

Characterization and Optical properties of Lead doped Poly Vinyl Alcohol Films

الخواص البصرية لاغشية بولي فنائيل الكحول المطعم بالرصاص

Muna M. Abbas¹, Tariq J. Alwan² and Inaam M. Abdulmajeed³

^{1,3} Baghdad University, College of Science, Physics Department

² Al-Mustansiriyah University, College of Education, Physics Department

Corresponding author email:muna_moussa@yahoo.com

Abstract

Pure and Lead-doped poly vinyl alcohol (Pb-PVA) films were prepared by volume mixture using casting technique by different concentrations (2% and 6%). The characteristics of composites was investigated by FTIR spectroscopy. The optical properties, absorption and transmission of films were investigated through the transmission measurements at room temperature in wavelength range of (200-1100 nm). Overall we observe that the values of E_g decreases by the increasing of concentration. Values of E_g determined to be 6.2, 4.745 and 4.75 eV for pure PVC, 2% and 6% Pb respectively.

Keywords: Composite polymer; Poly vinyl alcohol, Pb; Optical properties

الخلاصة :-

اغشية بولي فنائيل الكحول النقية و المطعمة بالرصاص تم تحضيرها بمزج حجمي بنسب مختلفة (2% و 6%) بطريقة الصب. خصائص المركب شخّصت بواسطة طيف الاشعة تحت الحمراء. الخواص البصرية، الامتصاصية و النفاذية شخّصت بواسطة قياسات الامتصاصية في درجة حرارة الغرفة عند مدى للطول الموجي (200-1100) نانومتر. قلت قيم فجوة الطاقة بزيادة نسب التطعيم حيث كانت قيم فجوة الطاقة 6.2 و 4.75 و 4.745 إلكترون فولت للنماذج PVC 2% و 6% على التوالي.

Introduction

One of the goals of material research is to create new materials with properties tailored to a particular application and to understand the physical and chemical mechanisms that determine these properties.

Polymers opened a tremendous flurry of worldwide research, because of their promise potential industrial and technological of applications. The most frequently used polymeric material is polyvinyl alcohol (PVA), poly (methyl methacrylate) (MMA) and polyvinyl chloride (PVC) [1].

Polymers, on the other hand, are flexible lightweight materials and can be produced at a low cost. They are also known to allow easy processing and can be shaped into thin films by various techniques such as dip-coating, spin-coating, film-casting, and printing. Polymers are already widely used in the optoelectronics industry and are playing important roles in various applications.

Many researches done by mixed two or three polymers (polymer blend) or added materials to in order to improve the properties of polymers [2-7]. One of these materials metals or salts. A metal, in atomic or ionic state, introduced into a polymer matrix, generally improve the polymer behavior and as a rule of composite materials, new properties, different of both matrix and filler ones, could be evidenced.

Rabee [8] showed that the absorption coefficient increases and energy gap of the indirect allowed and forbidden decreases with increase the weight percentage of silver carbonate, the extinction coefficient increases with increase the silver carbonate content.

Prosanov [9] found that , the compositions such as PVA-ZnO-Pb(CH₃COO)₂ can be used as the reversal photographic materials with a direct blackening besides he showed another interesting property of lead nanoparticles in a PVA-ZnO composition is their ability to activate excitonic luminescence of zinc oxide.

The aim of the present work is to investigate the optical properties of polyvinyl alcohol (PVA) doped with varying concentration of Lead nitrate Pb (NO₃)₂.

Experimental Details

Casting method used to prepare pure and doped thin films. PVA with molecular weight of 107 g/mol from (BDH) company was used as a host polymeric material and Pb (NO₃)₂ from (BDH) company used as doping. To prepare pure PVA solution films, PVA grains of weight 0.2g were dissolved in 5 ml of distilled water to obtain a solution PVA. The mixture stirring continuously to obtain homogenous solution for about 15 min at 80°C. Doped solution films were fabricated by dissolving Pb (NO₃)₂ in distilled water of ratios (2% and 6%) and added to the polymeric solution with continuous stirring. Those solutions were poured into flat glass plate dishes and dried in oven at 60 °C for 3hr. Evaporation leads to increase the viscosity and formation of films; the dried homogeneous films were then removed easily by using tweezers clamp. Other similar films were prepared in order to ensure dried samples without bubbles and thermal damage. The thickness of the prepared films was about (0.05-0.07mm) measured by using a digital micrometer. The characterization of materials PVA and PVA/Pb have been carried out using Shimadzu FTIR-8400S Fourier Transform infrared spectrophotometer with range 400–4000 cm⁻¹.

Absorbance and transmittance measurements were carried out by using a double beam UV/VIS spectrometer Shimadzu Japan UV-160A in the wavelength range (190-1100) nm.

Results and discussion

The characterizations of pure and 6% PVA/Pb films are shown in Figs.1 and 2 respectively. The spectra show a strong broad absorbance at (3324- 3338 cm⁻¹) for pure PVA and (3173-3441 cm⁻¹) for 6 % Pb (NO₃)₂ doped PVA. This band could be assigned to O-H stretching vibration of hydroxyl group of PVA, the band corresponding to C-H asymmetric stretching vibration occurs at 2921 cm⁻¹ and 2941 cm⁻¹ for the doped PVA. A strong absorbance at 1710 cm⁻¹ for doped PVA corresponds to C=C stretching vibration Absorbance at 1649 cm⁻¹ corresponds to an acetyl C=O group, which could be explained on the basis of intra/inter molecular hydrogen bonding with the adjacent OH group. The sharp band 1095 cm⁻¹ corresponds to C-O stretching of acetyl groups present on the PVA backbone that remains the same for undoped but broadens for doped samples [10].

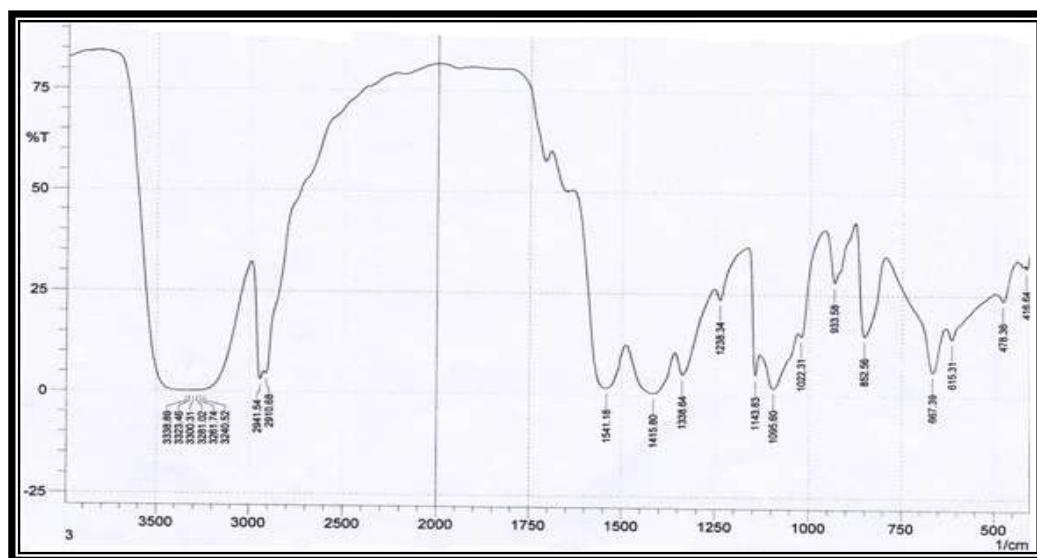


Fig.1: FTIR for pure PVA film

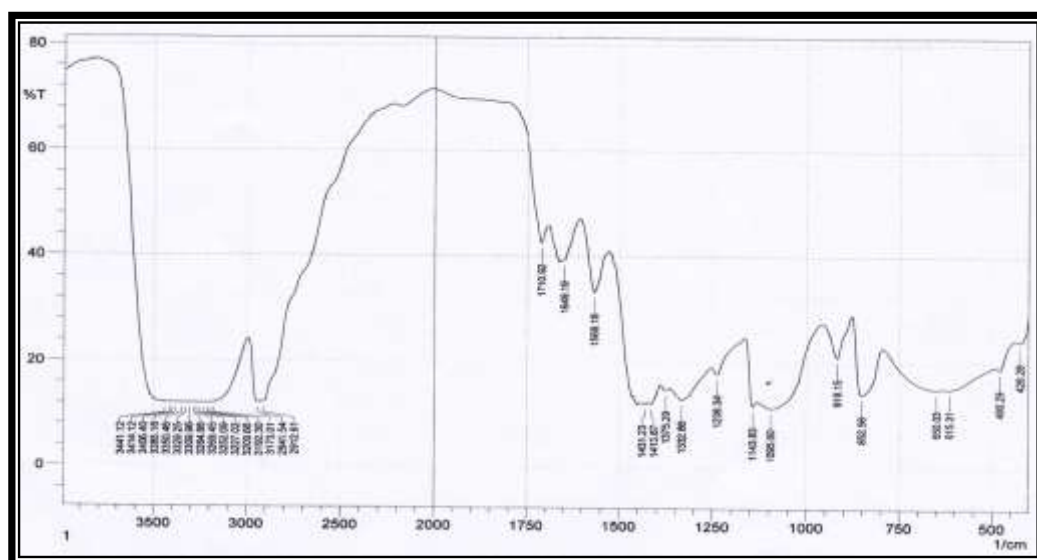


Fig.2: FTIR for 6% PVA/Pb film

Optical absorption measurements are carried out in particulars to check the presence of the Pb ionic form in the polymer matrix. The ultraviolet visible absorption spectra of pure, 2 and 6 wt % $\text{Pb}(\text{NO}_3)_2$ -doped PVA films are shown in Fig 3. It is observed that the shapes of the curves were similar there is a relatively sharp delimitation between the areas of high and low absorption in the UV region; a shifting in the peak position while the intensity of these peak increased as a result weight percentages of Pb . The most intense band belongs to the ligand PVA matrix, increasing the concentration [11] have more atoms present hence more states are available for the photon energy to be absorbed.

The transmittance and reflectance spectra of pure, 2 and 6 wt % $\text{Pb}(\text{NO}_3)_2$ -doped PVA films are displayed in Figs.4 and 5. The transmittance spectra for pure and doped films showed a sharp increase in UV below 300 nm subsequent by a steady state. The decreasing in transmission wavelength with increasing the concentrations, leads to a decrease in light scattering losses.

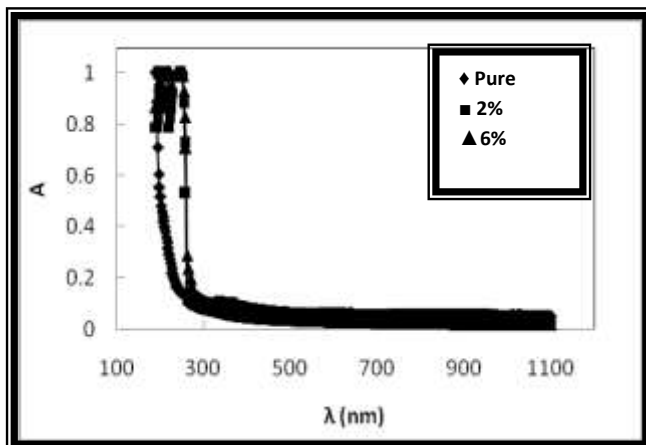


Fig.3: The absorption spectral for PVA/Pb films with different concentrations

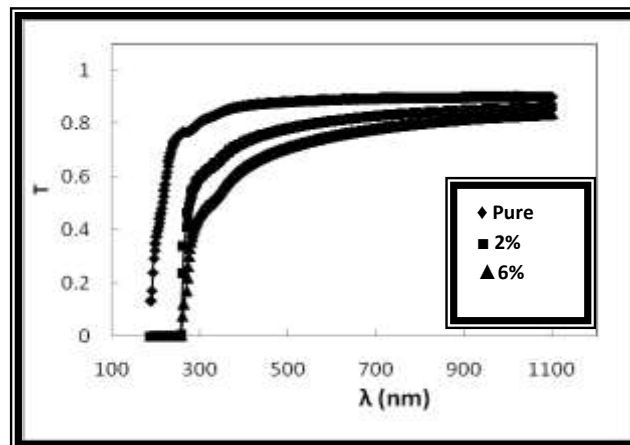


Fig.4: The transmission spectral for PVA/Pb films with different concentrations

Pure films showed increases the reflectance to form saturation and steady with increasing wavelength. Doped films showed different behavior, meanwhile, there is a relatively sharp delimitation between the areas of high and low absorption in the UV region; it had been shown that the reflectance increases with increasing Pb concentration due to the increase in the Pb atoms.

The optical absorption coefficient α behavior for PVA/Pb films is given in Fig. 6, it resembles the absorption spectra. The figure indicates the absorption coefficient increases by the increase of Pb concentration; this may be attributed to increase the absorbance [12].

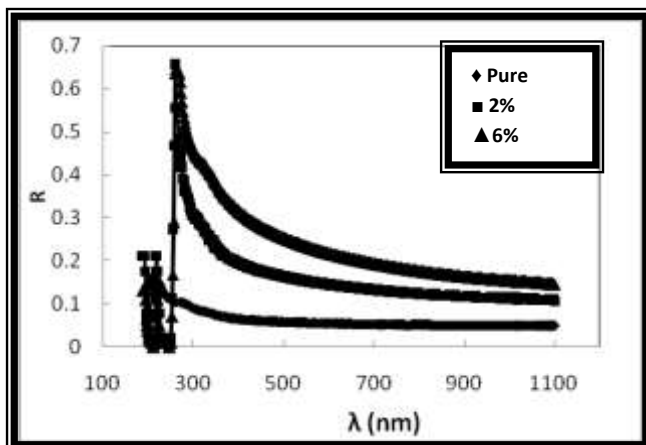


Fig.5: The Reflectance spectral for for PVA/Pb films with different concentrations

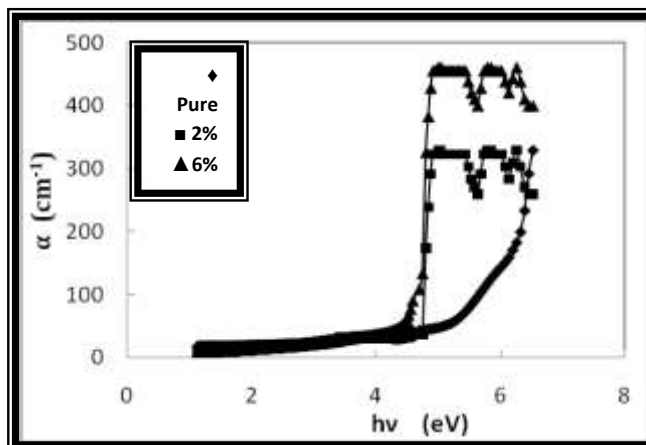


Fig.6: The absorption coefficient spectral for PVA/Pb films with different concentrations

The optical energy gap E_g of thin films is calculated by using the following equation [13]:

$$\alpha h\nu = A(\alpha h\nu - E_g)^n \quad (1)$$

where A is a constant, h is Planck's constant, E_g the optical energy gap of the material, ν is the frequency of the incident photon and n the exponent which depends on the type of transition [14] that occurred.

The plots of the $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ for various films with varying concentrations of Pb source are shown in Fig.7.

Values of E_g determined to be 6.2, 4.745 and 4.75 eV for pure PVC, 2% and 6% Pb respectively. Overall we observe that the values of E_g decreases by the increasing of concentration this is attributed to the presence of doping and its interaction results in the creation of new molecular dipoles, which could be results of point defects created within the band gap.

The values of Urbach energy E_u called the width of localized states in the optical band gap [15] are 2.479, 0.148 and 0.474 eV for pure PVC, 2% and 6% Pb respectively decreases with increasing concentration this is attributed to the increases of the defects and localized state in the energy gap.

The relationship between the extinction coefficient k and wavelength of the films are shown in Fig. 8. It can be clearly seen that the extinction coefficient increase as the doping percentage increased, this may be attributed to high absorption coefficient. This result indicates that the doping atoms of Pb will modify the structure of the host polymer. Similar behavior has been noticed by Ahmed *et al.* [16].

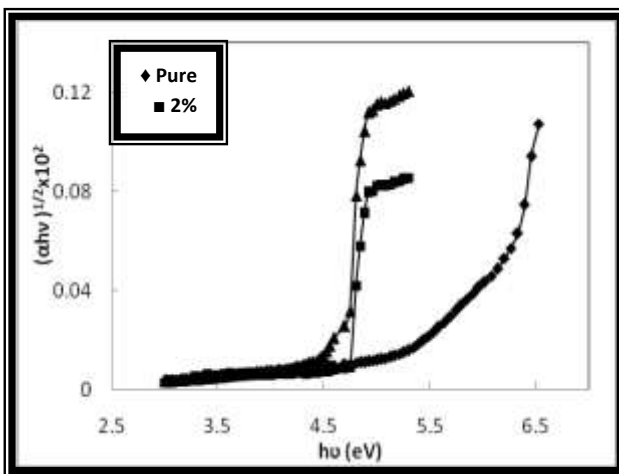


Fig.7: Plot of $(\alpha hv)^{1/2}$ vs. $h\nu$ for PVA/Pb films with different concentrations

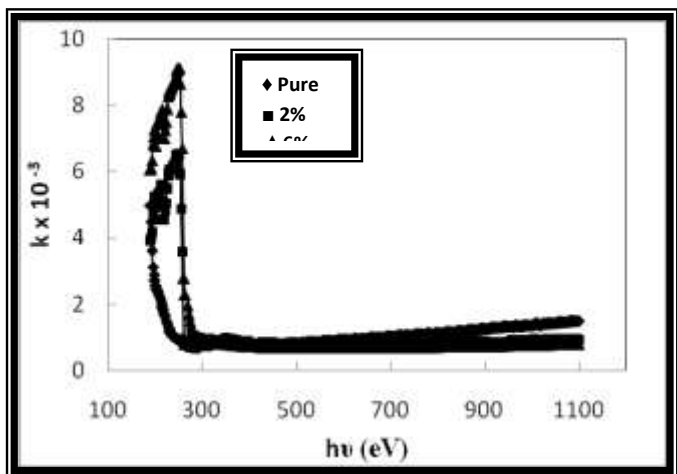


Fig.8 The extinction coefficient as a function of $h\nu$ for PVA/Pb films with different concentrations

The refraction index n value provides the optical properties of the film and it is related by the following equation [17].

$$n = \left(\frac{1 + \sqrt{R}}{1 - \sqrt{R}} \right) \quad (2)$$

Fig.9 illustrated the values of n as a function of the energy for films, was found that the value of refractive index increases by the increasing of the concentration of Pb (NO_3)₂ which results in the increase of the number of the atomic refractions due to the increase of the linear polarizability in agreement with Lorentz - Lorentz formula [12 and 18]. Moreover, they exhibit higher values of n in the UV-VIS regions for films with the increasing doping percentage, but lower values in the NIR region. This is an indication that the rate at which light is slowed down in the film is very high in the UV-VIS region and decays to relatively low rate in the NIR region.

Optical conductivity σ_o is calculated using the following equation [19]:

$$\sigma_o = \alpha nc / 4\pi \quad (3)$$

The plots of σ_o against $h\nu$ of films with different concentration are displayed in Fig. 10. Doped films showed a sharp increase subsequent by a steady state steady in high range of energy with increase of Pb (NO_3)₂ concentration; especially films with 6% have highest optical conductivity value.

The real and imaginary part of the dielectric constants ϵ_r and ϵ_i for films are shown in Figs. 11 and 12 respectively, the behavior of ϵ_r is similar to the refractive index because of the smaller value of k^2 comparison of n , while ϵ_i is mainly depends on the k values, which are related to the variation of absorption coefficient.

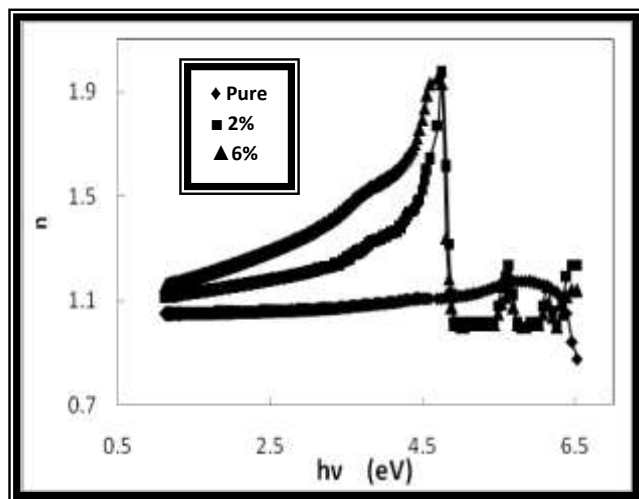


Fig.9: The values of refractive index as a function of $h\nu$ for PVA/Pb films with different concentrations

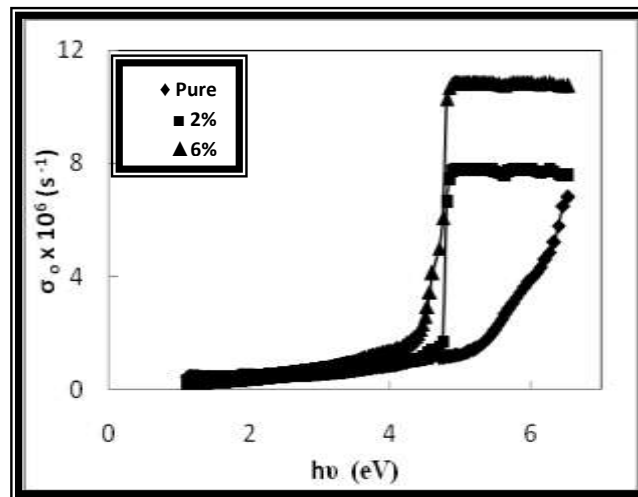


Fig.10: Optical conductivity as a function of $h\nu$ for PVA/Pb films with different concentrations

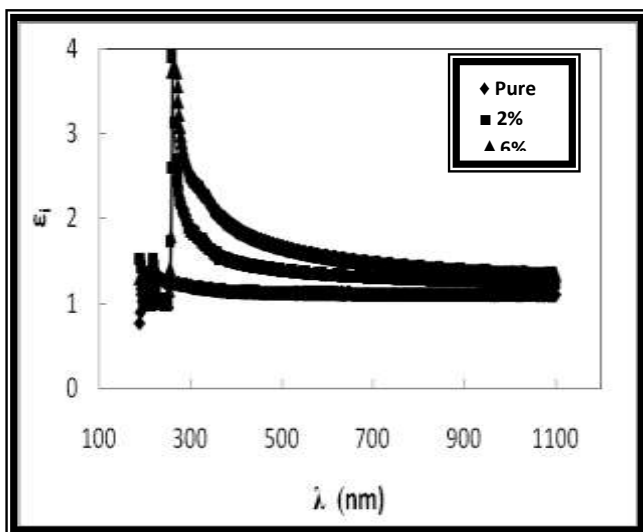


Fig. 11: The imaginary part of the dielectric constant function of wavelength for for PVA/Pb films with different concentrations

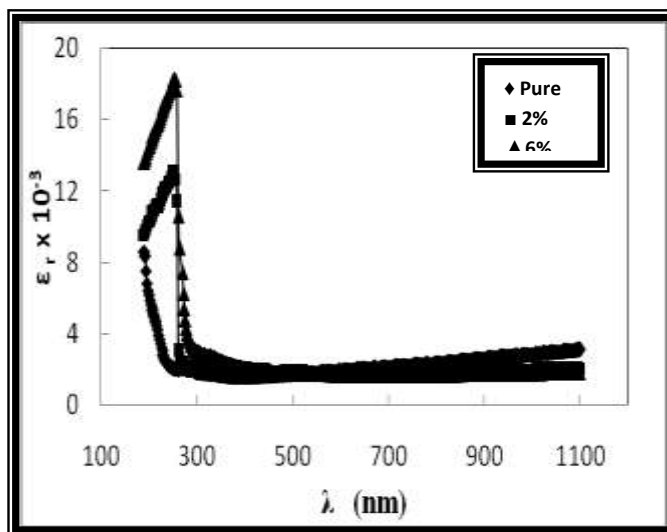


Fig.12: The real part of the dielectric constant as a function of wavelength for for PVA/Pb films with different concentrations

Conclusions

Pure and Pb-doped poly films were prepared by casting technique with different concentrations (2% and 6%). The absorption spectral analysis showed that the optical energy band is due to the indirect allowed optical transitions, the optical energy band gap (6.2-4.75) eV of the films decreases with increasing doping. The values of Urbach energy E_u are 2.479, 0.148 and 0.474 eV for pure PVC, 2% and 6% Pb respectively decreases with increasing concentration. Extinction coefficient and refractive index increase as the doping percentage increase.

The First Scientific Conference the Collage of Sciences 201 3

References

- [1] T. J. J. Meyer, Photon Transport in Fluorescent Solar Collectors, University of Southampton, School of Engineering Sciences, Ph D Thesis, 2009.
- [2] P.Uthirakumar,E.K.Suh,C.H.Hong and Y.S.Lee,Polym.,46,2005p.4640.
- [3] p.Uthirakumar,C.H.Hong,E..K.Suh and Y.S.Lee.Reactive &Funct polymer(2007)p1-16.
- [4] S. Nam, J. Jaeyoung, K. Kim, W.M. Yun, D..S Chung, J. Hwang, O.K. Kwon, J. Mat Chem. 21,2011,p. 775.
- [5] Z. R.Ali, A.M.Zeadan & K. M.Ziadan, J. Basrah Science A, 20, 1 ,2008, p.22.
- [6] H.M. Jabbar,E. M. Jaboori and A.Q. Abdullah, J. of Basrah researches Sciences)36,2010,15.
- [7] S. Gp. Gratzel, J. of chemical Education,75,6, 1998,p. 27.
- [8] B. H. Rabee, European Journal of Scientific Research ISSN 1450-216X 57,4 , 2011, p.583.
© EuroJournals Publishing, Inc. 2011.<http://www.eurojournals.com/ejsr.htm>
- [9] I.Y. Prosanov, Photochemical Formation of Metal Lead in A Polymeric Matrix, Far Eastern Transport University, Department of Physics. 680021, Khabarovsk, Seryshev str. 47, Russia.
- [10] J.McMurry. Organic Chemistry, sixth edition, Thomson Learning , Inc 2004.
- [11] F. H. Abd El-Kader, G. A Ttia and S. S. Ibrahim. J. of Applied Polymer Science. 50, 1993,p. 1281.
- [12] A.H. Ahmad, A.M. Awatif and N. Zeid Abdul-Majied, J. of Eng. & Technology,25, 4, 2007,p.558.
- [13] P. K. Ghosh, M. K. Mitra, K. K. Chattopadhyay, Nanotechnology 16, 2005, p.107.
- [14] J. Hwang, M. O. Oh, I .Kim, J. K. Lee and C. S. Ha. Curr. Appl.Phys. 5, 2005,p.31.
- [15] O. G. Abdullah and D. R. Saber. Optical Absorption of Polyvinyl Alcohol Films Doped with Nickel Chloride.2011 International Conference on Applied Physics and Mathematics, 2011 .
- [16] A. Hashim, A.J. Kadham Algidsawi and S. Hadi . American Journal of Scientific Research ISSN 1450-223X Issue 37,2011, p.20.
- [17] M.S.Aziz and H.M.El-Mallah, Indian Journal of pure &Applied Physics , 47, 2009,530.
- [18] M. Muhsien, A. Hashim, K. Mahdy, Doping Effect on Constants of Poly- Vinyl Alcohol, Proceedings of the First Scientific Conference of physics/ Al- Kufa University, Iraq,2010.
- [19] A. Osherov, V. Ezersky, Y. Golana, , Eur. Phys. J. Appl. Phys. 37,1,2007,p 39.