THE OPTICAL PROPERTIES OF THIN FILMS OF POLYMER PMMA /MR-EOSIN PREPARED BY CASTING METHODS

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Abstract

Thin films of polymer PolyMethyl Methacrylate (PMMA) grafted with Methyl red and Eosin dyes for different weight ratio (0, 1, 2.5, 5, 10) % were prepared by cast method. The Absorption spectra of thin films was studies at the range wave number (300-700) nm. This is represented by The Absorption spectra (A) and Reflectivity (R). The Absorption coefficient (α), direct and indirect energy gaps (Eg), Urbach (Localized State) energy (Eu) , reflective index (n), the extinction coefficient, Real and imaginary part of dielectric constant were computed. We found that the polymeric films having indirect energy gap which is increases with increase the weight ratio of dyes. Also we see that the energy gap for direct and indirect transitions was decreases from (5.06)eV for PMMA pure to(2.15±0.1) with graft the polymer PMMA by dyes for all ratio. Urbach energy was calculated and we found that its semi-stable for the ratios (1,2.5,5)%(equal to 0.06±0.01)and then increased to become (0.136) for the ratio (10%) with increase the dyes.

Keywords: PMMA, Eosin, Thinfilms, cast methods

Introduction:

Poly (Methyl Methacrylate) PMMA has been considered attention in recent year owing to its low cost, good tensile strength and hardness, high rigidity, transparency, low optical loss in the visible spectrum, low glass temperature, good insulation properties, and thermal stability dependent on tactility [1]. The Polymer (PMMA) are used in clinical applications [2], and have been widely used due to attractive physical and optical properties decisive about its broad applications [3]. It can be considered as a good host for organic nano particle due to their high surface to bulk ratio which can significantly affect the properties of PMMA matrix [4,5].The physical properties of polymers may be affected by doping and thickness. A graft copolymer is a type of branched copolymer with the side chain being different and separate from the main chain. Detailed studies of doped polymer with different dopant concentrations and thickness allow the possibility of choice of the desired properties

[6]. On the other hand, methyl red and methyl blue is interesting in terms of optical, electronic and UV-absorbing properties [7].Its major characteristics include rigidity, transparency, high refractive index, good electrical insulation characteristics, low water absorption, and ease of coloring and processing [8]. A more serious limitation of (PMMA) in many applications is its brittleness. This limitation led to investigation a mixture of (PMMA) with material having rubber properties [9].

Dye – doped polymers (DDP) are new materials which existing optical properties. DDP find application in fields of modern photonic technology apart from its use as an alternative to solid state laser media [10].

The study of optical absorption and particularly the absorption edge is a useful method for the investigation of optically-induced transitions and for the provision of information about the band structure and energy gap in both crystalline and amorphous materials. The measurements of the optical absorption coefficient, particularly near the fundamental absorption edge, provide a standard method for investigation. Detailed studies of doped polymer with different dopant concentrations and thickness allow the possibility of choice of the desired properties [6].

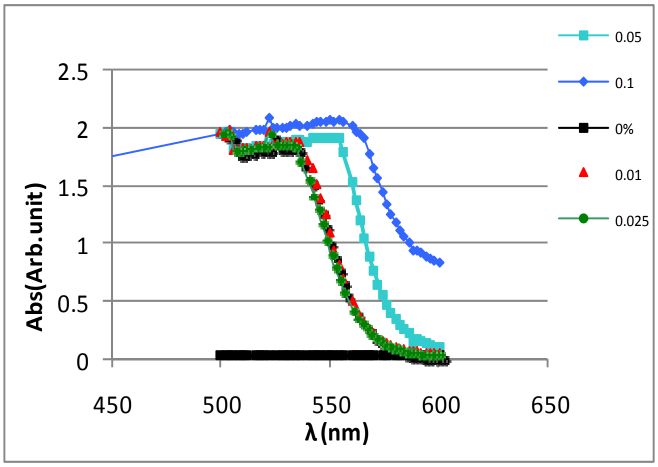
The aim of this work was prepared thin films of PMMA grafted by Methyl red and Eosin dyes using cast methods and studies their optical properties for it represented by the Absorption and Transmittance spectra, Reflection coefficient (R), energy gap (E_g) and Urbach (Localized State) energy (E_u) to know the effect of dyes on (PMMA).

Experimental methods:

Thin films of poly methyl methacrylate(PMMA) graft with dyes such as (Methyl red and Eosin) was prepared by cast methods, it's solved by Tetra hairdo furan (THF) at temperature(40^0 C). The solution of PMMA was prepared by taking 1gm with 30mel of THF and put it on hotplate stirrer for (120) minutes. Appropriate mixtures of PMMA and (methyl red, Eosin) solutions were mixture with (1%, 2.5%, 5%, 10%) weight ratio of dyes and stirred continuously until we get on a homogeneous solutions. The solution was poured into flat glass plate dishes for 24 hr, these homogeneous solutions were spread on a glass plate and allowed to evaporate the solvent slowly in air at room temperature. The thickness of the prepared films was measured using the optical interferometer method employing He-Ne laser 0.632μm. The absorbance and transmittance spectra were recorded using UVspectrophotometer (SP -8001) double-beam spectrophotometer in the wavelength optical a range 190-1100nm, the measurements were carried out at room temperature.

Results and Discussion:

The Absorption spectra (A) for polymer (PMMA) graft with Methyl red and Eosin dyes as thin films were recorded using UV-Vis Spectrophotometer in the wavelength range 0f (500-600) nm as Fig.(1).



Fig(1): Absorption Versus wave length

From fig(1) we see that the Change in absorbance values at the range (500-600)nm are clear after the addition dyes for it, and for all weight ratios the Absorbance spectra were decreases with increase the wave length but its dependent on the type of dyes and the ratio. Also we see that the Absorbance spectra are increases with increase the weight ratio of dyes [11].

The Absorption coefficient (α) of thin films can be estimated after the correction of the reflectivity by [12]:

$$\alpha = \frac{2.303}{t} A \qquad \ldots\ldots\ldots\ldots\ldots(1)$$

Were, t, is the thickness of the film and, A, is the Absorbance.

The study of α was very important to defined type of transition for the electron such as [allowed direct, forbidden direct, allowed indirect and forbidden indirect]. This case dependent on α values; if $\alpha > 10^4$ that is lead to the transition was allowed or forbidden direct and when $\alpha < 10^4$ these values lead to allowed or forbidden indirect. The absorption coefficient data of Fig(2) were analyzed to obtain information on the non-vertical allowed transitions in frame of the theory of bardeen et all[13]:

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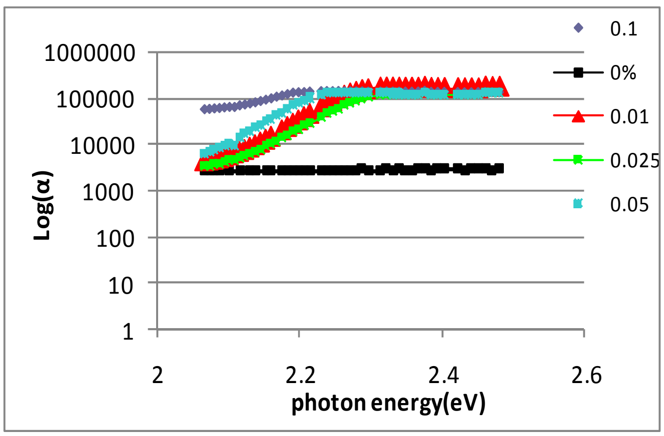
$$\alpha = \frac{A(h\upsilon - Eg \pm Ep)^r}{h\upsilon} \qquad \text{................(2)}$$

Where r=*1/2* or *2*

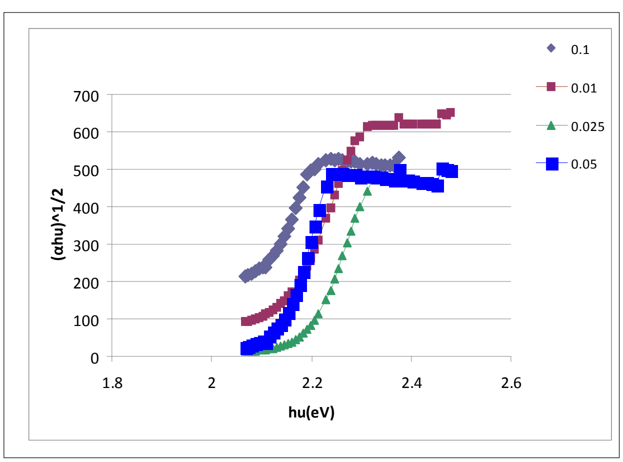
Eg // is the indirect band gap.

Ep // the energy of the absorbed (+) or emitted (-) phonons.

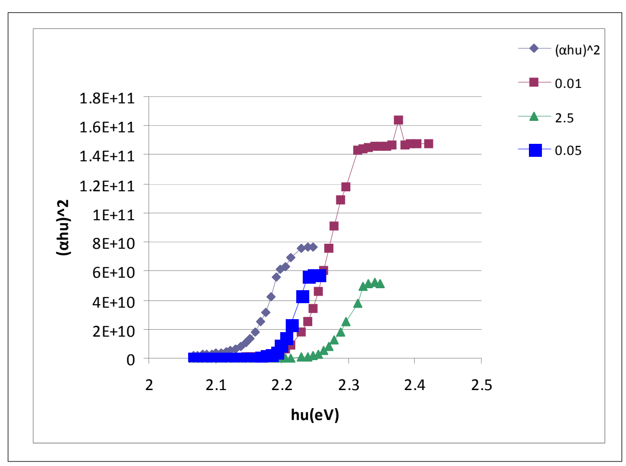
The plot of $(\alpha h\upsilon)^{1/2}$ versus photon energy are shown in Fig (3) with two straight lines are obtained for each case, one at lower energy corresponds to phonon absorption transition and the photon energy intercepts at Eg-Ep. The other lines correspond to phonon energy emission processes and photon energy intercept at Eg+Ep. From intercepts its found Eg and Ep. the plot of $(\alpha h\upsilon)^2$ versus photon energy are shown in Fig (4) and the direct energy gap are obtained for each case when the photon energy intercepts at $(\alpha h\upsilon)^2$=0,See table (1).



Fig(2): Log(α) versus photon energy



Fig(3): $(\alpha hu)^{1/2}$ versus photon energy



Fig(4): $(\alpha hu)^2$ versus photon energy

From the Absorption coefficient data, can be calculate the extinction coefficient (K) by:

$$K = \frac{\alpha\lambda}{4\pi} \quad ....(3)$$

Where ,λ, is the wavelength

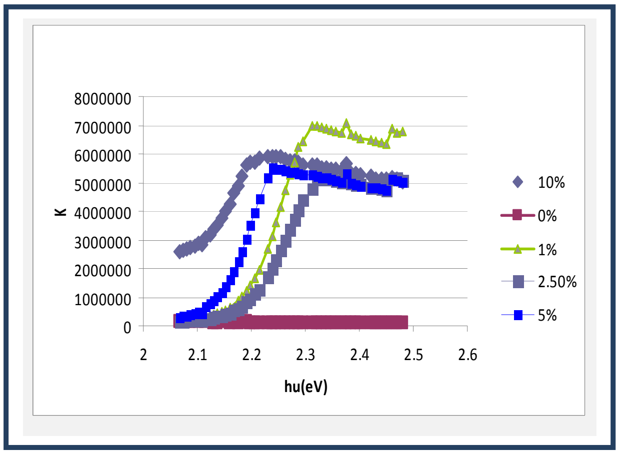
Table (1): shows the energies values for different weight ratioof Polymers.

N0.of Sample	W%	Eg (eV) (direct)	Eg (eV) (indirect)	Ep(eV)	Eu(eV)	Reference
1	0%	5.06	5.06	0	-------	[14]
2	1%	2.23	2.08	0.04	0.076	Current study
3	2.5%	2.26	2.16	0.02	0.073	Current study
4	5%	2.2	2.13	0.01	0.05	Current study
5	10%	2.15	2.05	0.08	0.136	Current study

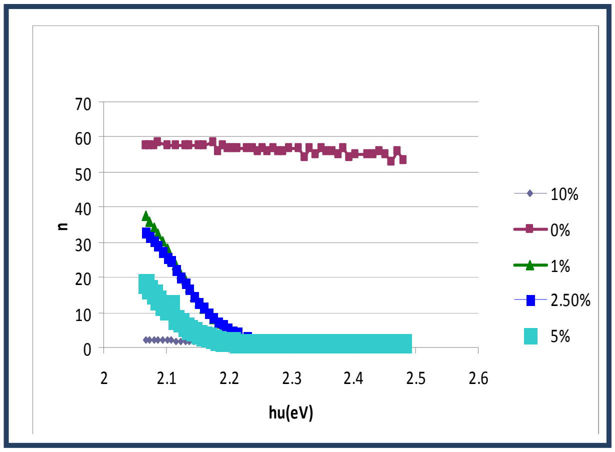
This result was very important to improve polymer (PMMA) to use it in different application such as:

- Optics: Dust covers for hi-fi equipment, sunglasses, watch glasses, lenses, magnifying glasses;
- Vehicles: Rear lights, indicators, tachometer covers, warning triangles;
- Electrical engineering: Lamp covers, switch parts, dials, control buttons;
- Office equipment: Writing and drawing instruments, pens;
- Medicine: Packaging for tablets, pills, capsules, suppositories, urine containers, sterilisable equipment;
- Others: Leaflet dispensers, shatter-resistant glazing, shower cubicles, transparent pipelines, illuminated signs, toys.

Fig(5) represent the relation between (K) and photon energy. From figure we see that the extinction coefficient was increasing with increase the photon energy and with increase the weight ratio of dyes at the range (2.05-2.5)eV and we see from this figure the maximum value for it was for the ratio (1%) at the range(6-7)X$10^6$from extinction coefficient. But when we see the Fig.(6) that is represented the relationship between Refractive index and photon energy we find that is inverse to the extinction coefficient in the behavior.



Fig(5): extinction coefficient versus photon energy



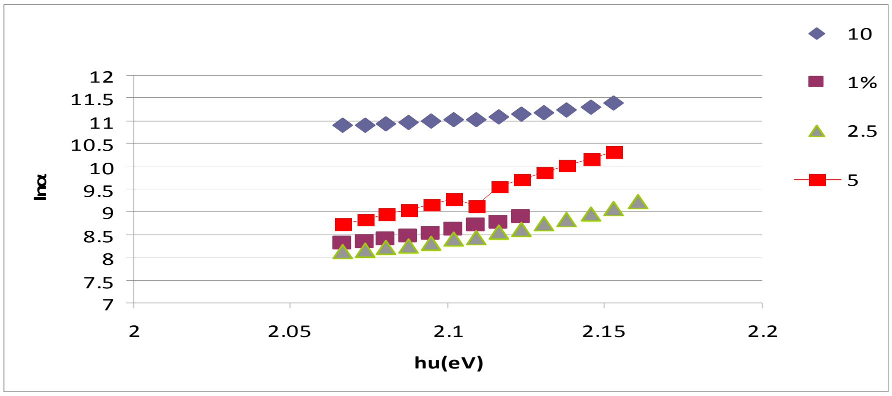
Fig(6):refractive index versus photon energy

The absorption coefficient $\alpha(h\upsilon)$ near the band edge for non-crystalline materials shows an exponential dependence on the photon energy $(h\upsilon)$ which follows the Urbach's formula [14]:

$$\alpha(h\upsilon) = \alpha_o \exp(h\upsilon / E_u) \ldots\ldots\ldots\ldots\ldots(4)$$

Where α_o is constant, E_u is an energy that represents the width of the tail of localized states in the forbidden band gap, υ is the frequency and h is planck's constant. The origin of E_u is considered as thermal vibrations in the lattice.

Figure (7) shows the logarithm of the absorption coefficient as a function of the photon energy for polystyrene with KPF_6 at different weight ratios. The values of the Urbach′s energy were calculated by taking the reciprocal of the slopes of the linear portion in the lower photon energy regions of these curves and listed in Table (1). The instable in the Urbachs energy is case of PS may be due to the crystalline nature of the polymer [15].



Fig(7): logarithm Alpha (lnα)versus photon energy

The optical properties solids are usually described in terms of the complex dielectric function [13]:

$\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$ ………………..(5)

Where, $\varepsilon_1(E), \varepsilon_2(E)$ are the real and imaginary parts of the dielectric respectively which can be calculated by:

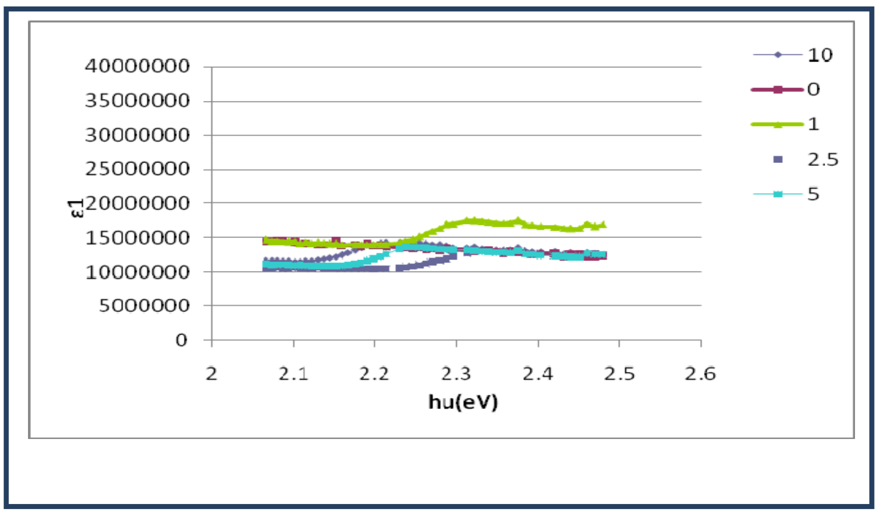
$\varepsilon_1(E) = n^2 - K^2$ …………………(6)

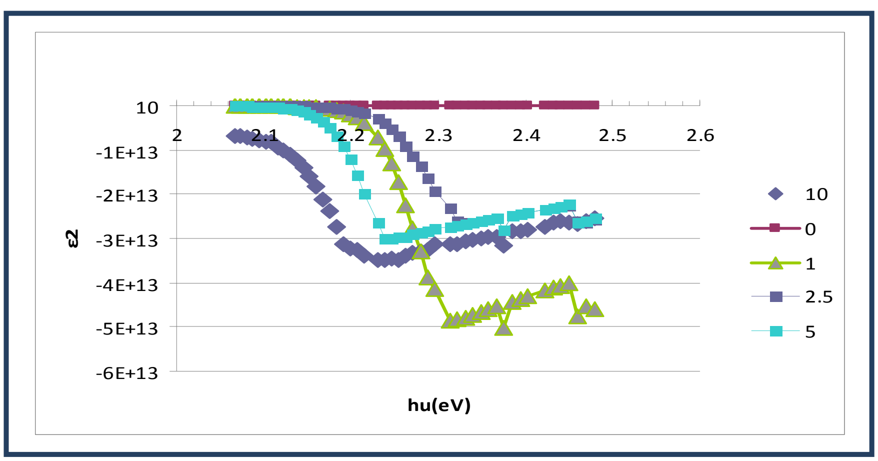
$\varepsilon_2(E) = 2nK$ ……………………(7)

Where ,n, is the refractive index which is dependent on reflection and absorption coefficient and calculated by:

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \quad \text{………………..(8)}$$

Fig(8) Show the relationship between the real and imaginary parts of the dielectric constant with the photon energy, from figure we see that $\varepsilon_1(E)$ was semi stable with increase the photon energy, while the $\varepsilon_2(E)$ decreases with increase the photon energy and having a minimum value of it's at the ratio (1%).





Fig(8): $\varepsilon_1(E), \varepsilon_2(E)$ versus photon energy

Conclusions:

1. For all weight ratios the Absorbance spectra were decreases with increase the wave length but its dependent on the type of dyes and the ratio.
2. The energy gap was decreases to the half value of PMMA when we added the dyes for it.
3. The behavior of the Refractive index is the opposite of the behavior ofthe extinction coefficient.

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