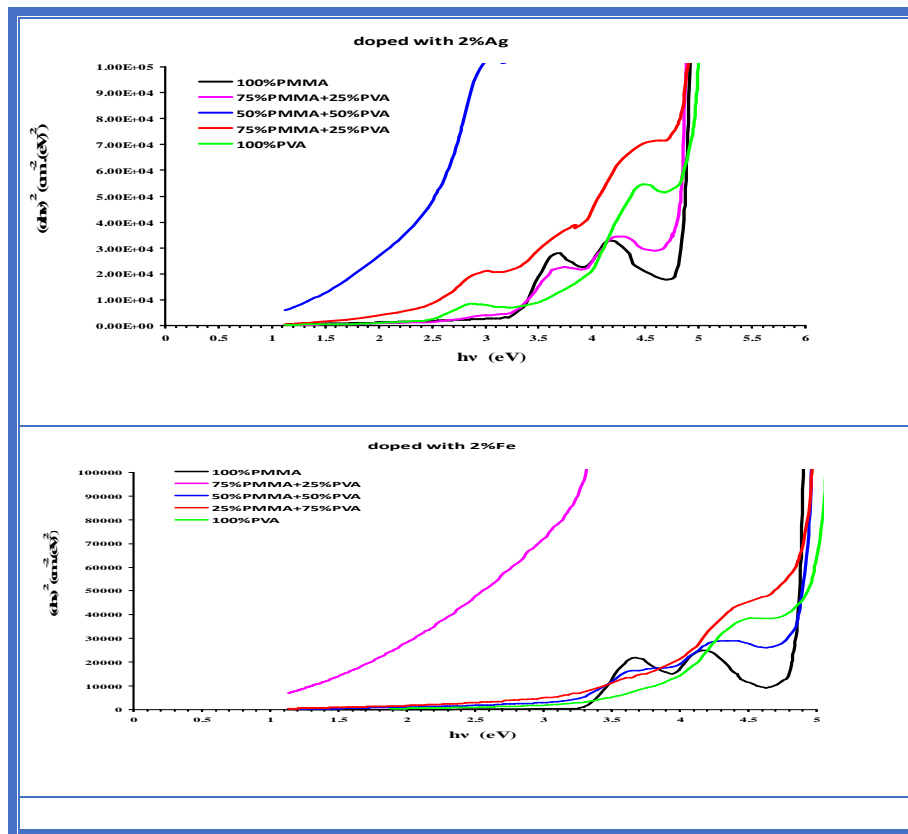


Fig. 2: Variation of $(\alpha hv)^2$ versus (hv) of (PMMA-PVA) undoped and doped with Ag, Sn, and Fe.

The wavelength (λ) dependence of the refractive index (n) for (PMMA-PVA) films prepared with different ratios, undoped and doped 1% Ag, Fe and Sn are shown in Fig.3. It is obvious that (n) values decrease with increase of wavelength of the incident photon, on the other hand n of undoped and doped exhibit to change in non systematic sequence (i.e. increasing then decreasing) with increase of PVA ratio. It is found from that the refractive index increases as PVA added to PMMA and then decreases with further addition. Indeed n increase from 1.23 to 2.18 when PVA ratio increases from 0 to 25% and then decreases to 1.28 for neat PVA sample, see table 1 to 4. The increase of (n) may be explained on the basis of formation of miscible blends and hence to the increase of molecular weight, while more addition of PVA to the host polymer lead to formation of immiscible blends and hence to decrease the molecular weight. In order to compare our results with a published data the value of ($n_{PMMA} = 1.23$, $n_{PVA} = 1.28$) were determined at ($\lambda = 600\text{nm}$), while the published data referred that $n = 1.49$ and 1.54 , at $\lambda = 587\text{nm}$ for PMMA and PVA respectively. Doping with 1% Ag, Fe and Sn as shown from Figure 3, in general leads to increasing

of n values of all blends samples, maximum values occurred at 50/50 for blends doped with Ag, 25/75 for blends doped with Sn and Fe respectively. The behavior refractive index reflects the decrease of the transmittance i.e. the sample becomes more opaque to the incident wavelength as expected from the simultaneous decrease of the energy gap.

The dependence of extinction coefficient (k) on the wavelength (λ) of PMMA/PVA blend samples undoped and doped with 1% Ag, Sn and Fe are shown in Fig.4. It is remarked that the values of (k) changes with (λ), indeed (k) for pure and blends samples. It is obvious that k shows the same behavior of refractive index, i.e. k increases as PVA introduced to the host polymer but then decreases with further increase of PVA, moreover it is found that (k) increases from 2.54×10^{-5} to 1.91×10^{-4} at ($\lambda = 600\text{nm}$) when PVA content increases from 0 to 25% (see table (1)). This behavior is related with the corresponding absorption coefficient (α) according to equation (4), hence (α) showed increment with PVA content. The same observation of refractive index can be given here i.e. doping also increases k values compared with those of undoped blends.

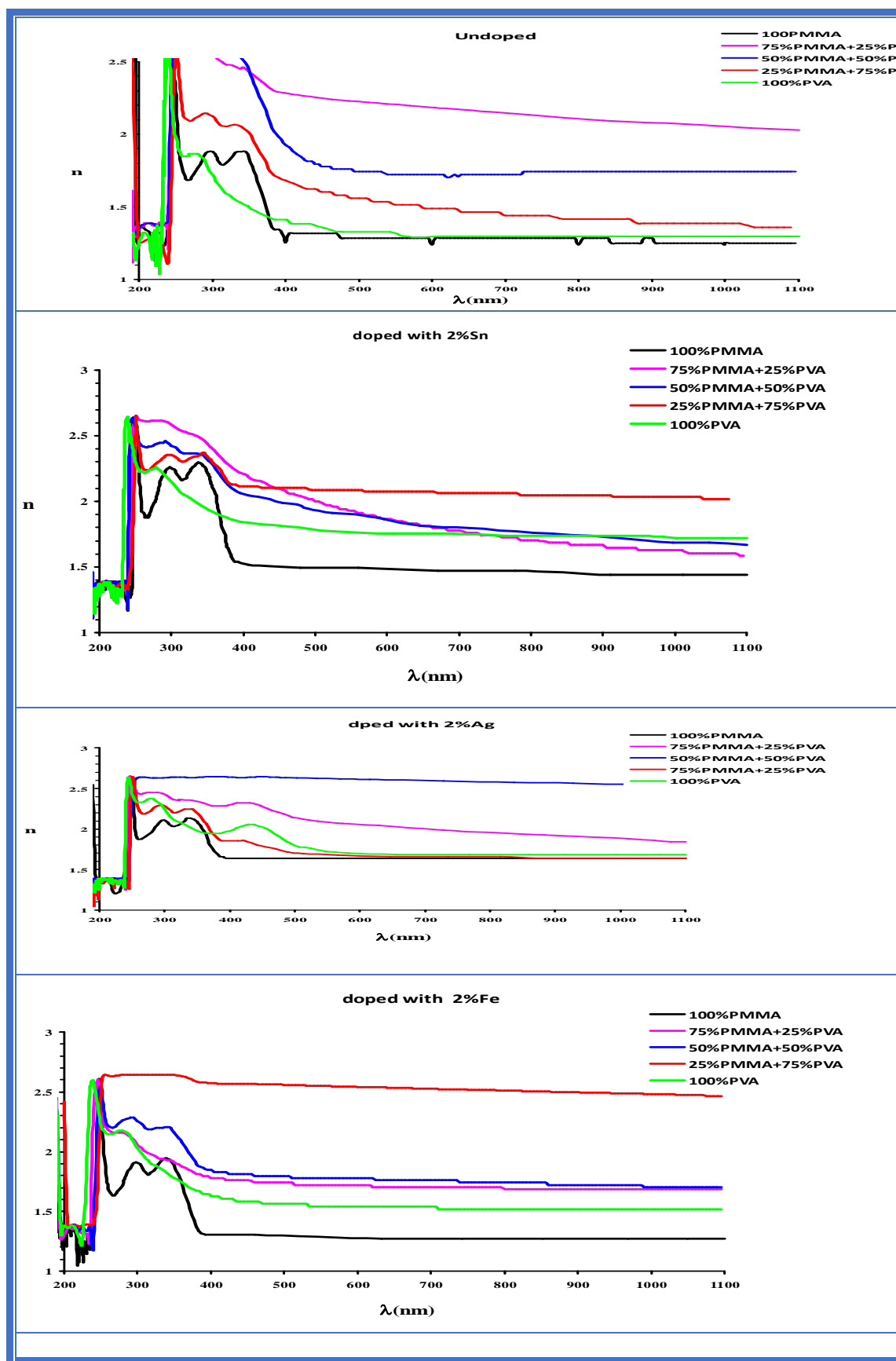


Fig. 3: Variation of refractive index versus wavelength of (PMMA-PVA)undoped and doped with Ag,Sn,and Fe.

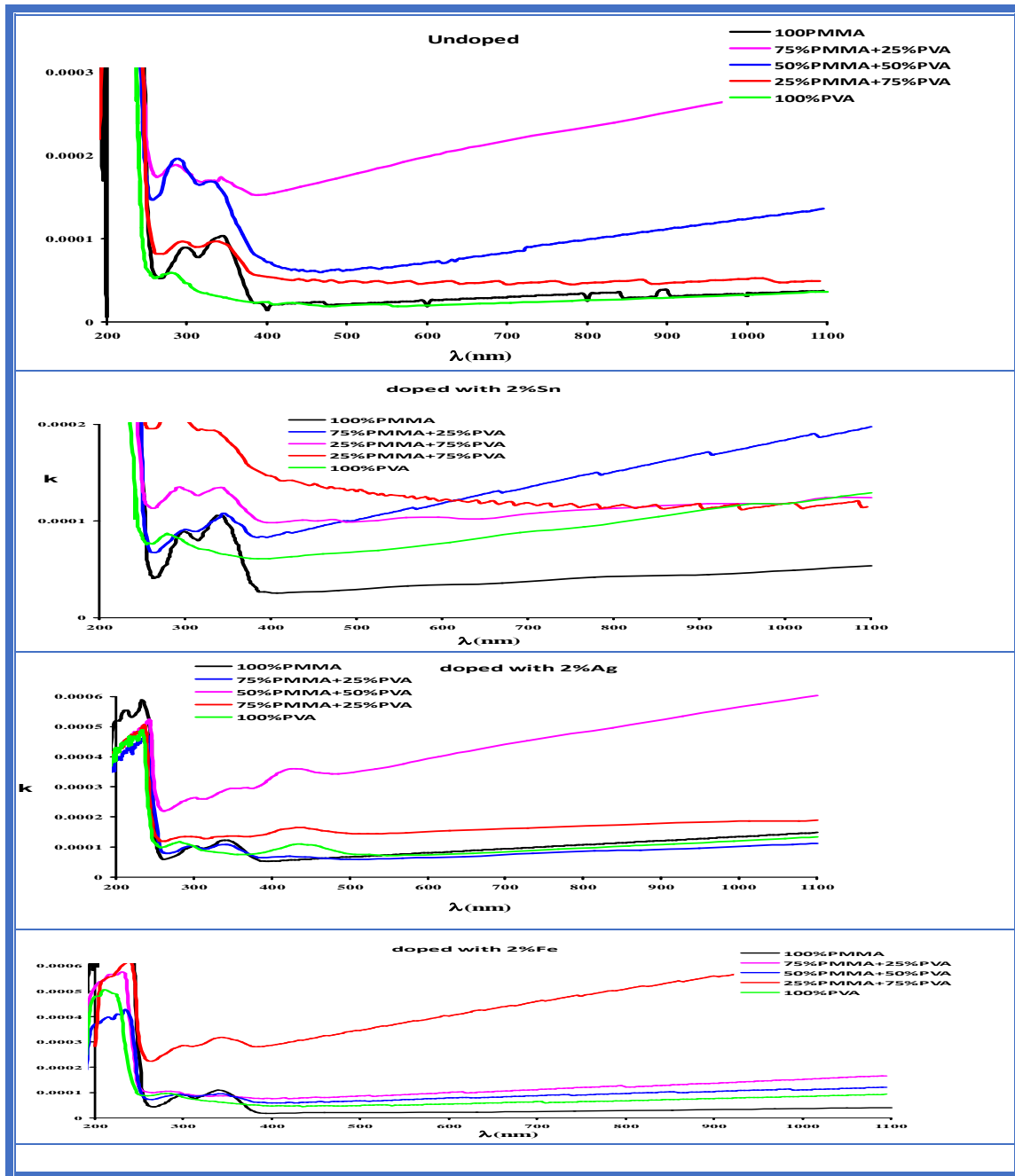


Fig. 4: Variation of extinction coefficient versus wavelength of (PMMA-PVA)undoped and doped with Ag,Sn,and Fe.

The real ϵ_r and imaginary part ϵ_i of the dielectric constant as function of wavelength are shown in Figures (5 and 6) for (PMMA-PVA) films prepared with different blend ratios undoped and doped with different elements. It is clear that the variation of ϵ_r mainly depend on the values of (n^2) as a results of

small values of (k^2) comparison with (n^2) , while (ϵ_i) mainly depend on the (k) values which are related to the variation of absorption coefficient. It is remarked that the values of doped values exceeded those of undoped blends.

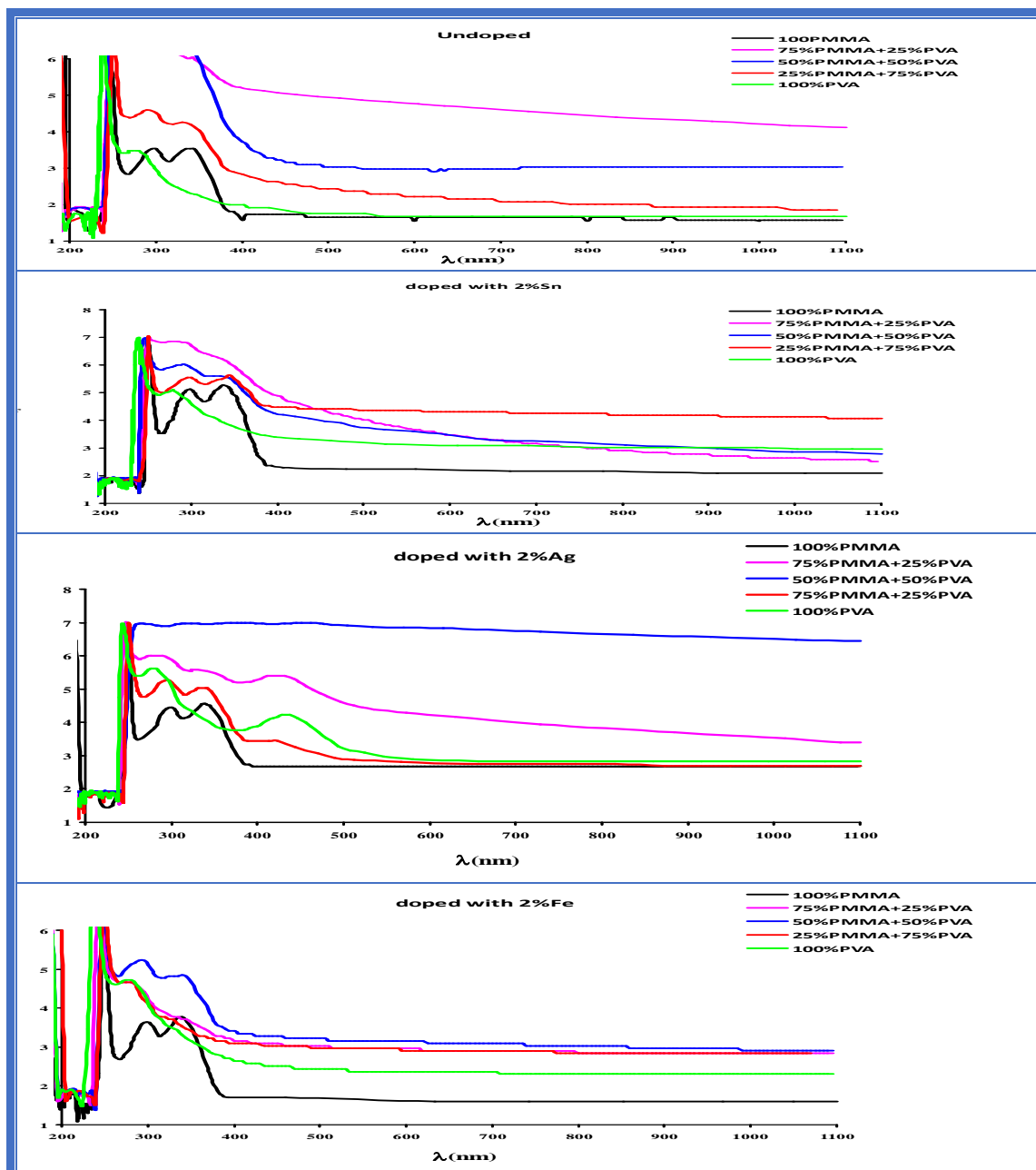
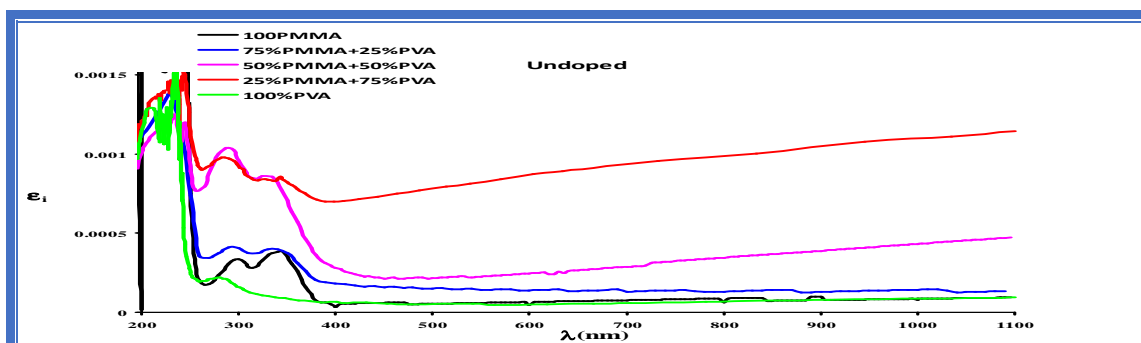


Fig. 5: Variation of real dielectric constant versus wavelength of (PMMA-PVA)undoped and doped with Ag,Sn,and Fe.



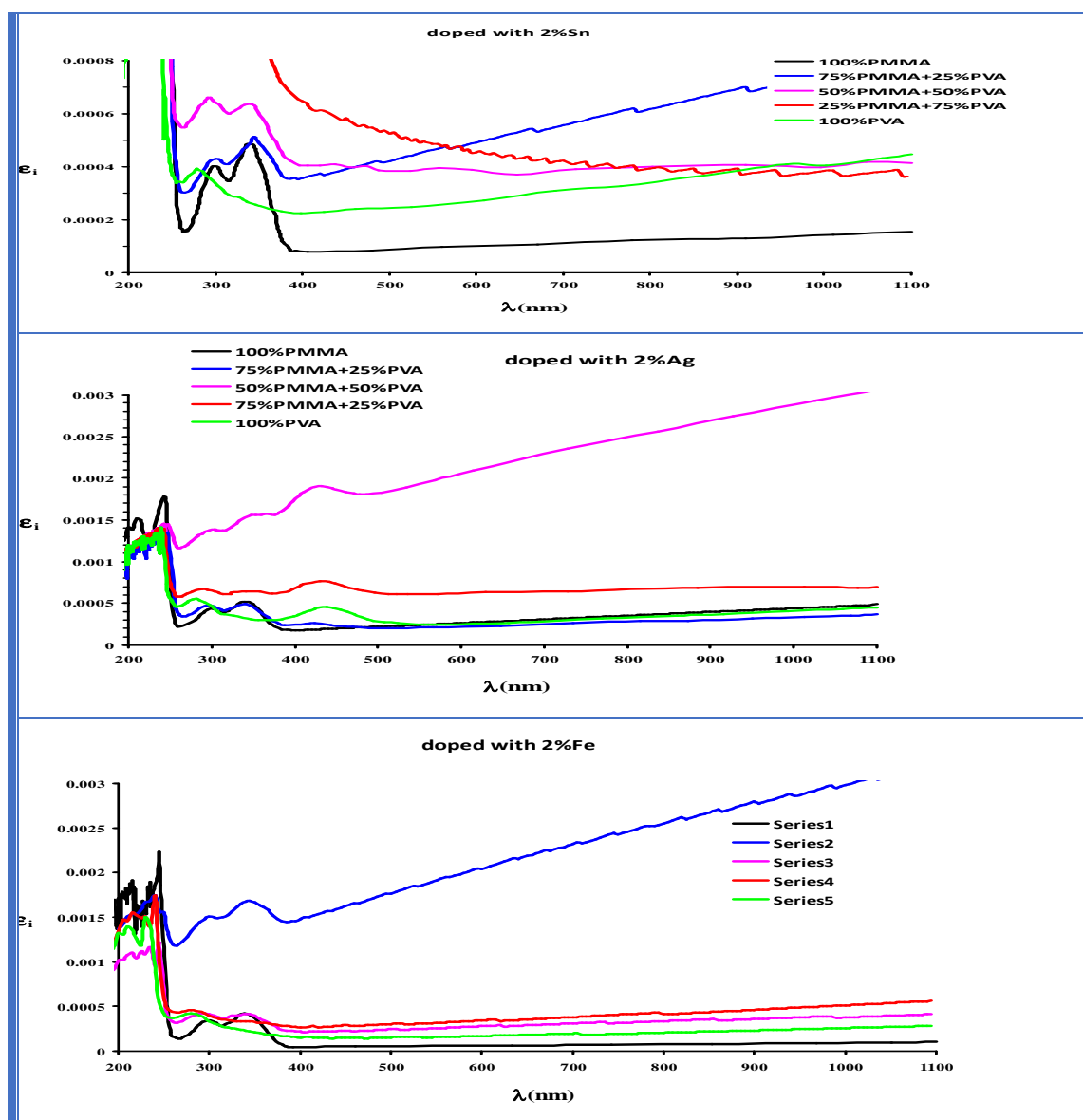


Fig. 6: Variation of imaginary dielectric constant versus wavelength of (PMMA-PVA)undoped and doped with Ag,Sn,and Fe.

Table 1: the values of optical parameters of undoped (PMMA-PVA) blend.

Blend sample	T%	Pure E_g (eV)	n	k	ϵ_r	ϵ_i
100% PMMA	97.97	4.7	1.23	2.54E-05	1.53	6.52E-05
75% PMMA+25% PVA	71	4.6	2.18	0.000191	4.76	0.00087
50% PMMA+50% PVA	86.7	3.2	1.72	7.05E-05	2.97	0.000245
25% PMMA+75% PVA	92	2.8	1.49	4.85E-05	2.22	0.000136
100% PVA	97.95	4.85	1.28	1.87E-05	1.65	4.65E-05
Blend sample	T%	Ag E_g (eV)	n	k	ϵ_r	ϵ_i
100% PMMA	89	4.8	1.63	7.94E-05	2.67	0.000262
75% PMMA+25% PVA	75.8	4.8	2.04	6.30E-05	6.84	0.000214
50% PMMA+50% PVA	49	2.2	2.61	3.76E-05	4.2	0.00209
25% PMMA+75% PVA	88	4.25	1.67	0.000148	2.81	0.000653
100% PVA	87	4.7	1.74	7.36E-05	2.94	0.000251

Table 2: The values of optical parameters of (PMMA-PVA)blends doped with 2%Sn.

Blend sample	T%	E_g (eV) Sn	n	k	ϵ_r	ϵ_i
100% PMMA	92.8	4.85	1.49	3.30E-05	2.22	0.000105
75% PMMA+25% PVA	80.5	4.85	1.89	0.000112	3.59	0.000475
50% PMMA+50% PVA	82.5	4.5	1.86	0.000104	3.48	0.000388

25%PMMA+75%PVA	75.6	3	2.07	0.000125	4.3	0.000457
100%PVA	85	4.9	1.75	7.79E-05	3.39	0.000273

Table 3: The values of optical parameters of (PMMA-PVA)blends doped with 2% Ag.

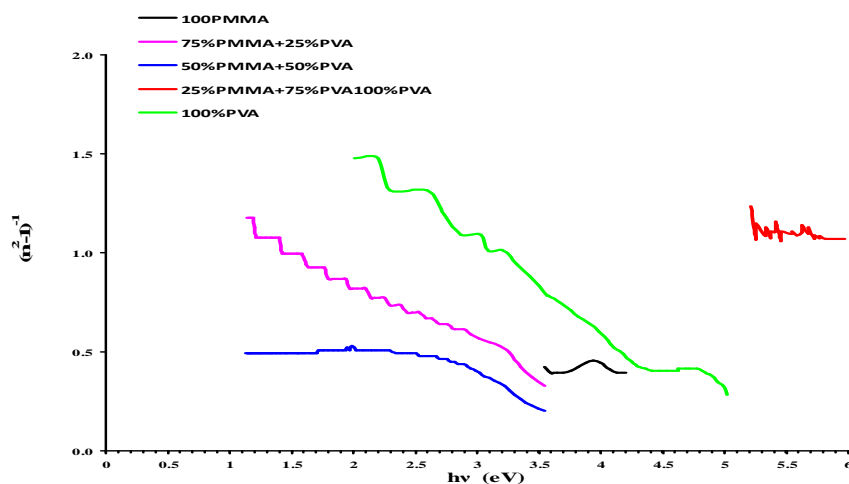
Blend sample	T%	Ag Eg(eV)	n	k	ϵ_r	ϵ_i
100% PMMA	89	4.8	1.63	7.94E-05	2.67	0.000262
75% PMMA+25% PVA	75.8	4.8	2.04	6.30E-05	6.84	0.000214
50% PMMA+50% PVA	49	2.2	2.61	3.76E-05	4.2	0.00209
25% PMMA+75% PVA	88	4.25	1.67	0.000148	2.81	0.000653
100% PVA	87	4.7	1.74	7.36E-05	2.94	0.000251

Table 4: The values of optical parameters of (PMMA-PVA)blends doped with 2% Fe.

Blend sample	T%	FeEg(eV)	n	k	ϵ_r	ϵ_i
100% PMMA	97	4.9	1.26	2.30E-05	1.6	5.88E-05
75% PMMA+25% PVA	86.8	2.4	1.72	0.000106	2.96	0.00195
50% PMMA+50% PVA	85.2	4.8	1.77	7.76E-05	3.15	0.000285
25% PMMA+75% PVA	55.5	4.65	2.54	0.000401	2.96	0.000336
100% PVA	91.7	4.85	1.53	5.44E-05	2.37	0.000169

In order to estimate many parameters like the values of the E_0 which is an average energy gap $E_0 \approx 2E_g$, and E_d can be determined from the intercept E_0/E_d and the slope $(E_0E_d)^{-1}$ according to (WDD) model, we must plot $(n^2-1)^{-1}$ versus $(h\nu)^2$ as shown in figure.7 The values of dispersion parameters, E_0 , E_d , static refractive index, and static dielectric constant, ϵ_s were put in Table 5. It was observed that, the single oscillator energy E_0 showed non systematic manner with increase of the PVA content while, both the dispersion energy E_d and n_0 decreases with the increase of PVA content, however they increases for PMMA/PVA =50/50. An important indication of the

WDD model is that the relation between the dispersion energy, E_d , and other physical parameters of the material like the effective coordination number of the cation nearest-neighbor to the anion, the formal chemical valency of the anion, the effective number of valence electrons per anion. Thus to evaluate the compositional trended of E_d it is suitable to proposed that, the observed decrease in E_d with increasing PVA is primarily due to the change in the ionicities (Wemple, S.H., M. DiDomenico, 1971), which decreases with increasing PVA content (see Table.5).

**Fig. 7:** Variation on $(n^2-1)^{-1}$ versus $(h\nu)$ for (PMMA-PVA) blends.**Table 5:** The values of E_d , E_0 , n_0 , ϵ_s , and E_g .

Blend sample	E_d	E_0	n_0	$\epsilon_s=n_0^2$	$E_g=E_0/2$
100% PMMA	230.8754	85.47	3.701243	13.69	1.85
75% PMMA+25% PVA	2.570156	3.63	1.707564	2.91	0.85
50% PMMA+50% PVA	116.3873	50	3.327747	11.07	1.66
75% PMMA+25% PVA	6.9185	11.11	1.622665	2.63	5.55
100% PVA	1.093541	2.470	1.442556	2.08	1.23

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