Raghad S. Al-Khafaji
University of Baghdad College of EducationIbn - Al-Haithem, Department of Physics Baghdad , Iraq

Kareem A. Jasim
University of Baghdad College of EducationIbn - Al-Haithem, Department of Physics Baghdad , Iraq

Adil M. Ibraheim
Ministry of Education Baghdad – Al-Rusafa 2 Baghdad , Iraq
Adilmahmoud488@yahoo.com

Received on: 11/5/2017
Accepted on: 20/12/2017
Published online: 25/05/2019

Optical and Thermal Characterizations of PMMA Composites

Abstract: *Thick composite films were prepared employing hand – lay-up method . A definite quantity of PMMA (98%wt) , fixed content (2% wt) of rutile titanium dioxide TiO_2 , gamma alumina (γ- Al_2O_3) and Zirconia powder (ZrO_2) , were added to polymer solution gradually and separately. Optical constants were obtained of the prepared samples using spectrometer (UV- VIS). The prepared composite samples were thermally characterized by differential scanning calorimeter (DSC). We notice increasing value of glass temperature and differential heat capacity (ΔCp) for composites compared with pure PMMA .*

Keywords: Binary composite, PMMA , TiO_2 , Al_2O_3 , ZrO_2 , Optical constants , thermal analysis.

How to cite this article: R. S. Al-Khafaji. , K. A. Jasim and A.M. Ibraheim , " Optical and Thermal Characterizations of PMMA Composites" , *Engineering and Technology Journal* , Vol. 37, Part B, No. 2, pp. 61-66, 2019.

1.Introduction

UV energy which absorbed by plastics can be stimulate photons , which then generate free radicals . Absorbing of electromagnetic energy in the UV-district transmissions the accurate amount of energy levels of the bonds molecule and consequence in agitation of electrons at the ground situation into an activated state. However, absorption will only happen if the energy of the photon exactly agrees to that of the transition edge. The experimental conclusions for optical absorption in glassy materials have been described by Mott and Davis [1]. There are two dominant optical transitions (direct and indirect) depending of optical absorption [1,2].

The mobility gap value and shape of the amorphous semiconductors can be influenced by on the planning state such as substrate, annealed temperature, amount of impureness and imperfection of the prepared composite. Any dissimilarity in so much parameters conduct to an alteration in the absorption edge was near upper or lesser of the energy [3,4].

Composites, the miracle materials are fetching and necessary part of today's materials due to their benefits. Composites of polymer as matrix-ceramic as filler are getting increased care due to their remarkable of electrical and optoelectronic characterizations , such as, , angular acceleration of accelerometers , acoustic emission of sensors, integrated decoupling of capacitors, electronic packaging are some potential applications and optoelectronic device elements such as light emitting diodes (LED), solar cells, and laser diodes. Materials of ceramic are usually brittle, dielectric strength is low and are problematic to be performed which requiring high temperature . But then , polymers are flexible , easily treatment at low temperatures and display in height dielectric break-down [5,6].

Titanium oxide (TiO_2) is a very significant material due to its multi-functional request in photo catalysis , photovoltaic cells, hydrophobic material, photochromic and electro chromic devices , gas sensor, optical device, among others[7] . Poly methyl methacrylate (PMMA) is amorphous transparent thermoplastic that frequently used as a light or fragment-resistant alternate to glass (glass plastics). PMMA is multipurpose polymeric materials for applications technological areas contain optics and electro-optics , transistors filed effect, developing capacitors , also, due to its high transparency in the visible region and low refractive index, hence diminished of optical losing [8].

The combination and properties of trialkoxysilane-capped poly-(methyl methacrylate)-titania hybrid of optical thin films carried out by Chen et al.(1999) [9]. K. NARASIMHA (2003) synthesized and characterized of (single and multi) -layer films for CeO_2 , TiO_2 , Al_2O_3 , MgF_2 and SiO_2 by

http://dx.doi.org/10.30684/etj.37.2B.5
2412-0758/University of Technology-Iraq, Baghdad, Iraq

electron beam evaporation on together glass and PMMA substrates for optical applications [10].

Fu-Der Lai et al.(2007) investigated the optical possessions of Al_2O_3-TiO_2 composite monolayer amorphous films employed as HT-APSM blanks for ARF submersion lithography. The optical properties of the polymers can be fittingly modified by adding of dopants dependent on their reactivity with the host matrix. Rui- Juan and Thomas calculated the optical parameters of polymer composites and they clarified that they are strongly influenced by particle size, particle content, and particularly by difference in refractive indices between polymer as matrix and particles as fillers. The present work looking for the effect of Al_2O_3, TiO_2 and ZrO_2 as fillers on some of the optical constants such as absorption coefficient, refractive index, extinction coefficient and energy gap, as well as, thermal features like heat capacity and glass temperature T_g of PMMA composite.

The applications such as prepared composite could be act in fields of transparent ceramics(high-pressure sodium lamps and EP-ROM window), sensor devices and furnace tubes.

2.Experimental Setu

A definite quantity of PMMA (98%wt), acquired from (sigma Aldrich, GMBH Germany, 99.8% purity) was dissolved in chloroform solution with purity 99.98% with concentration of 15 % g/ml. Fixed content (2% wt) of rutile titanium dioxide TiO_2 of particle size (20-15) μm supplied from (Fluka , Switzerland), gamma alumina (ɤ- Al_2O_3) with particle size < 35μm and Zirconia powder (ZrO_2) particle size < 20μm obtained from (riedel-de haen company, German), were added to polymer solution gradually and separately. Continuous stirring using (magnetic stirrer device) at temperature 50ºC for about (3-4) hours. Prior of film fabrication the starting materials are grounded using ball mill and dried in a convection oven at 100°C for 3h to avoid local inhomogenities. Each solution was transferred to clean mold (quartz substrate), on which cleaned using ultrasound bath with diluted HNO_3 solution, acetone and distilled water respectively, furthermore, it was dried and stored in the drying oven at 40 ^{o}C. The prepared films were then dried at room temperature for 1 day, and further dried in an convection oven at curing temperature 70°C for 2 h to finish the polymerization. The thickness of the films was measured, to be ranging (0.200-0.294)mm. Optical constants were calculated through the absorbance and transmittance spectrum were recorded utilizing double beam UV/VIS-160 a SCHIMADZU (Japan) in wavelength range of (300-900)nm for composite material samples of dimensions (25 × 35) mm , all the measurements were carried out at room temperature. The prepared composite samples were thermally characterized by differential scanning calorimeter (DSC) . It was sealed in aluminum pans by pressing , and put in the furnace of DSC were conducted from room temperature to(120 ̊C) with a rate of heating 10 ̊C / min .The heat flow rate as function of temperature was recorded automatically.

Optical constants (extinction coefficient, refractive index , optical energy gap and absorption coefficient have been calculated from spectrum of absorption[11,12].

$$I = I_0 e^{-\propto t} \quad \ldots..(1)$$

Equation (1) is the mathematical formula of Lambert's law :

Transmittance (T) can be calculated from equation:

$$T = \exp[-2.303\ A] \quad \ldots..(2)$$

Reflectance correlated with absorption and transmission spectra as following :

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

Absorption coefficient (α) can be calculated from equation:

$$\propto = 2.303A/t \quad \ldots..(4)$$

Where The Refractive index (n) and The extinction coefficient (k) were obtained from following equations :

$$R = ((n-1)^2 + k^2) \quad ..(5)$$

$$k = \propto \lambda/4\pi \quad ..(6)$$

Where

t: thickness of sample

I_o: Intensity of light incident on sample

I: Intensity coming out from sample.

α : Absorption coefficient.

A: Absorption of the material

The samples were sealed in aluminum pans by pressing , and put in the furnace of DSC were conducted from room temperature (RT) to (120 ̊C) with a heating rate of 10 ̊C / min .The heat flow rate as function of temperature was recorded automatically

3.Results and Discussions:

Absorption spectrum analysis in a lower energy section provides data about vibrations of atomic while the higher energy section of the spectra offers cognition about the electronic vibrations . The bonds between the atoms in many polymer have separation energies that are very comparable to the quantum energy which present in UV radiation those reported in references [13,14].

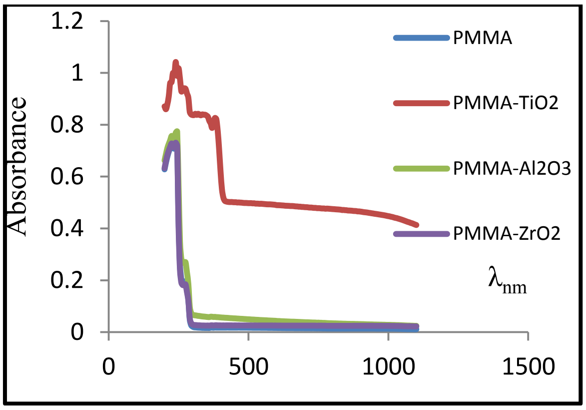


Figure 1 The Absorbance for PMMA composite as a function of wavelength.

The absorbance (A) correlation of the length of wave (λ) of incident (I_o) light for PMMA prepared composites of several fillers of Al_2O_3,TiO_2 and ZrO_2 is shown in fig1 . The spectrum reveals that all the thick films show more absorbance in ultraviolet region UV. There are a sharp fall towards the visible region. All the films show low absorbance (A) in the visible range VIS, this behavior can be explained as follows: at high wavelength , the incident photon do not have sufficient energy to act together with atoms , therefore the photons will transmitted. When decreasing wavelength (λ) (at the vicinity of the essential absorption edge), the interaction among incident photon with material will happen, then the photon will absorbance.

PMMA/TiO_2 exhibit highest value of absorbance, the reason behind of this result attributed to strong dispersion of titanium at visible and near ultraviolet.

All the films demonstrate more transmittance in fig 2 , and the maximum value depends upon of radiation energy, as well as, the combination of the film. The extremely transmittance is due to crystalline nature of the synthesized films which there are indicated in our work(not seem in these research) Below 400 nm there is a sharp reduction in the transmittance of the films, which is referable to robust absorbance in this region. UV-VIS transmittance calculations have shown that our films are extremely transparent in the visible wavelength section, which build them favorable for sensor applications. This clarifies the opportunity of using prepared films as a protective window of solar cells which permit the passage of solar radiation amid the visible light region and protects it from the radiation place within the UV region which is considered disagreeable.

fig 3, shows the correlation of the absorption coefficient (α) and wave length (λ) of the incident light for prepared composites PMMA we noticed the alteration in the coefficient of absorption are slight at low optical energies this is designates the opportunity of electronic transitions is a few. On elevated energy , variation the coefficient of absorption is great which revealed the great probability for electronic transitions are the absorption border of the region, this agree with [16].

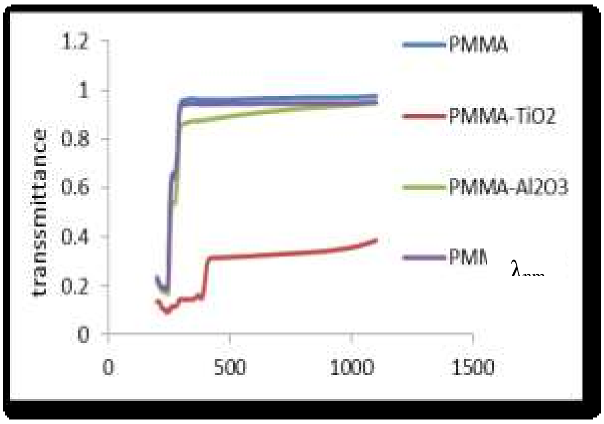


Figure 2 The transmittance for PMMA composite as a function of wavelength.

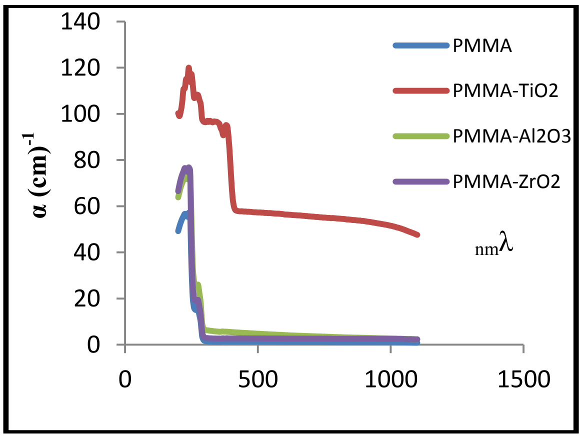


Figure 3 The absorption coefficient for PMMA composite as a function of wavelength.

The result behavior in fig 3 was similar to the absorption spectra, which indicated the direct correlation between absorption and absorption coefficient as shown in equation(4).

The extinction coefficient (k) was illustrated in figure 4 as a function of wavelength of the prepared composites PMMA. The behavior of the extinction coefficient has increased in the visible and near infrared regions, while decreased at low wavelength of absorption edge.

The extinction coefficient correlated to the absorption coefficient, increasing absorption coefficient lead to extinction coefficient increases because of linear correlation between them. Refractive is winding of an incident light beam when it enters a dielectric material . The physical cause for this is that the velocity of light is changed inside the dielectric. The refractive index (n) is a parameter straight correlated to the density of material . Less dense polymorphs of a specific material will have a more open structure and hence a lower (n) than their denser similitude.

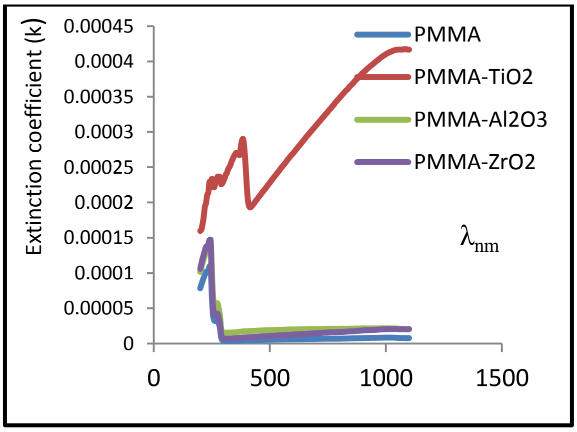


Figure 4 the extinction coefficient for PMMA composite as a function of wavelength .

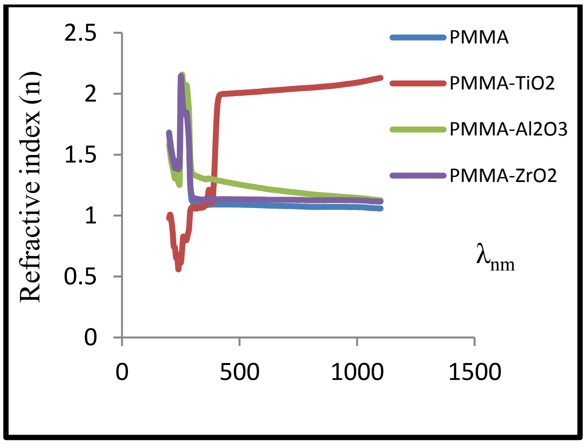


Figure 5 the refractive index for PMMA composite as a function of wavelength.

The coefficient of absorption (α) assistances to determine the character of electronic transitions, when the values coefficient of absorption $(\alpha > 10^4 cm^{-1})$ at great energies we predictable direct of electronic transitions , then the energy in addition of momentum reservation of the electron and photon , when the values coefficient of absorption is $(\alpha < 10^4 cm^{-1})$ at lesser energies we estimated in this case indirect electronic transition[5].The coefficient of absorption for the (PMMA-TiO_2),(PMMA-Al_2O_3)and(PMMA-ZrO_2)composites is less than $(\alpha < 10^4 cm^{-1})$which designated indirect electron transitions[15] .

$$\alpha h\nu = B(h\nu - Eg_0)^m \quad \ldots\ldots(7)$$

Where

hν: photon energy

B: proportionality constant

E_{go} : forbidden energy gap.

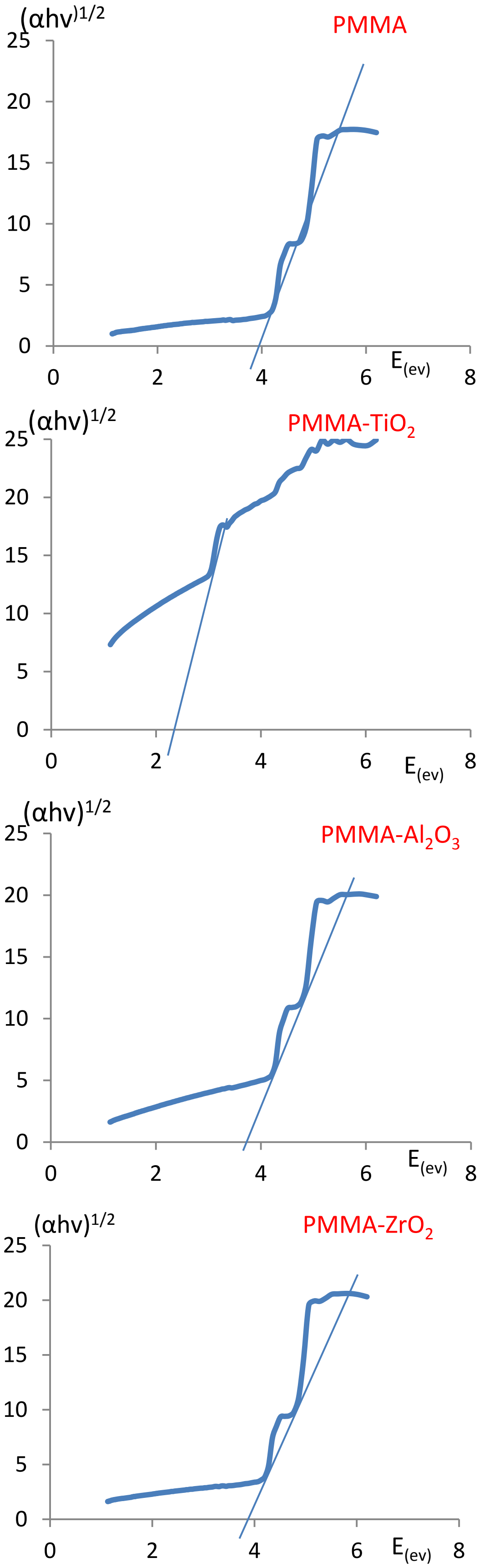
If the value of (m=2) shows to allow of indirect transition . while the value (m=3) display to forbidden of indirect transition. fig(٦) shows the $(\alpha h\nu)^{1/2}$ $(cm^{-1}.eV)^{1/2}$ as a function of the photon energy. Figure(7) shows the correlation with $[(\alpha h\nu)^{1/3}(cm^{-1}.eV)^{1/3}]$ and energy of photon.

The values of energy gap dependency generally on the structure of crystal for the composites and (organization and dissemination way) of atoms in the crystal lattice ,so decreasing of energy gap which is attributed increasing of disorder in the material [5].But then , during mixing of composite, formation of defects may occur, like, voids, which result rise to desirable localized states in the band gap of the material, furthermore, decreasing in cluster size of the parent solution.

Table (1) glass temperature (T_g) and differential heat capacity (ΔC_p) for PMMA and composites specimens

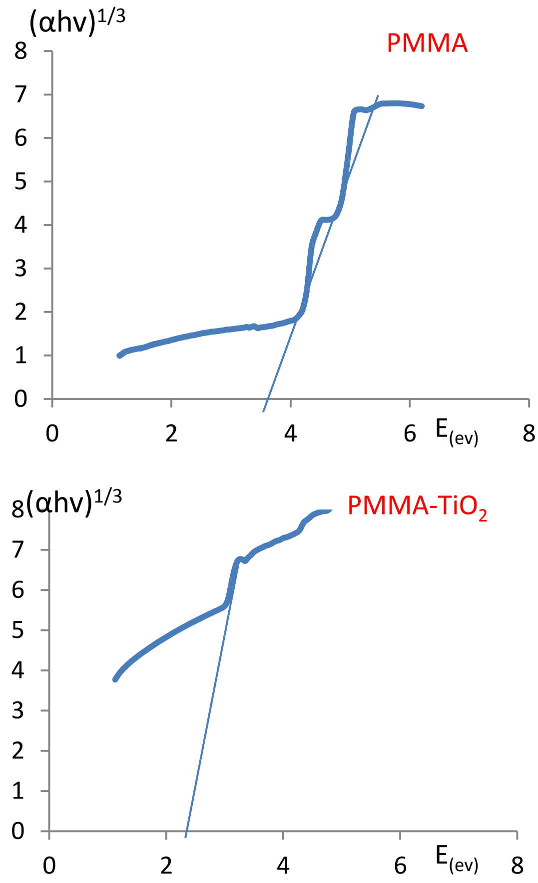
Samples	T_g (°C)	ΔC_p (μV)
100% PMMA	72.981	0.693
98% PMMA+ 2% Al_2O_3	75.656	0.298
98% PMMA+ 2%TiO_2	75.348	0.00813
98% PMMA+ 2%ZrO_2	74.56	0.018

We notice increasing value of glass temperature and differential heat capacity (ΔC_p) for prepared composites compare with pure PMMA , these result can be explained at reduction the mobility of PMMA chains due to formation of highly



immobile layer around each particle which reduce which reduce the mobility of PMMA chains and filling free space between PMMA chains and we can exegesis by increase the restriction of PMMA chains which reason to increase glass temperature (T_g) .

Figure 6 shows the correlation with (αhv)$^{1/2}$ and energy of photon



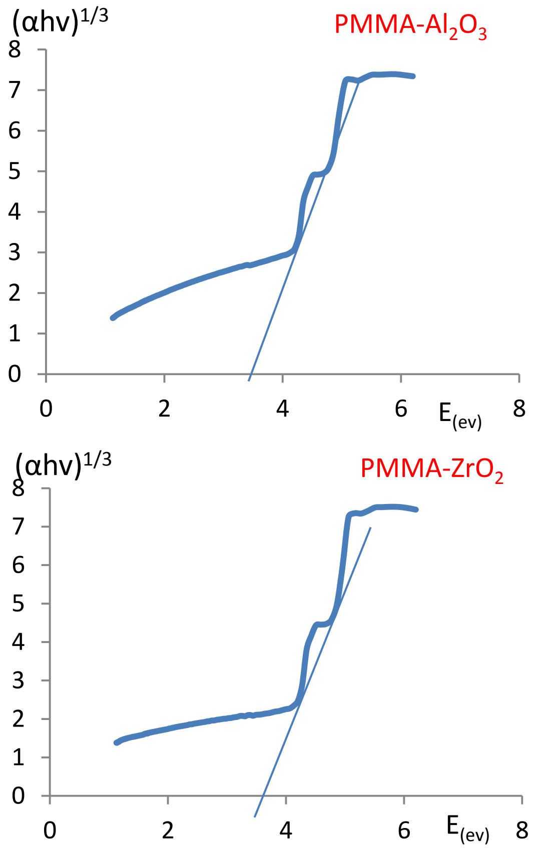


Figure 7 shows the correlation with $(\alpha h\nu)^{1/3}$ and energy of photon.

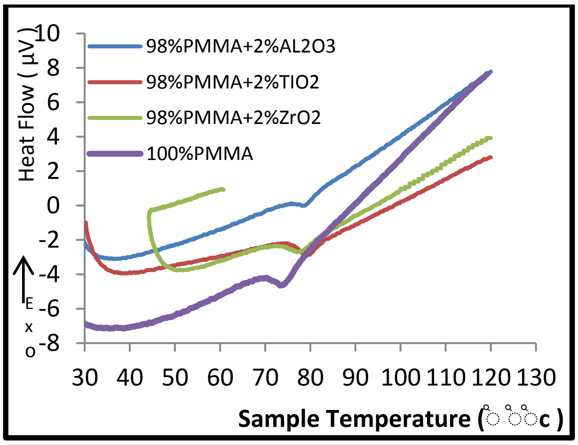


Figure (8) DSC curve of heat flow versus temperature for pure polymer and blends with different compositions.

4.Conclusion:

The composites are prepared employing hand – lay- up method. The spectrum reveals that all the thick films show more absorbance in ultraviolet region UV. There are a sharp fall towards the visible region. UV-VIS transmittance calculations have shown that our films are extremely transparent in the visible wavelength section, which build them favorable for sensor applications. It was noticed for prepared composites PMMA, alteration in the coefficient of absorption are slight at less optical energies this is designates the opportunity of electronic transitions is a little. At high energy , variation the coefficient of absorption is great which revealed the great probability of electronic transitions are in the absorption border of the region. The behavior of the extinction coefficient has increased in the visible and near infrared regions, while decreased at low wavelength of absorption edge. Refractive coefficient (n) is a parameter straight correlated to the density of material, thus it is high in case of PMMA- ZrO_2 . Energy band gap increasing from PMMA- ZrO_2 down to PMMA. The prepared composite are capable in UV-VIS filters and sensors applications. From thermal analysis results we notice increasing value of glass temperature and differential heat capacity (ΔC_p) for prepared composites compare with pure PMMA.

References:

[1].J. singh " Electronic and Optoelectronic properties of semiconductor structures " pp 364 , 2003 .

[2].A. S.Ayesh " Electrical and Optical characterization of PMMA doped with $y_{0.0025}$, $Si_{0.025}$, $Ba_{0.9725}$ ($Ti_{(0.9)}$ $Sn_{0.1}$) Q_3 ceramic , chinese Journal of polymer science Vol.28 , No.4 , pp 537 – 546-2010 .

[3].R. Boylestad and Louis Nashelsky " Electronic Devices and Circuit Theory" seventh edition pp 5-8 1999. [4].V.Raghavan " Materials Science and Engineering " fifth edition pp 356-360 , 2010 .

[5].S.L.Rosen .Fundimental principles of polymeric materials , John Willey &Sons . Inc . Newyork , 1993 .

[6].A. K.Kaw " Mechanics of compsite Materials " 2th edition , Taylor & Francis Group , 2006 .

[7].J.Brandup , E.H.lmmergut and E.Grulk , " polymer Handbook " 4th edition , John Wiley , Newyork , 1999 .

[8]. S. kalbandhe , Ankita Thikane and shubhashree munot " P_{mma} Nano – Composites" International conference on Ideas , Impact and Innovation in mechanical Engineering , V. 5 ,pp 1627-1632 , 2017 .

[9]. B.S.Hayes and L.M.Gammon " Optical Microscopy of fiber-Reinforced composites " , ASM International , pp 17-22 , 2010 .

[10]. D.Lukkassen and Annete Meidell " Advanced Materials and Structures and their Fabrication processes

" book manuscript , Navvik university college , Hing , pp190-192 , 2007 .

[11]. P.S.Kireev , " Semiconductor physics " , 2nd edition , Translated from The Russian by M.samokhvalov , Mir publishers Moscow , pp .16-331 , 1978 .

[12]. S.Rani and J.shanthi " Effect of annealing on the optical transmittance behavior of electron beam evaporated CdSe thin films " international Journal of Recent Scientific Research , Vol .5 , pp 118 – 119 , 2014

[13]. M.A.Diab,,N.A.ALGhamaz , "conducting polymers VIII optical and electrical " polymer testing , Vol.63,pp440-447,201

[14]. S.Sun , Yu Wang "In situ synthesis of poly nano composites and their optical properties " springer , polymer science , vol. 59, pp 630-638 , 2017

[15].A.Ehsani , Shirin Adeli "Electrochemical and optical properties of TIO_2 nanoparticales / poly composites films " journal of Electro analytical "Vol . 713 , pp 91-97 ,2014

[16].S.M.Scholz, G.Carrot and J.Hilborn,"Optical properties of Gold-Containing Poly (Acrylic Acid) ",Lausanne-Switzerland,(2008).