Optical properties of polymer composite PS-PC thin films

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Abstract

The optical properties of polymer composite polycarbonate-polystyrene (PC-PS) films prepared by casting technique were studied in the visible and ultraviolent wavelength regions. It was found that the optical absorption is due to direct allowed transitions for pure and composite polymer films, while the energy gaps and the width of the tail localized states of the composite was lied in the mid values of the pure samples. The optical constants refractive index n, extinction coefficient k, the real ϵ_r and the imaginary ϵ_i parts of the dielectric constant have been also calculated. The dielectric constant and refractive index become more stable for composite sample.

Introduction

Polystyrene is very low cost and is extensively used where price alone dictates. Its major characteristics (Chanda, 2009) include rigidity, transparency, high refractive index, good electrical insulation characteristics, low water absorption, and ease of coloring and processing. A more serious limitation of polystyrene in many applications is its brittleness. This limitation led to investigation a mixture of polystyrenes with material having rubber properties (Kim, 2008).

It is well known that composites can be produced exhibiting enhanced properties that the constituent materials may not exhibits (Akram, 2005; Golden, 2001). For instance, from the combination of different polymer matrices one can produced polymer-matrix composites, a material important to the electronic industry in the use of capacitors (Aoi, 1997; Jo et al, 1997). The study of optical absorption and particularly the absorption edge is a useful method for the investigation of optically-induced transitions and for the provision of information about the band structure and energy gap in both crystalline and amorphous materials. 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 aim of the present work is to concern with the investigation the optical properties of pure polycarbonate and polystyrene polymer films, and its composite (PC-PS).

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 (Ballato &Foulger, 2003):

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

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 $A = log\ (I_o/I_t)$.

The extinction coefficient K, is related to the absorption coefficient α, through $K = \alpha\lambda/4\pi$, (Ballato &Foulger, 2003) where λ is the wavelength of light.

The transmission coefficient was calculated using the formula $T = 10^{(-A)}$, while the Reflection can be obtained from the values of absorbance and transmission coefficient from the equation:

$$R = 1 - (A + T) \qquad \qquad \dots(2)$$

The refractive index as a function of wavelength can be determined from the reflection coefficient data R and the extinction coefficient K using equation (Ballato &Foulger, 2003):

$$n = \left(\frac{4R}{(1-R)^2} - k^2\right)^{\frac{1}{2}} - \frac{(R+1)}{(R-1)} \qquad \qquad \dots(3)$$

The absorption edge for direct and non-direct transitions can be obtained in view of the models proposed by Tauc et al.(1970):

$$\alpha\ hv = C_o(hv - E_g^{opt})^n \qquad \qquad \dots(4)$$

where C_o is an energy - independent constant related to the properties of the valance and conduction bands (Reicha et al, 2003), hv is the photon energy, α is the absorption coefficient, E_g^{opt} is the optical energy band gap of the material, and $n = 1/2, 3/2, 2, or\ 3$ for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively (Khare & Sandeep, 2000).

A plot of $(\propto hv)^{1/n}$ versus (hv) often yields a reasonably good straight line fit to the absorption edge and the extrapolated (hv) at which $(\propto hv)^{1/n} = 0$ provides a convenient experimental benchmark for the optical band gap E_g^{opt}. The optical absorption coefficient $\propto (v)$ near the band edge shows an exponential dependence on photon energy (hv) and obeys an empirical relation due to (Urbach, 1953),

$$\propto (v) = \propto_o \exp (hv/E_t) \qquad \qquad …(5)$$

where $\propto_o$ is a constant and E_t is related to the 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 absorption region ($\propto = 10^3 - 10^4 \, cm^{-1}$).

The real and imaginary parts of dielectric constant (ϵ_r & ϵ_i respectively) can be calculated as follows (Ezema et al, 2007):

$$N^* = n - i K \qquad \qquad …(6)$$
$$\epsilon^* = \epsilon_r - i \, \epsilon_i \qquad \qquad …(7)$$

where N^* is the complex refractive index and ϵ^* is the complex dielectric constant. From the relation $N^* = \sqrt{\epsilon^*}$, there are:

$$(n - i K)^2 = \epsilon_r - i \, \epsilon_i \qquad \qquad …(8)$$
$$\epsilon_r = n^2 - K^2 \qquad \qquad …(9)$$
$$\epsilon_i = 2nK \qquad \qquad …(10)$$

Experimental detail

The cast technique was used to prepare two types of polymer PC and PS polymers supplied from Sigma-Aldrich company, the two polymer were dissolved in dicholoro methylene, one gram from each polymer was dissolved in 10 ml of solvent to prepare pure PC, pure PS, and composite PC-PS polymer blends, the solution was stirred continuously for $2h$ to obtain a homogeneous solutions, these homogeneous solutions were spread on a glass plate and allowed to evaporate the solvent slowly in air at room temperature for $24h$. The thickness of the films was in the range of $(180 - 470) \mu m$, it was determined using micrometer at different places in each film and an average was taken.

Results and Discussions

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 pure, and composite PC-PS polymers, for low wavelengths, near the UV region the absorption coefficient is decreasing exponentially for PC polymers results of reflectance R.

The reflection for the pure, and composite PC-PS polymers thin film was given in Fig (2). It was clear that the films exhibit low reflection and high transmittance, and the reflection values decrease with increasing frequency for all samples.
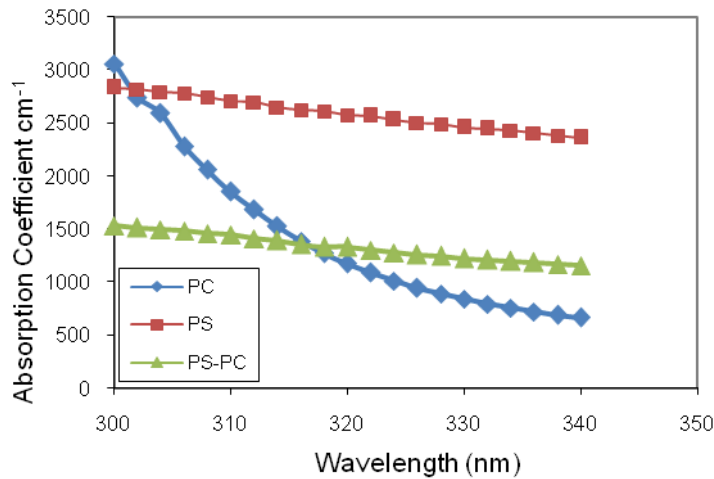

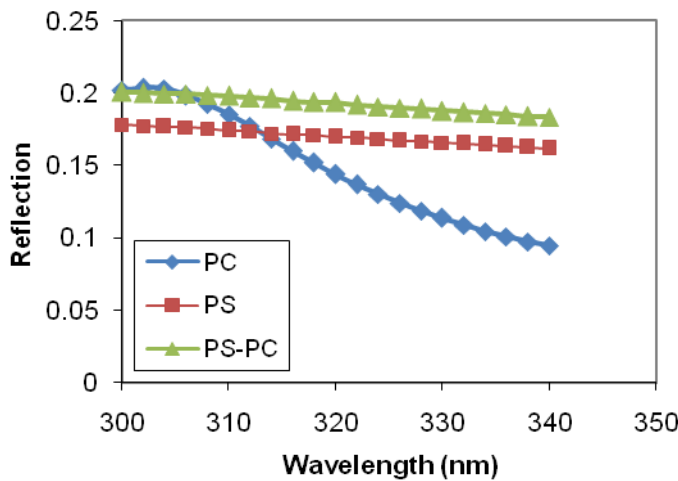**Fig (1): Optical absorption coefficient for pure and composite PC-PS films.**

Fig (2): Reflection R as a function of wavelength for pure and composite PC-PS films.

The extinction coefficient K over the absorption region $(300-340)nm$ for all polymer samples are given in Fig(3). The variations of refractive indices n of all films with photon energy are shown in Fig(4). It is clear from these figures, that the refractive indices n, and extinction coefficient

K are decrease with increase of wavelength. The change of values for extinction coefficient K and refractive indices n for composite polymer with wavelength are smaller comparing with the pure samples.
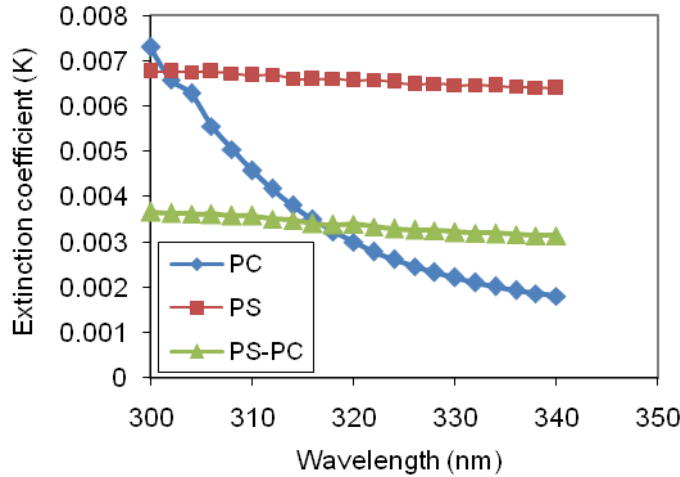

Fig (3): Extinction coefficient K as a function of wavelength for pure and composite PC-PS films.
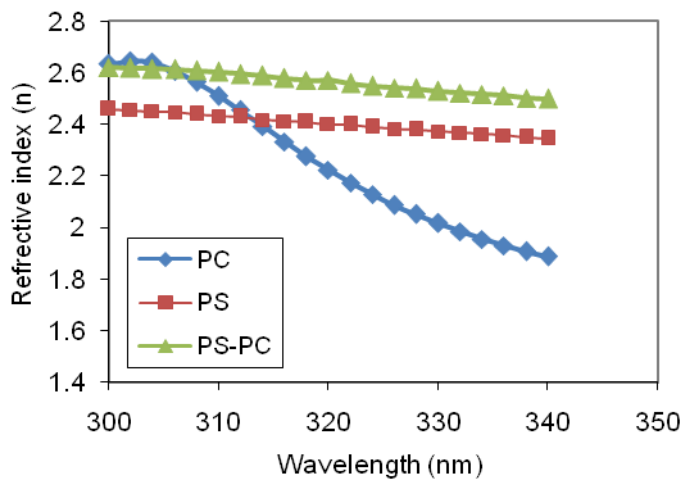

Fig (4): Refractive index as a function of wavelength for pure and composite PC-PS films.

Fig (5) shows the dependence of $(\propto h\nu)^2$ on the photon energy $(h\nu)$ for direct allowed transitions. It is to be noticed that the curve for PC 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 E_g^{opt} of composite was in the mid of the values of pure

samples. The plot show straight line with some deviations from linearity at the lower value of $\propto$, which were suggested by Redfield and Afromowitz, (1967) as possibly due to imperfections in the material, but this region of the curve is still not fully understood.

The mean vale of E_g^{opt} for direct allowed transitions are tabulated in Table (1).
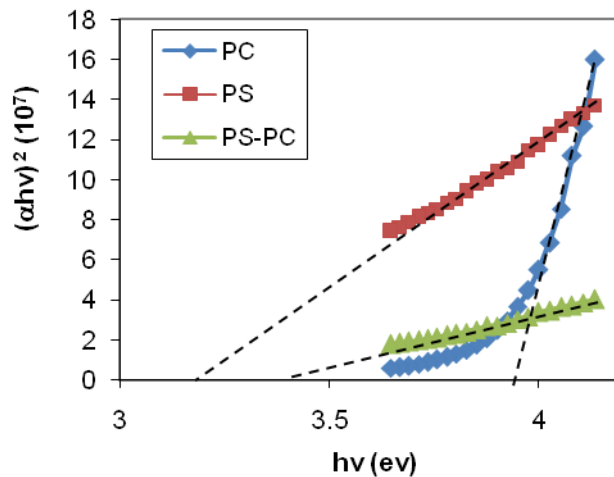

Fig (5): Relation between the $(\propto hv)^2$ and hv for pure and composite PC-PS films.

The Urbach plot is presented in Fig (6) in which the natural logarithm of absorption coefficient is plotted as a function of photon energy hv. The slop of each line yields the magnitude of $1/E_t$ where (E_t is the value of width tail localized states). The measured values of width tails localized states in the band gap for all samples are tabulated in Table (1).
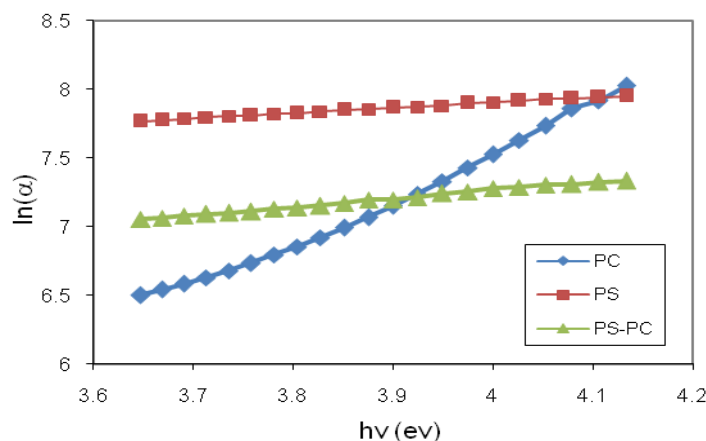

Fig (6): Relation between the $ln(\propto)$ and hv for pure and composite PC-PS films.

Table (1): Optical energy band and band tail for pure and composite PC-PS films.

	pure PC	pure PS	PC-PS composite
Direct allowed (eV)	3.9381	3.1752	3.3969
Width of band tail (eV)	0.3107	2.5974	1.6393

Table(1) shows that the optical energy gap E_g^{opt} for direct allowed transition, and the width of the band tails of the localized state stay in the mid values of pure polycarbonate and polystyrene films. Since the width of the band tail of localized state increase with degree of disorders (Edder et al, 2006), one can conclude that the polycarbonate PC have greater degree of crystallization than that of polystyrene PS films. This is in support of the theory of (Mott & Davis, 1971) which suggests that the extent of the localized state near the mobility edge increases with increase of the disorder in the amorphous structure.

Figs (7 and 8) show the real part of dielectric constants ϵ_r, and the imaginary dielectric constant ϵ_i versus the photon energy for all samples. The significant decrease of dielectric constant can be observed in the wavelength range $(300-340)nm$. Because of the small dipole polarization effect, the ϵ_r , ϵ_i for PC exhibit stronger wavelength dependence than PS and the composite PC – PS polymers.
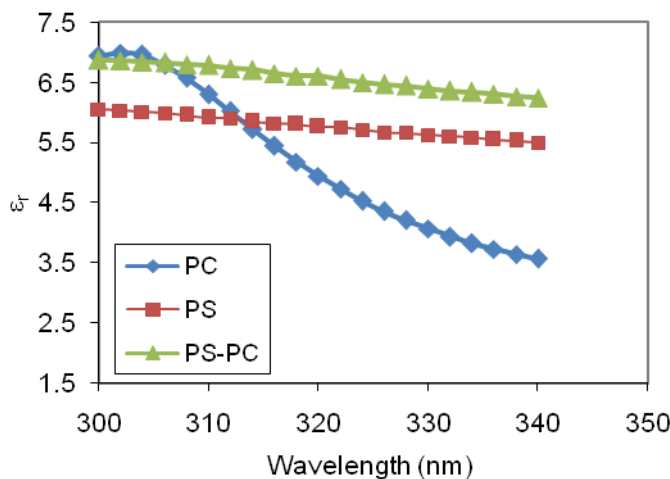

Fig (7): Relation between the real part of dielectric constant ϵ_r and wave length for pure and composite PC-PS films.
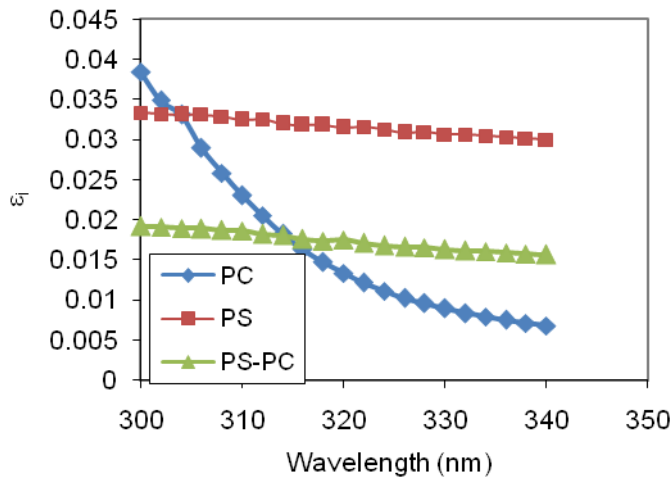
Fig (8): Relation between the imaginary part of dielectric constant ϵ_i and wave length for pure and composite PC-PS films.

Both the electric nature of the pure polymers and the effect of 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 (Netra et al, 2005). 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.

Conclusion
The optical properties of pure and composite (PC-PS) polymers films 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 and the width of the band tail of localized state of the composite lain in the mid values of pure polymer samples. The value of refractive indices and dielectric constant become more stable for composite PC-PS films, through the investigated range (300 – 340) nm.

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الخصائص البصرية للأغشية الرقيقة لمركب البوليمرPS-PC

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الخلاصة

تمت دراسة الخصائص البصرية لأغشية مركب البوليمر بوليكاربونايت-بوليستايرين (PC-PS)المحضرة بالطريقة الصب في مناطق الاطول الموجية المرئية و فوق البنفسجية. و قد وجد أن الامتصاص البصري ناتج عن الانتقالات المسموحة المباشرة لكل من ألاغشية البوليمرات النقية و المركبة، تبين ان فجوة الطاقة و اتساع المناطق الممتدة لبوليمرات المركبة يقع بين متوسط قيم النماذج النقية. تم أيضا حساب الثوابت البصرية الاتية: معامل الانكسار، معامل اكتلاشى ، الجزء الحقيقي و الجزء الخيالى لثابت العزل. بينت هذه الدراسة ان ثابت العزل و معامل الانكسار يصبحان اكثر استقرارا للبوليمرات المركبة.