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Optical study of poly(methyl methacrylate)/rare earth composite luminescent materials

Nabawia A.El- Zaher[1], Asmaa A.Hendi[2], Osiris W.Guirguis[3]*

[1]Textile Metrology Lab, National Institute for Standards, Giza, (EGYPT)

[2]Physics Department, Sciences Faculty for girls, King Abdulaziz University, Jeddah, (SAUDI ARABIA)

[3]Biophysics Department, Faculty of Science, Cairo University, Giza, (EGYPT)

E-mail : osiris_wgr@yahoo.com

ABSTRACT

In the present work, composites of poly(methyl methacrylate)/alkali rare earth aluminate photoluminescent pigment (PMMA/AREAPP) (100/0, 98/2, 96/4, 94/6, and 92/8 wt/wt%) were prepared using mixture technique. The pigment has the composition formula of $MeO.xAl_2O_3.ySiO_2$:Eu (Me = Ca, Mg, Sr, Ba, x = 0.5-2.0, y = 0.005-0.5) which is activated by rare earth element (Eu). The reflectance spectra and the tristimulus values as well as the color parameters were employed to characterize and reveal the miscibility map and the relationship of the structure properties. The study has been extended to include the absorption and extension coefficients of the prepared composites, the band tail width and band gap energies for the composites. From the obtained results, it is found that the organic parts are attached with the inorganic parts in the PMMA/AREAPP composites. Also, it is clear that the AREAPP powder has a great effect on improving the performance properties of PMMA and greatly depends on its concentration in the composite.

KEYWORDS

Poly(methyl methacrylate);
Rare earth element;
Luminescent materials;
Tristimulus values and color parameters;
Absorption and extension coefficients.

INTRODUCTION

Polymer blending is one of the most important contemporary ways for the development of new polymeric materials[1]. Polymer blends often exhibit properties that are superior to any one of the component alone. However, the manifestation of superior properties depends upon the miscibility of homopolymers on the molecular scale. Methods for the experimental study of polymer miscibility are numerous and very diverse, and may be divided into several main groups such as[2]: (1) methods based on the determination of optical homogeneity of the mixture; (2) methods for determination of interactions on molecular levels; and (3) indirect method for miscibility.

One of the decisive factors in the design of any material based on polymer blends is miscibility, compatibility or component solubility, as computability has a major effect on the final properties.

Poly(methyl methacrylate), PMMA, is a versatile polymeric material, which is very suitable for numerous microelectronic applications, including as photoresist for direct-write-e-beam, X-ray and deep UV micro-lithographic processes. PMMA is adopted in photonic of nanotechnology because of the uniform optical index of its structure[3], and in prosthetic composites used in dentistry because of its excellent cell adhesion and biocompatibility[4,5]. PMMA is also widely used in cosumer products due to its excellent mechanical properties and performance under various processing conditions[6]. The properties of polymers, such as PMMA, are governed distinctively by molecular weight, temperature and gas atmosphere during decomposition, all of which can change the material characteristics and have been investigated[7].

Luming photoluminescent pigment (has 6 series) is a kind of rare earth photoluminescent powder, with no radioactive component. Luming photoluminescent pigment powder can be used as an additive among the transparent agents. It can be added in coating, ink, paint, plastics, printing paste, ceramics, glass, and fiber etc., to activate the emitting functions of the agents and then the medium can glow in the dark. The products made from the pigment can be safely applied in different fields such as: indication position; safety fields; building; toys; clothing, decorations and others as: arts and crafts, amber, sand crystal, glass, painting works and the systems of transportation, military industry, architecture, etc. Furthermore, some applications of rare earth luminescence are: Lighting technologies, white LED approaches, LED conversion phosphors, persistent phosphors, scintillator phosphors[8]. Applications are numerous in both the commercial and domestic markets.

Poly(methyl methacrylate)[9]; oxide glasses[10] are well known as excellent hosts for rare-earth ions. The present phosphorescent pigment (type PLO-6D from six series) used in the present work is a type of long persistence phosphorescent pigment powder of alkaline earth aluminate. The main characteristic of this material is the particular structure of its crystal with the strong capacity of absorbing-storing-emitting light. This luminous pigment is a light-yellow powder which turns to green color after activated by visible light. Compared with the traditional luminous material ZnS, it has the advantages of short activating time, long afterglow time, long lifetime (can be 10 years), high brightness, various environmental adaptation, non-toxic, harmless, non-radioactivity, non-flammability and non-explosive etc. All of these advantages make it sure that the new pigment is an environmental friendly one. It can be easily and widely used in many fields. It has good stability and weather ability. Excitation and emission can be repeated indefinitely.

In the present work, the matrix polymer used is poly(methyl methacrylate) (PMMA). PMMA is mixed with different concentrations (2, 4, 6 and 8 wt%) from an alkali earth aluminate-silicate photoluminescent pigment powder activated by rare earth element (Eu) (AREAPP). Optical analyses are employed to characterize and to reveal the relationship of the structure properties of PMMA. Also, the study has been extended to include the changes in the color parameters, absorption and extinction coefficients, the band tail width and band gap energies for the composites.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) (PMMA) powder CAS:9011-14-7 043982 of chemical formula [-$CH_2C(CH_3)(CO_2CH_3)$-]$_n$ with average molecular weight of 320,000 and melting point > 150 °C was supplied from Alfa Aesar (A Johnson Matthey Company, *Massachusetts*, USA). Phosphorescent pigment powder (type PLO-6D) of alkaline earth aluminate (AREAPP) has a formula: $MeO.xAl_2O_3.ySiO_2$:Eu (Me = Ca, Mg, Sr, Ba, x = 0.5-2.0, y = 0.005-0.5) activated by rare earth element (Eu) was supplied by Dalian Luminglight Science and Technology Co. Ltd., Shanghai, China and its physical and luminescent properties are given in TABLE 1 (Ref. [11]).

Energy dispersive X-ray spectroscopy

The elemental analysis of the alkaline earth aluminate phosphorescent pigment powder was done by using Energy Dispersive X-ray Spectroscopy (EDX, Oxford Instruments INCA X-sight) accompanied by the Scanning Electron Microscope (SEM, Jeol JXA 840) operating in liquid nitrogen atmosphere with 5% error (TABLE 2) (Ref. [11]).

Sample preparation

The PMMA powder is mixed with AREAPP powder for five different concentrations (2, 4, 6 and 8 wt%). The starting materials were ground using a Phillips PW 4018/00 MiniMill for 15 minutes with a rotating speed

TABLE 1 : Typical physical and luminescent properties of the alkaline earth aluminate phosphorescent pigment powder (AREAPP)

Typical physical properties	
Appearance	Yellowish
Density	3.6 g/cm^3
Temperature resistance	250 ^{o}C
Average particle size	10-15 μm
Luminosity life	10 to 20 years depending on manufacturing process, mixing and moisture content of the vehicle
Typical luminescent properties	
Excitation	UV radiation, white light (any visible light)
Excitation wavelength	200-450 nm
Peak value	520 nm
Glowing color	yellow-green
Brightness of afterglow	> 12 hours after absorbing the light for 10-30 minutes
Temperature resistance	250 ^{o}C

TABLE 2 : Elemental analysis of the alkaline rare earth aluminate phosphorescent pigment (AREAPP) powder

Element	Mg	Al	Si	P	S	Ca	Ni	Cu	Zn
Weight%	0.449	0.016	7.672	0.881	40.378	0.828	0.017	0.034	49.727

of 3400 rpm to form a homogenous mixture[11].

Visible spectroscopic measurements

The measurements in the visible region from 400 to 700 nm for PMMA/AREAPP were carried out using a Shimadzu (VIS) Double Beam Spectrophotometer with standard illuminant C (1174.83) Model V-530 and band width 2.0 nm covers the range 200–2500 nm with accuracy ±0.05%. The color properties were analyzed using the CIE Colorimetric System, CIE 1931 2-degree Standard Observer[12,13].

The tristimulus reflectance values (x_r, y_r and z_r), the relative brightness (L), the color constants 'a' and 'b', the whiteness index (W), and the color difference (ΔE) are calculated using the CIE relations previously reported[12-14].

The absorption coefficient (α) of the present materials strongly depends on optical transmission, reflection and thickness of film which is evaluated using the relation[15,16]:

$$\alpha = (1/d)\, \ell n\, (1-R)^2/T \quad (1)$$

Where R is the reflectance, T is the transmittance and d is the thickness of the sample (= 0.01 cm). The optical energy gap (E_g) of the thin films has been determined from absorption coefficient data as a function of photon energy (hυ in eV). According to the generally accepted model proposed by Tauc for higher values of absorption coefficient where the absorption is associated with interband transitions, it yields the power part which obeys the Tauc[17] and Mott and Davis[18] relations as:

$$\alpha\, h\, \upsilon = B\, (h\upsilon - E_g)^n \quad (2)$$

Where B is the slope of the Tauc edge called the band tail parameter and n is the type of electronic transition responsible for absorption, being 0.5 for direct transition and 2 for indirect one. In the low absorption region the absorption coefficient (α) shows an exponential dependence on photon energy (hν) and obeys the Urbach relation[15]:

$$\alpha = \alpha_0 \exp\, (h\nu / E_b) \quad (3)$$

Where α_0 is a constant and E_b is the Urbach energy, interpreted as the width of the tails of localized states in the band gap. The absorption edge (E_e), the band tail (E_b), the direct energy gap (E_d) and the indirect energy gap (E_{ind}) were also calculated from the graphs of: α versus hν, ℓn α versus hν, $(\alpha h\nu)^2$ versus hν and $(\alpha h\nu)^{1/2}$ versus hν, respectively.

The extinction coefficient (K) is important parameters characterizing photonic materials. Value of K can be calculated from transmission and reflection spectra using the relation[16]:

$$K = \alpha\lambda/4\pi \quad (4)$$

Where λ is the wavelength in cm and α is the absorption coefficient in cm^{-1}.

RESULTS AND DISCUSSION

Reflection measurements

Figure 1 represents the reflection spectra in the visible range (400-700 nm) for pure PMMA and PMMA mixed with 2, 4, 6 and 8 wt% AREAPP composites. It is clear that, the reflectance values decrease gradually

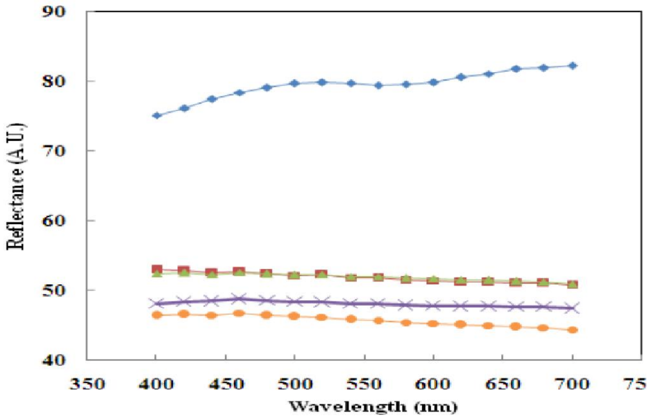

Figure 1 : The change in reflection percentage (R%) spectra for PMMA/AREAPP composites. (◆) 100/0, (■) 98/2, (▲) 96/4, (x) 94/6 and (•) 92/8 (wt/wt%)

with increase the concentration of AREAPP.

From the values of reflectance (Figure 1), the tristimulus reflectance values (y_r) are calculated and plotted as a function of wavelength (400-700 nm) and shown in Figure 2 for PMMA/AREAPP composites. It is observed from the figure that the behavior of y_r for all the composites is similar and no change in peak position (about 560 nm) is detected. It is noticed that, y_r values decreases with increasing AREAPP concentration up to 8 wt% (92/8 wt/wt% composite).

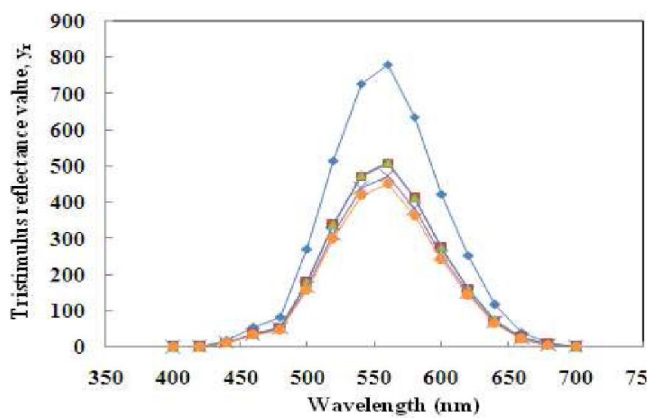

Figure 2 : Variation of the tristimulus reflectance value (y_r) with wavelength for PMMA/AREAPP composites. (◆) 100/0, (■) 98/2, (▲) 96/4, (x) 94/6 and (•) 92/8 (wt/wt%)

Figures 3 and 4 show the variations of the tristimulus reflectance values x_r and z_r, respectively, with wavelength in the range 400-700 nm for PMMA/AREAPP composites. It is clear from the figures that the behaviors for each x_r and z_r for all the composites are similar and their values decrease with increasing AREAPP concentration and also show no change in their peak positions.

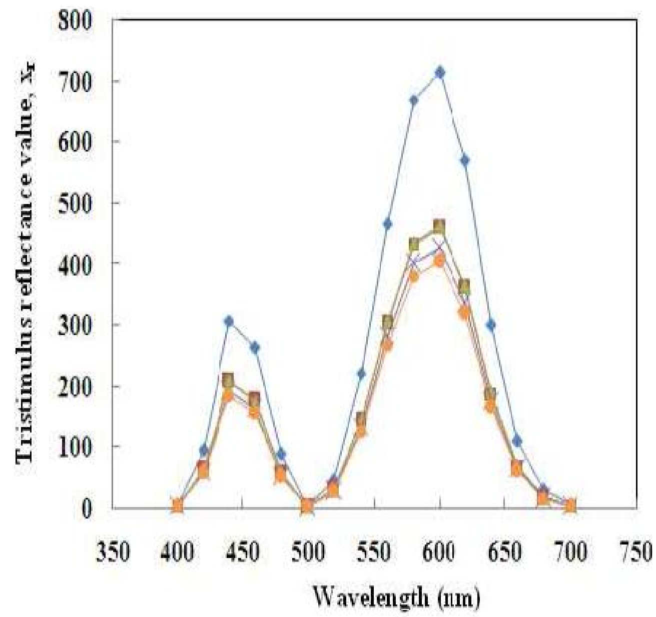

Figure 3 : Variation of the tristimulus reflectance value (x_r) with wavelength for PMMA/AREAPP composites. (◆) 100/0, (■) 98/2, (■) 96/4, (x) 94/6 and (•) 92/8 (wt/wt%)

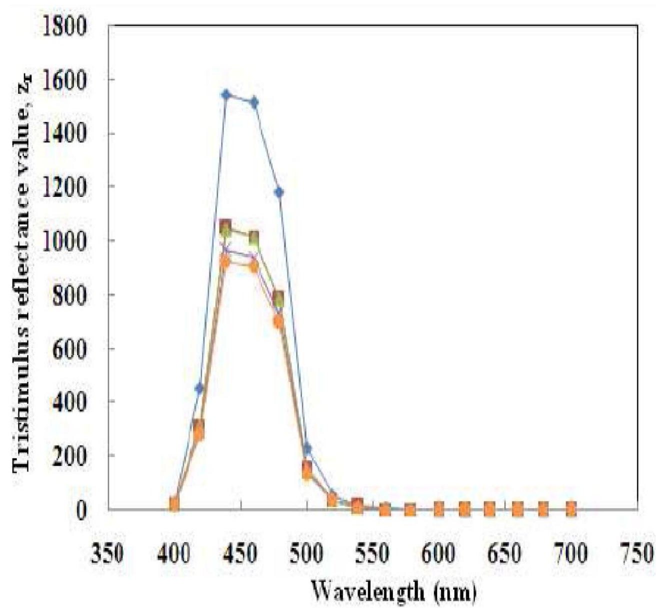

Figure 4 : Variation of the tristimulus reflectance value (z_r) with wavelength for PMMA/AREAPP composites. (◆) 100/0, (■) 98/2, (▲) 96/4, (x) 94/6 and (•) 92/8 (wt/wt%)

TABLE 3 illustrates the values of x_r, y_r and z_r at the peak positions for PMMA/AREAPP composites. It is noticed from the table that the tristimulus reflectance values x_r, y_r and z_r decrease with increasing the concentration of AREAPP up to 8 wt%. The observed results are in agreement with that obtained for the color parameters.

The observed changes in the color parameters (L,

TABLE 3 : The x_r, y_r and z_r tristimulus reflectance values of PMMA/AREAPP composites

PMMA/AREAPP composites (wt/wt%)	x_r		y_r	z_r
	λ = 440 nm	λ = 600 nm	λ = 560 nm	λ = 440 nm
100/0	308.14	614.67	781.28	1545.59
98/2	208.57	459.80	509.37	1042.56
96/4	207.85	462.57	511.73	965.40
94/6	192.47	427.85	472.66	926.40
92/8	184.72	404.85	449.73	780.57

a, b, W, Ye and Δ E) calculated from the reflectance curves of PMMA/AREAPP composites under investigation are tabulated in TABLE 4. As well known, L parameter measures the brightness of the composite and varies from 100 for perfect white to zero for black. It is clear from the table that the 92/8 wt/wt% PMMA/AREAPP composite is darker in color than the other composites while 96/4 wt/wt% PMMA/AREAPP acquires the brightest color. The color constant 'a' varies from green for negative value and red for positive value. It is noticed from TABLE 4 that 'a' values increase in case of 94/6 wt/wt% composite which means that this composite tendering towards red color and on other hand the lower value of 'a' is that for 92/8 wt/wt% composite which indicates that this composite had more green coloration. In considering the color constant 'b', it was found that a considerable decrease in b value for 92/8 wt/wt% composite, which indicates the tendering of this composite towards blue color instead of yellow one. By following the values of whiteness (W), it is noticed that the whiteness index (W) shows nearly the

TABLE 4 : Values of the color parameters for PMMA/AREAPP composites and their percentage changes

Color parameters	PMMA/ AREAPP composites (wt/wt %)				
	100/0	98/2	96/4	94/6	92/8
L	89.82	77.13	77.26	74.85	73.34
ΔL%	-	0.58	1.91	2.07	2.54
a	-0.47	-0.23	-0.28	-0.19	-0.37
Δa%	-	17.02	46.81	-2.13	-12.77
b	2.20	-0.81	-1.05	-0.52	-0.96
Δb%	-	1.36	-37.73	6.36	1.36
W	65.40	56.12	54.50	50.93	51.07
ΔW%	-	1.68	12.08	5.50	7.80
ΔE	-	8.93	9.08	6.68	5.45

same behavior as the color constant 'b'. The obtained results indicate that variations in color difference between samples are occurred by the presence of AREAPP by different concentrations with PMMA.

The observed changes in the color parameters calculated from the reflectance curves with the increase in the concentration of AREAPP in PMMA/AREAPP composites may be due to the change in the physical bonds and then change in the molecular configuration of PMMA which may lead to formation of new centers of the polymeric material. In addition, the obtained results of the color parameters are of great importance for the improvement of the optical properties of PMMA polymer[14,19].

Optical absorption measurements

The total absorption spectral response (α) for the composites under investigation is calculated in the visible wavelength range from 400 to 700 nm and in the photon energy (hν) range 3.10-1.77 eV. Figure 5 shows the relation between the absorption coefficient (α) as a function of wavelength in the visible range (400-700 nm) for PMMA/ARAEPP composites. It is clear from the figure that the absorption coefficient (α) decreases gradually with increasing AREAPP content up to 8 wt%.

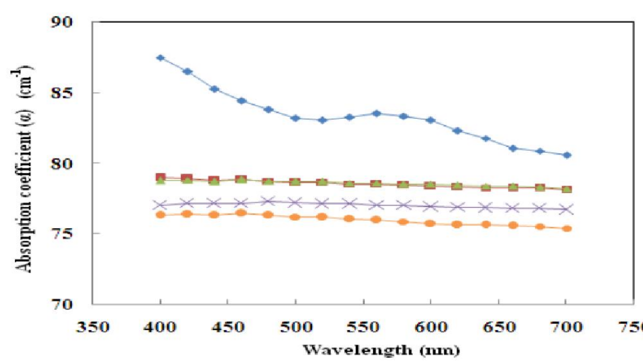

Figure 5 : The absorption coefficient (α) of PMMA/AREAPP composites as a function of wavelength. (◆) 100/0, (■) 98/2, (▲) 96/4, (x) 94/6 and (•) 92/8 (wt/wt%)

The change in the absorption coefficient may be due to the change in the chemical bonds between the PMMA polymer and the inorganic material AREAPP, which form other molecular species[20]. This in turn leads to the formation of new color centers[21], i.e., preferential light absorption at particular wavelength. AREAPP components role is to strength the linkage formed between the reactive species of the PMMA chemical groups and their polar groups. Besides, hydrogen bonds are found between hydroxyl group of PMMA polymer and the chemical groups of AREAPP.

Figure 6 illustrates the variation in the absorption coefficient (α) with photon engery (hν) for PMMA/AREAPP composites under investigation. It is clear that for pure PMMA, the absorption coefficient values increases with increasing photon energy. The behavior of absorption coefficient for the composites of PMMA/AREAPP for different weight percent shows unremarkable increase with increasing photon energy.

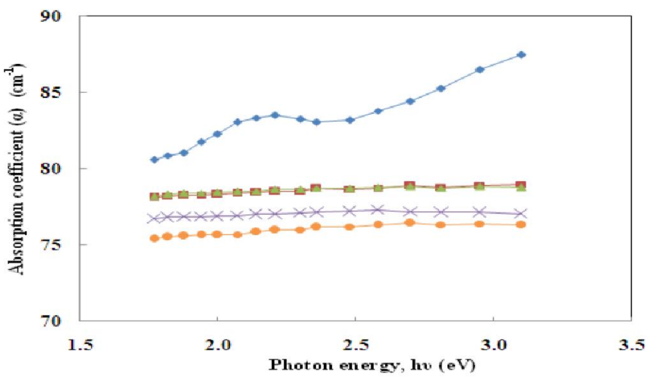

Figure 6 : The absorption coefficient (α) of PMMA/AREAPP composites as a function of photon energy (hυ). (◆) 100/0, (■) 98/2, (▲) 96/4, (x) 94/6 and (•) 92/8 (wt/wt%)

Figure 7 shows the relation between –!n α and hυ for PMMA/AREAPP composites. The straight lines obtained suggest that the absorption follows the quadratic relation for inter-band transitions given by Mott and Davis and the Urbach rule is obeyed[16,19]. The values of band tail energy (E_b) can be deduced from the slopes of the straight lines and are listed in TABLE 5. The E_b values decrease with increasing AREAPP concentration contained in PMMA polymer matrix up to 4 wt%

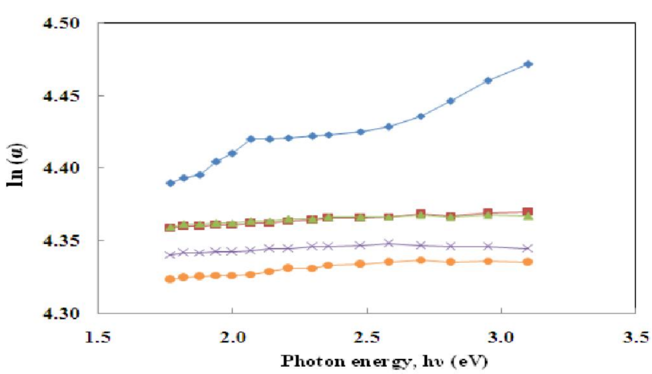

Figure 7 : Urbach law plots for PMMA/AREAPP composites. (◆) 100/0, (■) 98/2, (▲) 96/4, (x) 94/6 and (•) 92/8 (wt/wt%)

and then increase at AREAPP 8 wt%. This change in the band tail at different concentration of AREAPP may arise from the random fluctuations of the internal fields associated with structure disorder in the amorphous region of the polymer material[19].

TABLE 5 : Values of band tail energy (E_b) and direct energy gap (E_d) of PMMA/AREAPP composites

PMMA/AREAPP composites (wt/wt%)	E_b (eV)	E_d (eV)
100/0	0.368	1.81
98/2	0.206	1.54
96/4	0.186	1.56
94/6	0.232	1.57
92/8	0.237	1.58

Figures 8 and 9 show the dependence of $(\alpha h\upsilon)^2$ and $(\alpha h\upsilon)^{1/2}$ on photon energy (hυ) for PMMA/ARAEPP composites, respectively. From the figures, it is observed that the allowed direct energy gap (E_d) is determined by extrapolating the linear parts of the curves to zero absorption and the values are given in TABLE 5. It is noticed from these intercepts that the values of E_d are closed together for all the PMMA/AREAPP composites and lower than that of the pure PMMA. So the obtained values for E_d show the dependence on the composition of the sample. The decrease of them may be due to the number of ions per unit length available for conduction and the change in molecular configuration induced by increasing AREAPP concentration in the PMMA matrix[22].

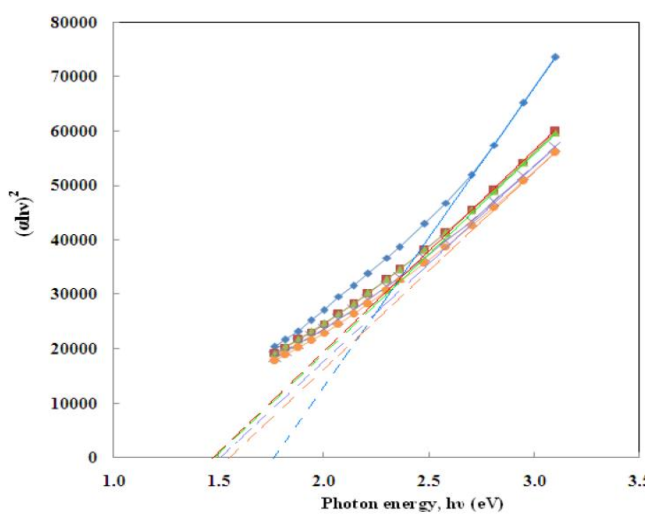

Figure 8 : The variation of $(\alpha h\upsilon)^2$ for PMMA/AREAPP composites as a function of photon energy (hυ). (◆) 100/0, (■) 98/2, (▲) 96/4, (x) 94/6 and (•) 92/8 (wt/wt%)

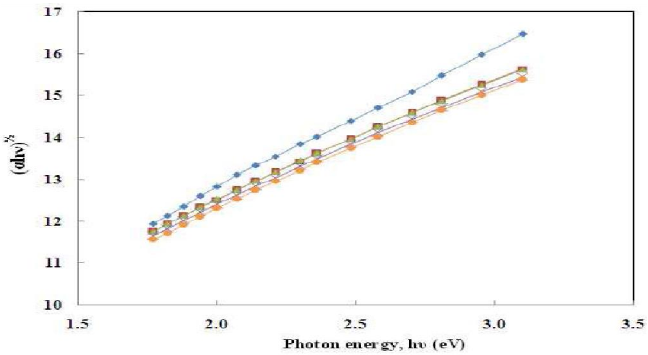

Figure 9 : The variation of $(\alpha h\upsilon)^{1/2}$ for PMMA/AREAPP composites as a function of photon energy (hυ). (◆) 100/0, (■) 98/2, (▲) 96/4, (x) 94/6 and (•) 92/8 (wt/wt%) Extinction coefficient

Extinction coefficient

The extinction coefficient (K) describes the properties of the material to light of a given wavelength and indicates the amount of absorption loss when the electromagnetic wave propagates through the material, i.e., represents the damping of an EM wave inside the material. Figure 10 shows the variation in the extinction coefficient with wavelength of PMMA/AREAPP composites. It is clear from the figure that similar behavior for all composites are observed and the values of K are found to be small in the order 10^{-4} throughout the studied wavelength range (400-700 nm) which indicate that the composites under investigation are considered to be insulating materials at room temperature[23]. It is also clear that, the composite 92/8 wt/wt% indicates the lowest value of K through the whole range of wavelength. In addition, the behavior of the absorption coefficient is preserved for all samples near the absorption edge.

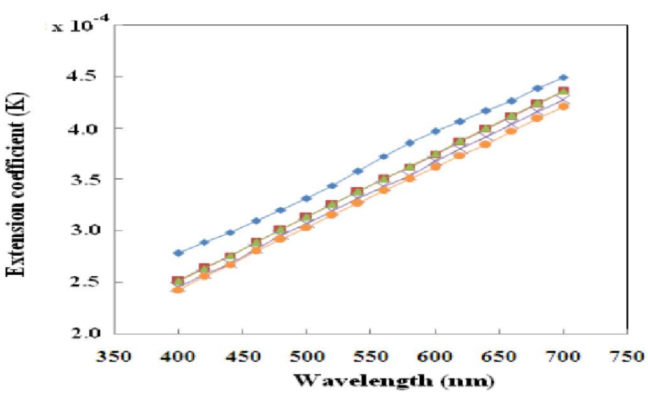

Figure 10 : Variation in the extinction coefficient (K) as a function of wavelength (λ) for PMMA/AREAPP composites. (◆) 100/0, (■) 98/2, (▲) 96/4, (x) 94/6 and (•) 92/8 (wt/wt%)

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