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Effect of TiO_2 concentration on the optical properties of polymer composite PC-PS films

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تأثير اوكسيد تيتانيوم على الخواص البصرية لاغشية مركب البوليمر بولي كاربونايت- بولي ستايرين

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الخلاصة

تمت دراسة الخصائص البصرية لأغشية مركب البوليمر بولي كاربونايت - بولي ستايرين مع نسب مختلفة لأكسيد التيتانيوم في المنطقتين المرئية و فوق البنفسجية. و قد وجد أن الامتصاص البصري ناتج عن الانتقالات المسموحة المباشرة، و ان فسح الطاقة تزداد من 3.4863 eV ل 5% من أكسيد التيتانيوم الى 3.9034 eV ل 7.5% من محتوى أكسيد التيتانيوم، في حين يقل اتساع المناطق الممتدة مع زيادة محتوى أكسيد التيتانيوم. تم أيضا حساب الثوابت البصرية الاتية: معامل الانكسار، معامل الخمود، الجزئين الحقيقي و التخيلي لثابت العزل. بينت هذه الدراسة ان ثابت العزل و معامل الانكسار يتأثران كذلك بمحتوى أكسيد التيتانيوم.

Abstract

The optical properties of polymer composite polycarbonate-polystyrene (PC-PS) films with different filling levels of Titanium oxide (TiO_2) were studied in the visible and ultraviolent wavelength regions. It was found that the optical absorption is due to direct allowed transitions, and the energy gaps increase from *3.4863 eV* for *2.5%* TiO_2 to *3.9034 eV* for *7.5%* TiO_2 filler content, while the width of the tail localized states decrease with increasing TiO_2 content. The optical constants refractive index *n*, extinction coefficient *k*, the real ϵ_r and imaginary ϵ_i parts of the dielectric constants have been also calculated. The dielectric constant and refractive index are also affected by TiO_2 content.

Key words: polymer, optical properties, filler, complex dielectric constant.

Introduction:

Polymer composites incorporating metal, semiconductor, carbon black, nano-materials, and magnetic materials have been widely used and studied as multi-function and materials with inherent polymer properties [1]. Composites of polymer are the subject of extension research in view of the technological importance which includes high density data storage, electromagnetic shielding, electronic circuitry, switch, and biomedicine sensors [1,2].

It is well known that the physical properties of polymers may be affected by filling. Certain structural, optical, mechanical, electrical and magnetic properties of the selected polymer can be controllably modified owing to the type of the filler used, its concentration and the way in which it penetrates and interacts with the chains of the polymer. Detailed studies of polymer with different levels of a certain filler allow the choice of the desired properties [3]. The measurement of the optical absorption coefficient, particularly near the fundamental absorption edge, provide a standard method for investigation of optically induced electronic transitions and provide some ideas about the band structure and energy gap in both crystalline and non-crystalline materials.

The present work is concerned with the investigation of the effect of TiO_2 filler on the optical properties of polymer composite (PC-PS) films.

Optical band gap:

Practically the optical absorption coefficient α which is a function of wavelength can be calculated from the optical absorbance spectra by using the relation [4]:

$$ln\left(\frac{I_o}{I_t}\right) = 2.303\ A = \alpha d \qquad (1)$$

where I_o and I_t are the intensities of the incident and transmitted beams respectively, A the optical absorbance, and d is the film thickness, and absorbance is defined by $A = \log\left(I_o/I_t\right)$.

The extinction coefficient K, is related to the absorption coefficient α through $K = \alpha\lambda/4\pi$, where λ is the wavelength of light.

The refractive index as a function of wavelength can be determined from the reflection coefficient data R and the extinction coefficient K using equation:

$$n = \left(\frac{4R}{(1-R)^2} - k^2\right)^{\frac{1}{2}} - \frac{(R+1)}{(R-1)} \qquad (2)$$

The absorption edge for direct and non-direct transitions can be obtained in view of the models proposed by Tauc et al [5]:

$$\alpha h v = C_o\left(h v - E_g^{opt}\right)^{\gamma} \qquad (3)$$

where C_o is a constant related to the properties of the valance and conduction bands [6], hv is the photon energy, α is the absorption coefficient, E_g^{opt} is the optical energy band gap of the material, and $\gamma = 1/2, 3/2, 2, or\ 3$ for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively [7].

A plot of $(\alpha hv)^{1/\gamma}$ versus (hv) often yields a reasonably good straight line fit to the absorption edge and the extrapolated (hv) at which $(\alpha hv)^{1/\gamma} = 0$ provides a convenient experimental benchmark for the optical band gap E_g^{opt}.

The optical absorption coefficient $\alpha(v)$ near the band edge shows an exponential dependence on photon energy (hv) and obeys an empirical relation due to Urbach [8]

$$\alpha(v) = \alpha_o \exp\left(hv/E_t\right) \qquad (4)$$

where α_o is a constant and E_t is related to width of the band tails of localized states in the forbidden band gap. It should be mentioned that this equation is applicable only in the low absorption region ($\alpha = 10^3 - 10^4\ cm^{-1}$).

The real and imaginary parts of dielectric constant (ϵ_r & ϵ_i respectively) can be calculated as follows [9]:

$$N^* = n - i\,K \qquad (5)$$

$$\epsilon^* = \epsilon_r - i\,\epsilon_i \qquad (6)$$

where N^* is the complex refractive index, and ϵ^* is the complex dielectric constant which consist of two combinations, the real part which is known as the relative permittivity and the imaginary part called the dielectric loss or dissipation factor. The complex dielectric permittivity ϵ^* as a function of wavelength can be represented found from relation $N^* = \sqrt{\epsilon^*}$,

$$(n - i\,K)^2 = \epsilon_r - i\,\epsilon_i \qquad (7)$$

$$\epsilon_r = n^2 - K^2 \qquad (8)$$

$$\epsilon_i = 2nK \qquad (9)$$

where ϵ_r is the true permittivity, describes the stored energy, and ϵ_i is the imaginary permittivity describes the dissipation energy.

Experimental detail:

The cast technique was used to prepare two types of polymer polycarbonate (PC) and polystyrene (PS) polymers supplied from Sigma-Aldrich company, the two polymer were dissolved in dicholoro methylene, each gram of polymer dissolved in *10 ml* of solvent to prepare 1:1 (PC-PS) polymer blends to obtain *5gm* of the total weight of blend, then these blends were dissolved and mixed with titanium oxide (TiO_2) for weight ratios (2.5, 5.0 and 7.5) wt%, to prepare the different filling levels of the PC-PS-TiO_2 composites. These homogeneous solutions were spread on a glass plate. The whole assembly was placed in a dust free chamber and allowed to evaporate the solvent slowly in a dry atmosphere at temperature $23^{o}C$, in this way; the film was prepared by isothermal evaporation technique. After $24\ hr$ the films was removed from the glass plate. The thickness of the films was in the range of $(250-560)\mu m$, determined using micrometer at different places in each film and an average was taken.

Results and Discussion:

The optical absorption spectra of all films were recorded at room temperature, by UV-VIS double beam spectrometer (Model: Lambda 25) in the wave length range from 190 to 1100 nm. The optical band gap of these samples was evaluated from the photon energy absorption plot.

Fig (1) shows the absorption coefficient as a function of the wavelength for PC-PS polymer with different concentration of TiO_2 filler, for low wavelengths, it is seen that in the UV region the absorption coefficient is decreases monotonically. The TiO_2 content was responsible enhance the absorbance spectrum of PC-PS films in the investigated wavelength region.

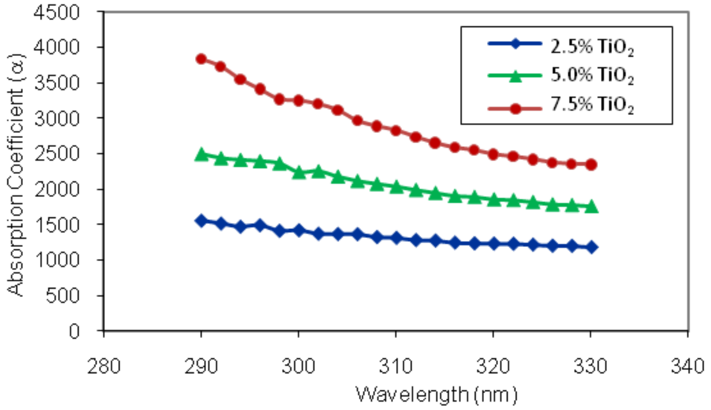
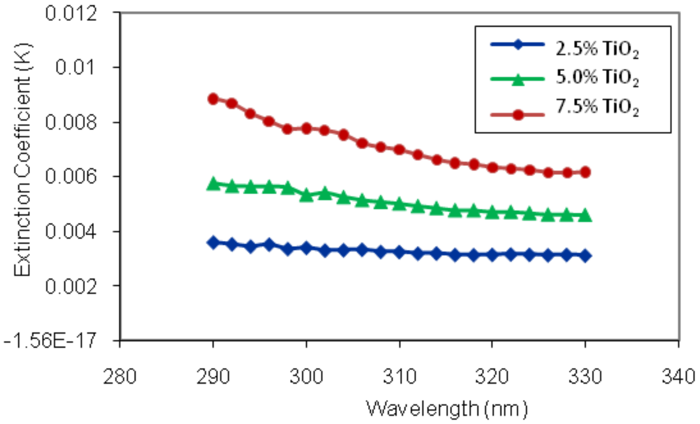
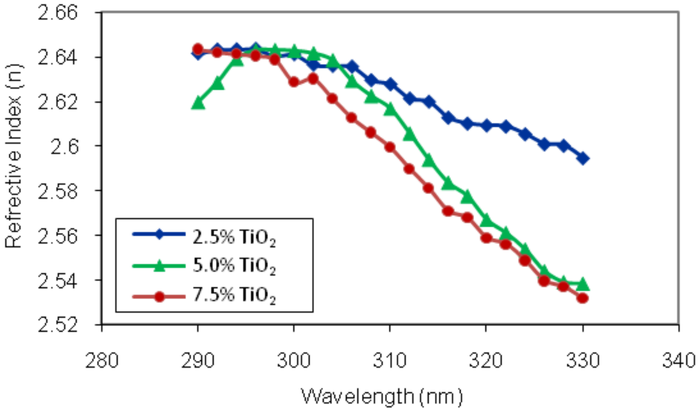


Fig (1): Optical absorption coefficient (α) as a function of wavelength for PC-PS Polymer with different TiO_2 content.

The extinction coefficient K over the exponential absorption region $(290-330)nm$ for all polymer samples is shown in Fig(2). Moreover, the refractive index values have been calculated from a combination of reflectance and absorbance measurements at normal incidence. Fig(3) shows the variation of refractive index n of all films with wavelength. It is clear from these figures, that the refractive index n, and extinction coefficient K decrease with increasing wavelength. The increase of TiO_2 content to the polymer lead to high values of extinction coefficient, and less affects in refractive index.

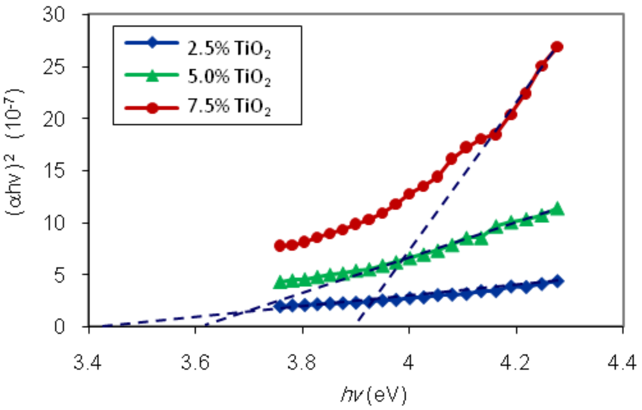


Fig(2): Extinction coefficient K as a function of wavelength for PC-PS polymer with different TiO_2 content.



Fig(3): Refractive index (n) as a function of wavelength for PC-PS Polymer with different TiO_2 content.

Fig (4) shows the dependence of $(\alpha h v)^2$ on the photon energy (hv) for direct allowed transitions. It is to be noticed that the curve is characterized by the presence of an exponentially decaying tail at low photon energy. The optical energy gap E_g^{opt} was estimated from the extrapolation of the linear portion of the graph to the photon energy axis. It is observed that the E_g^{opt} increased with increasing TiO_2 content. The plot shows straight line with some deviations from linearity at the lower value of α, which were suggested by Redfield and Afromowitz [10] as possibly due to imperfections in the material, but this region of the curve is still not fully understood.



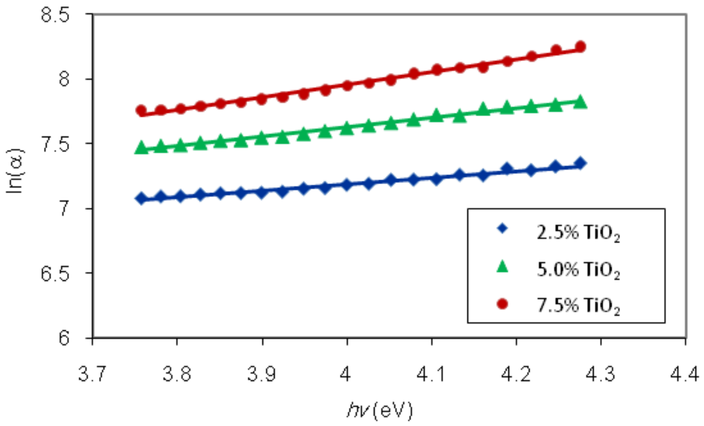
Fig(4): Relation between the $(\alpha h v)^2$ and hv for PC-PS with TiO_2 content.

The Urbach plot is presented in Fig (5) in which the natural logarithm of absorption coefficient is plotted as a function of photon energy hv. The solid line represent the best-fitted value to obtain slope. From the slope of parallel straight line, the width of localized state E_t was calculated. The values of E_t is essentially dependent of TiO_2 concentrations. The measured values of width tails localized states in the band gap for all samples are tabulated in Table (1).

Table(1): Direct allowed optical energy gap E_g^{opt} and width of tail localized state E_t for PC-PS Polymer with different TiO_2 content.

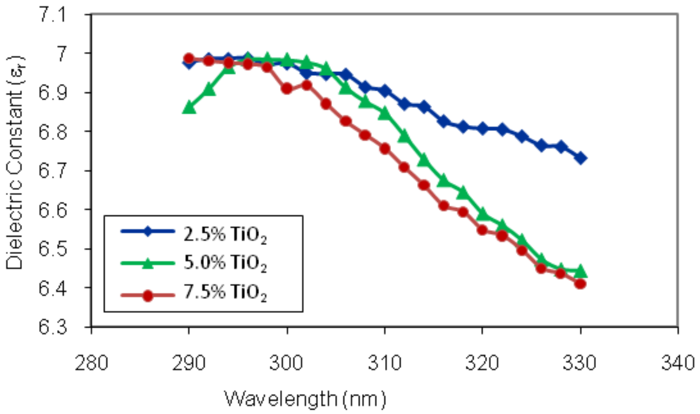
Samples	E_g^{opt} (eV)	E_t (eV)
PC-PS-2.5% TiO_2	**3.4863**	**1.9685**
PC-PS-5.0% TiO_2	**3.6266**	**1.3679**
PC-PS-7.5% TiO_2	**3.9036**	**1.0204**

Table(1) shows that the optical energy gap E_g^{opt} increases with increasing TiO_2 contents for direct allowed transition, from (*3.4863 eV)* for *2.5%* TiO_2 to (*3.9034 eV)* for *7.5%* TiO_2 filler content; on the other hand the width of the band tails of the localized state E_t shift towards lower energies from (*1.9685 eV*) for *2.5%* TiO_2 to (*1.0204 eV*) for *7.5%* TiO_2 filler content. This may be attributed to rearranged of TiO_2 fillers as an interstitial atoms in the space of the polymers, which caused the changes in the degree of crystallization, which is known to decrease the width of the localized states, thus increase the value of the optical energy gap. Such a change has been reported by others for different polymer compositions [11].

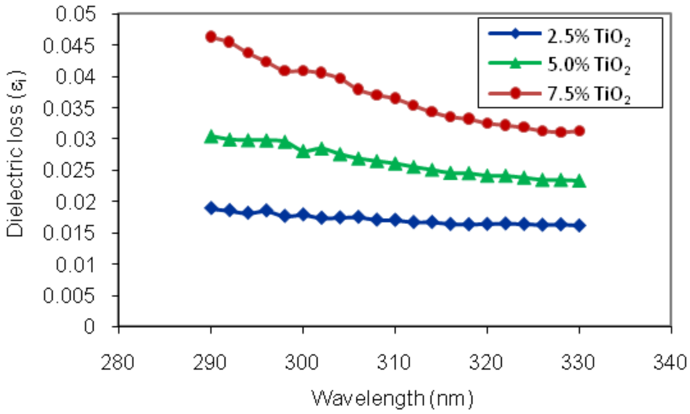


Fig(5): Relation between the $ln(\alpha)$ and hv for PC-PS with TiO_2 content.

The behavior of the real part of dielectric constant ϵ_r, and the imaginary part of dielectric constant ϵ_i against wavelength λ for all samples are displayed in Fig(6) and (7). It was observed that the dielectric permittivity decreases with increasing both wavelength and TiO_2 concentration, as well as the significant decrease of dielectric constant can be observed in the wavelength range $(300-330)nm$ as shown in Fig(6). The general trend for all composition is decreases the dielectric loss factor in the investigated wavelength region, while there are an increase in with increasing the TiO_2 concentration.



Fig(6): Relation between the real part of dielectric constant ϵ_r and wave length for PC-PS with TiO_2 content.



Fig(7): Relation between the imaginary part of dielectric constant ϵ_i and wave length for PC-PS with TiO_2 content.

Both the electric nature of the polymer and the effect of TiO_2 in the composites can be understood by correlating the dielectric constant values with the refractive index. If the sample is non-polar insulator, the dielectric constant ϵ_r for long wavelength can be expressed by Maxwell's equation $\epsilon_r = n^2$. The difference between the squared refractive index and the dielectric constant is a result of permanent dipoles and the semi-conductive character of the sample [12]. The difference between ϵ_r and n^2 for all samples is due to the permanent dipoles of PC, since the PS in non-polar plastics.

Conclusions:

The optical properties of composite polymers (PC-PS) films with difference concentrations of (TiO_2) were investigated at room temperature. The band tail width obeys Urbach's empirical relation. The optical absorption is due to direct allowed transition. Generally, the optical band gap increases with increasing TiO_2 contents. The value of refractive indices, and dielectric constant decreases by increasing the TiO_2 content in PC-PS matrix, through the investigated range.

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