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Investigation of optical properties of irradiated and unirradiated poly (vinyl chloride-co-vinyl acetate)

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الخلاصة

تضمن هذا البحث دراسة الخواص البصرية للبولي (فاينيل كلورايد – فاينيل اسيتات) بسمك (25μm) قبل وبعد التشعيع وقد وجدنا ان التشعيع يؤثر بشكل كبيرعلى بعض الخواص البصرية , وقد درست الخواص البصرية باستخدام مطياف الاشعة فوق البنفسجية و المرئية ضمن الطول الموجي nm (300-900)

Abstract

This work describes the studies of the optical properties of poly (vinyl chloride-co-vinyl acetate) film (25 μm Thick.) before and after irradiation, where we found that the irradiation has major effect on the optical properties. The optical properties studied by using ultraviolet - visible spectra in the wave length range (300-900) nm .

Introduction

Irradiation of solids with high energy radiation, like γ-rays, and UV light, electrons or neutrons expected to affect their physical properties. Studies on the changes in optical properties of ferroelectric thin films irradiated with ionizing radiations yield valuable information regarding the electronic processes in these materials. The radiation effects are strongly dependent on the structure of the absorbing substances. Ionization occurs and charged species, both ionic and free radical, are formed. The study of radiation-induced defects is not only important in observing the changes in the physical properties degradation or efficiency improvement in its applicability in a radiation environment, but it is also critical in getting basic informations on vacancies, interstitials and their interaction with impurities.

Optical absorption measurements is a standard technique for investigating band structure and it is therefore of interest to study absorption in thin films. The absorption spectra in the lower region (IR) are useful in studying the molecular vibrations. The higher energy region (UV) can be useful to manifest the electronic states of the atoms and other important phenomena affected by irradiation (1)

In recent years, studies on optical of polymer blend films have increased remarkably in view of their wide applications in radiation dosimetry and in optical and electronic devices(2). The manufacturing of these materials can be tailored to have unique optical, electrical and electrochemical properties by irradiating with the electromagnetic radiation such as x- and γ-rays or the participate radiation such as electron and ion beams or change their physicochemical properties through grafting and scission or dehydrochlorination(3,4,5).

The increase of ionic species in polymer blends upon in addition can be studied using absorption spectrometers, which provide details of the optical band gap energy and absorption edge and activation energy. The absorption spectra in UV region increase with increasing dose. Electromagnetic wave packet interacts with electron in the Valence Band (VB), which is then raised across the band gap on the Conduction Band (CB) via two possible types of electronic transition, i.e. direct transition and indirect transition(4).

2- Experimental part

2-1 Materials

a- Copolymer

Copolymer of vinyl chloride-co-vinyl acetate (B.D.H. Ltd A.R.Grade, purity 99%) was used at the test sample .

2-2 Film preparations

poly vinyl chloride-co-vinyl acetate of 0.04 gm/ml in a dichloromethane solvent is used to prepare polymer film (25 µm in thickness).The film was prepared by casting and evaporation techniques at room temperature for 2 hr.. The film sample was fixed on a special holder for irradiation (which is an aluminum plate (0.6mm) in thickness supplied from (Q-panel) company U.S.A.)

2-3 Irradiation process:

2-3-1 Accelerated testing technique:

We used the accelerated weather-o-meter, Q.U.V. tester, (Q panel company, U.S.A), for irradiation of polymer films. The accelerated weathering tester contains stainless steel plate with two cavities in the front and rear sides. Each side contains four lamps, type (U.V.B. 313), located horizontally, giving spectrum range of wavelength between (290 to 360) nm, and the maximum intensity is located at (313) nm.

The polymer film holders are fixed vertically and paralleled to the lamps, so that U.V radiation is vertically incident on the polymeric samples. The irradiated sample holders were changed in positions from time to time to ensure that all samples received the same intensity of light ($I_o = 3.49*10^{-5}$ einsteins.$dm^{-3}.S^{-1}$), the temperature of the tester chamber is constant at 50 °C for all samples, time of irradiation was 240 hrs .

During the irradiation process, the degree of photodegradation of the polymer films was monitored, by taking different times.

The intensity measurement of the incident light (I_o) was carried out with potassium ferrioxalate actinometer as described by Hatchard and Parker(6).

2-4 Photodegradation measuring methods:

The photodegradation rate of polymer film was measured using infrared spectrophotometery and ultraviolet-visible spectrophotometry (7).

Results and discussion

In Fig. (1) the optical transmittance (T%) of irradiated and unirradiated poly (vinyl chloride-co-vinyl acetate) film are shown.

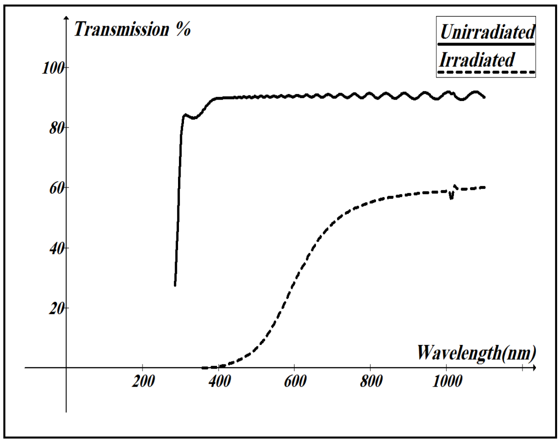


Fig. (1): Transmission % of irradiated and unirradiated Poly(VC/VAc) samples

It was found that the absorption edge shifts towards low energies due to irradiated (blue). Furthermore, the transmission was found to decrease with irradiated from about 80% to 90% in spectral region above 400 nm.

Fig. 2 illustrates the dependence of the absorption coefficient on the photon energy for irradiated and unirradiated poly (vinyl chloride-co-vinyl acetate) samples.

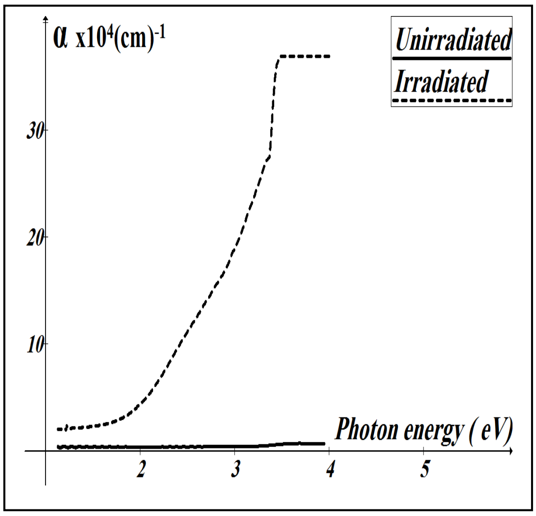


Fig.(2): Absorption coefficient versus photon energy for irradiated and unirradiated Poly(VC/VAc) samples

The study of the fundamental absorption edge in the IR-VIS-UV region is a useful method for the investigation of optical transitions and electronic band structure in crystalline and non-crystalline materials. The main feature of the absorption edge is an exponential increase of the absorption coefficient α with photon energy hν. The absorption coefficient α can be determined as a function of frequency using the formula

$$\alpha = \frac{A}{d} \times 2.303$$

where A is the absorbance and d is the thickness of the sample.

The marked decrease of the absorption coefficient at higher energies for unirradiated sample may be attributed to the absence of extra transition from the bonding molecular orbit to nonbonding molecular orbit(8)

The evaluation of refractive indices of optical materials is of considerable importance for applications in integrated optic devices such as switches, filters and modulators, where the refractive index of a material is the key parameter for device design(9).

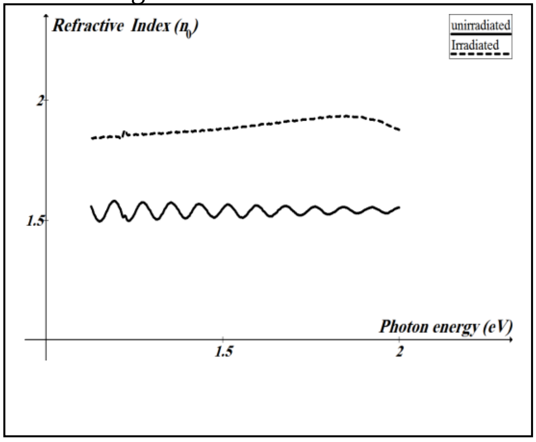


Fig.(3): Refractive index versus photon energy for irradiated and unirradiated poly (vinyl chloride-co-vinyl acetate) samples

From figure (3) show change of refractive index versus photon energy for irradiated and unirradiated film under investigation, the irradiated sample have value greater than unirradiated sample. The variation of (n_o) in investigated frequency range shows that some interactions take places between photons and electrons. (n_o) changes with variation of the wavelength of the incident light beam are due to these interactions(10).

The plot of figure (4) can be considered as an evidence for direct allowed transition. The energy gap decrease for irradiated sample. Narrowing of band gap for irradiated sample might be due to increasing the localized states as we will see later. Also, variation of optical energy gap Eg may be explained by invoking the occurrence of local cross linking, in such a way as to increase the degree of ordering in these parts.

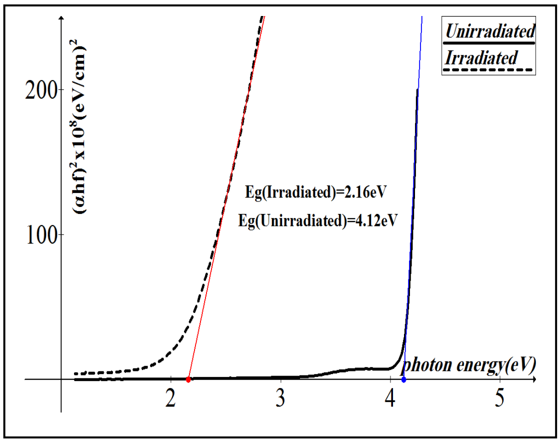
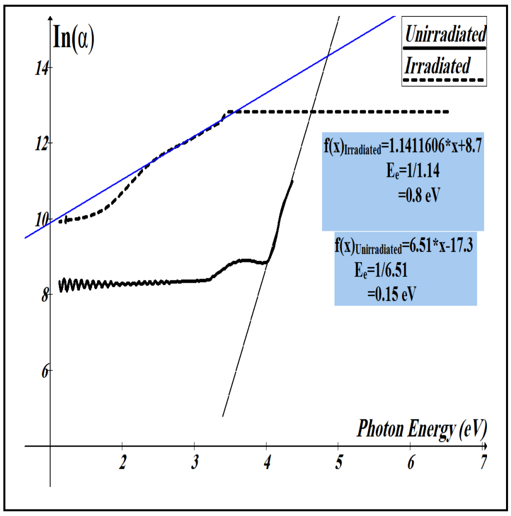


Fig.(4): Optical energy band gap of irradiated and unirradiated poly (vinyl chloride-co-vinyl acetate) samples

The absorption edge in many materials follows the Urbach rule .

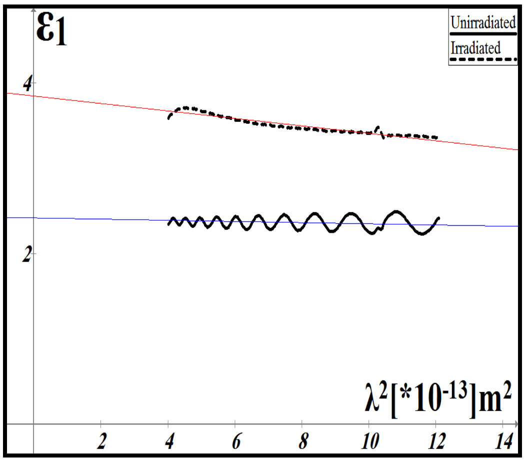
$$\alpha(f) = \alpha o \exp(\hbar f / E_e)$$

where, αo is a constant and (E_e) is the energy width of the tail of localized state in the normally forbidden band gap. E_e is often interpreted as the width of the localized states in the band gap of the material. E_e is estimated from the slopes of ln(α) vs hf plots, figure(5) represents such dependence. The energy width of the tail (E_e) could be obtained by extrapolating the linear portions of these curves.



Figure(5): Relation between lnα and photon energy

The shift of the energy gap in figure (4) to lower value for irradiated sample can be explained in terms of increasing dangling bonds, defects and the trapping of the generated carriers . This explanation can be supported by observing the increasing of band tail width as shown in figure (5), it's increased from 0.15 eV to 0.8 eV with irradiation.



Figure(6) :Calculation of carrier concentration

The carrier concentration N_{opt} can be obtained by using Drude's theory of dielectrics. The real dielectric constant ε_r, which results due to the contribution from the free carrier electric susceptibility, can be written by the following relation(11).

$$\varepsilon_r = \varepsilon_i - [\frac{e^2}{4\pi^2 c^2 \varepsilon_o}(\frac{N}{m^*})]\lambda^2$$

where ε_i is the residual dielectric constant due to the ion core , e is the electronic charge, c is the velocity of light, ε_o is the permittivity of free space ($\varepsilon_0 = 8.85 \times 10^{-12}$ C/N.m^2) and N/m* is the ratio of carrier concentration to the effective mass ($m^* = 9.10956 \times 10^{-31}$ kg). According to the free electron Drude model, ε_r should be a linear function of λ^2 (wave length) as it shown in figure (6). The values of carrier concentration N_{opt} for unirradiated and irradiated samples are N(unirra.)$=0.55*10^{25}m^{-3}$ and N(irra.)$=0.8*10^{25}m^{-3}$.

The electromagnetic will have its amplitude reduced by a factor 'e' after traversing a thickness (called the skin depth) such that:

$$\chi = \lambda / 2\pi k$$

Which may be the order of 100 to several thousand angstroms, depending on the material(12) . In long wavelength greater than absorption edge, skin depth increases with unirradiation as shown in figure (7), this might be due to decrease the probability of absorption with thickness and the amplitude of the incident photons will be reduced by a factor 'e' through the short distance within the film thickness .

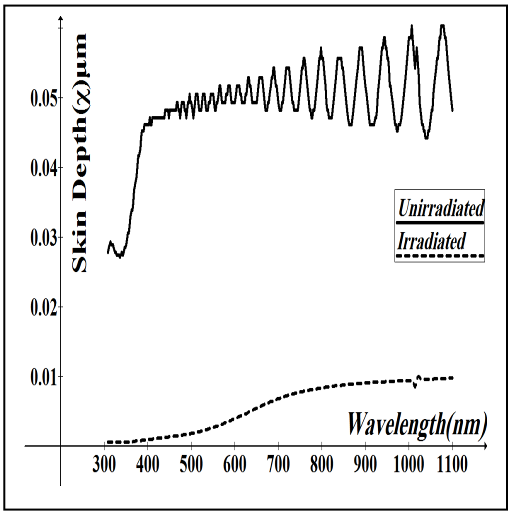
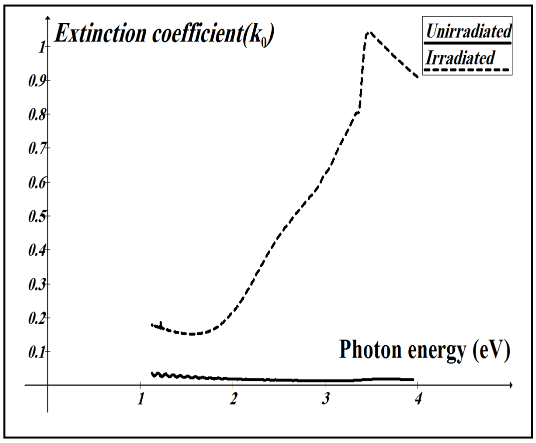


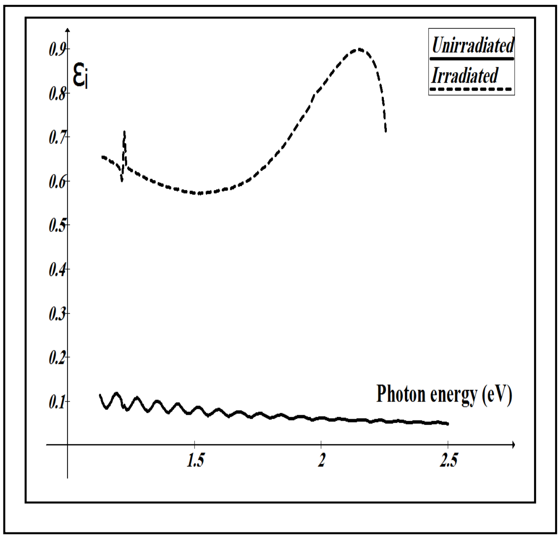
Fig. (7): Skin depth (χ) as a function of wavelength.

Extinction Coefficient (K_0) represents the imaginary part of complex refractive index and it can be defined as the amount of energy losing as a result of interaction between the light and the charge of medium(13) ; figure (8) shows the (k_0) as a function of Photon energy.

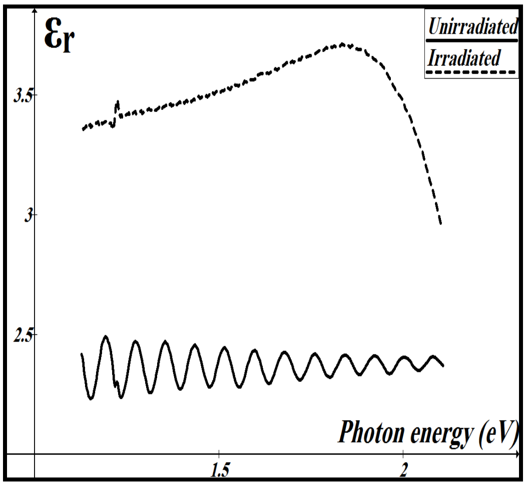


Figure(8): Extinction coefficient vs. Photon energy

The optical properties of a solid are usually described in terms of the complex dielectric function $\varepsilon = \varepsilon_r + i\,\varepsilon_i$. The real part ε_r and imaginary part ε_i of this description are both frequency-dependent quantities, which include all the desired response information. The complex dielectric constant ε_i is thought to contain much useful physical information about the material. In Figures (9) and (10) real and imaginary parts of dielectric constants increase with irradiation of sample.



Figure(9):ε_i vs.Photon energy



Figure(10): ε_r vs.Photon energy

Conclusions

The transmittance, energy gap, and skin depth decreases for irradiated poly (vinyl chloride-co-vinyl acetate) ; but on the other hand the absorption coefficient, localized states, Extinction coefficient ,carrier concentration and real part ε_r of dielectric constant increases for irradiated poly (vinyl chloride-co-vinyl acetate).

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