Study of the Optical Constants of the PMMA/PC Blends

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Abstract

The aim of the present work is concerned with the study of the optical constants of the PMMA/PC blend at different concentrations.

The samples are casted as films from the PMMA and PC homopolymers and blend. These polymer systems are evaluated spectrophotometically. The absorption spectra of homopolymers and PMMA/PC blends at different concertation showed absorption changes in the wavelength range, which depends on the polymer type, and the concentration of the polymer blends. It was found that 50% ratio from these polymers showed higher absorption values in comparison with the homopolymers, besides, the absorption spectroscopy of the polymer blends did not always effect the similar information obtained from the spectroscopy of the homopolymers .A phenomenon was attributed to immiscibility or phase separation as associated with the blends formation. The results of the optical constant proved that 50%ratio was the best, which was attributed to the lowest energy gap (2.5 eV). Morphological investigations for the casted polymer systems were introduced.

Keywords: PMMA/PC Blend, Optical constants, Optical properties.

دراسة الثوابت البصرية لخليط بوليمري PMMA/PC

الخلاصة

ان الهدف من البحث يتعلق بدراسة الثوابت البصرية لخليط PMMA/PC بمختلف التراكيز قولبت النماذج كأفلام من البوليمرات PC, PMMA, وخليط PMMA/PC بتراكيز مختلفة. حللت النماذج البوليمرية طيفيا. أن أطياف الامتصاص للبوليمرات والخليط البوليمريPMMA /PC بمختلف التراكيز. أظهرت تغيرا في مدى الاطوال الموجية, معتمدة على نوع البوليمر وتراكيز الخليط البوليمري. وجد ان نسبة 50% من هذه البوليمرات ذات أعلى قيم لامتصاصية مقارنة بأطياف الامتصاص للبوليمرات والخلائط البوليمرية الأخرى, اضافة الى ان اطياف الامتصاص للخلائط البوليمرية لاتعكس دائما نفس المعلومات الطيفية المستحصلة من اطياف البوليمرات قبل الخلط,أعزيت هذه الظاهرة الى كون الخلائط غير قابلة للخلط او حدوث فصل الاطور. اثبت نتائج الثوابت البصرية بان النسبة 50% هي افضل النسب, وقد أعزيت الى امتلاكها اقل فجوة طاقة بالنسبة للتراكيز الاخرى (2.5 eV). وقد تم إجراء الفحوصات الخاصة بالمجهر الضوئي للنماذج البوليمرية.

Introduction

Polymer blends (PB) is a mixture of at least two polymers or copolymers (polymeric material synthesized from more than single monomer).

In (2008) Deshmukh, S. H., et al recorded the optical transmission and UV-VIS absorption spectra with wavelength of (450-1000nm) range For different compositions of polyanline doped PVC-PMMA thin films. The absorption coefficient (α),

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optical energy gap (E_{opt}), refractive index (n) and optical dielectric constant had been evaluated. The effects of doping percentage of polyanilne on these parameters had been discussed and nonlinear behaviors for all the parameters were investigated [1]. Shwaya, A., [2] prepared (Pani/PVC) blends at different concentrations by casting method. The electrical properties and the energy gap were measured. The results proved increase in absorption coefficient, refractive index, extinction coefficient, and real and imaginary parts of dielectric constants with photon energy.

AL-Rubaie. N. J. O, [3] studied the influence of both deposition condition and doping on the physical properties of the lead iodide layers for different deposition conditions and dopant types .The optical measurement data were analyzed and interpreted in terms of direct electronic transitions. Transmission spectrum of undoped and doped lead lodide layers exhibited a sharp increment start around (~520nm) and it became sharper with doping .It was observed that lead iodide had wide direct band gap (2.3eV) , the energy gap was affected by deposition conditions and doping ;it decreased as samples deposited in dark and with increased doping weight.

Ahemed, R.M, [4] prepared transparent films of (PMMA/PVAc) blend with different concentrations by using solution cast technique. FTIR transmission spectra were carried out for the samples to detect the influence of UV radiation. In addition, optical absorption measurement was carried out for the samples at room temperature across the 190-900nm wavelength region before and after exposure to UV and filtered radiation using Xenon arc lamp. The study had been also extended to include the changes in the optical parameters including the band tail width and band gap energies for the samples. Moreover, the refractive index was calculated for samples from reflection and absorption spectrum before and after exposure to UV and filtered radiation. The results showed no minimum was found by absorption in the visible wavelength, which points to the fact that all the samples are colorless. In addition, the increase in the values of refractive index after exposure to UV radiation for 24 hours could be attributed to the increasing in localized density arising from photo induced cross-linking.

The optical constants are very important because they describe the optical behavior of the materials. The absorption coefficient of the material is very strong function of photon energy and band gap energy [5].

Absorptance (A) is defined as the ratio between absorbed light intensity (I_A) by material and the incident intensity of light (I_o).

$$\mathbf{A = I_A / I_o} \qquad \text{…….. (1)}$$

Transmittance (T) is given by reference to the intensity of the rays transmitting from the film(I) to the intensity of the incident rays on it (I_o) ($T=I/ I_o$), and can be calculated by [6]:

$$\mathbf{T = \exp [-2.303A]} \qquad \text{……. (2)}$$

And Reflectance (R) can be obtained from absorption and transmission spectra in accordance with the law of conservation of energy by the relation [6]:

$$\mathbf{R + T + A = 1} \qquad \text{…… (3)}$$

Absorption coefficient (α) is defined as the ability of a material to absorb the light of a given wavelength

$$\boldsymbol{\alpha = 2.303A/t} \qquad \text{……. (4)}$$

Where A: is the absorption of the material

t: the sample thickness in cm.

The Refractive index (n), the index of refraction of a material is the ratio of the velocity of the light in vacuum to that of the specimen [7-9].

$$R= ((n-1)^2+k^2)/ ((n+1)^2+k^2) \quad \text{…. (5)}$$

When the ($k \cong 0$)

$$R= (n-1)^2/ (n+1)^2 \quad \text{……. (6)}$$

$$n= (1+R^{1/2})/ (1-R^{1/2}) \quad \text{…… (7)}$$

The extinction coefficient (k) was calculated using the following equation [10]

$$K=\alpha\lambda/4\pi \quad \text{…… (8)}$$

Dielectric constant is defined as the response of the material toward the incident electromagnetic field. The dielectric constant of compound (ε) is divided into two parts real(ε_r), and imaginary (ε_i).The real and imaginary parts of dielectric constant ($\varepsilon_r$and ε_i) can be calculated by using equations [8, 10, 11]

$$\varepsilon=\varepsilon_r - i\varepsilon_i \quad \text{……... (9)}$$

$$\varepsilon_r=n^2-k^2 \quad \text{(real part) …..... (10)}$$

$$\varepsilon_i=2nk \quad \text{(imaginary part) …… (11)}$$

Experimental part

The homopolymer polymers were dissolved in methylene chloride and handly shaked until a homogenous solution was obtained, after which solution was transferred to clean glass Petri dish of (5.5cm) in diameter placed on plate form. The dried film was then removed easily by using tweezers clamp. The best concentration for film production for casting without bubbling and can be dismounted easily from the petri dish was found to be 7%wt/vol.

The polymer systems were evaluated spectra photometrically by using UV/160/Shimadzu spectrophotometer.

Energy gap of the polymer systems (homopolymer, and binary blends) at different concentrations were plotted as a function of the weight ratio of the blends involved.

The optical constants were calculated (absorption coefficient, refractive index, extinction coefficient, and the real and imaginary parts of the dielectric constant), by using equations (4), (7), (8), (10), and (11), for samples respectively.

The prepared samples morphology was examined by using optical microscope of (Nikon-73346) with digital camera(X10).

Results & Discussion

Ultraviolet and visible spectra for polymethylmethacrylate (PMMA), and polycarbonate (PC), the figure reveals a high absorption probability below 250and 290nm respectively. For PMMA, and PC, there is sudden decrease in the absorption values shown in Fig (1). In the visible region (PMMA), and (PC) were transparent. These results are in good agreement with Osawa, Fukuda [12], and Ayash, S.A [13]. The 50%PMMA/50% PC blend showed the higher absorption values in comparison with other concentration.

The reflection spectra for homopolymer (PMMA, PC), binary blends (PMMA/PC), at different concentrations, their behavior is shown in Fig (2). It was seen that it was of the same behavior of the absorption spectra. The best reflection was for the 50% PMMA/ 50%PC of the blends in different concentration.

Fig (3) shows the spectral transmittance over range of (200-700) nm for homopolymer and binary blends at different concentrations.

There is sharp increasing state in (250 and 290nm) region in transmittance of PMMA, and PC respectively and for the 50%PMMA/50%PC blend showed the lower transmittance than other concentration, it is obvious that its behavior is opposite to that of the absorption and reflection spectra.

The energy gap (E_g) was obtained by plotting $(\alpha h\nu)^{1/r}$ versus ($h\nu$) with (r) values equal to 1/2,3/2,2,and 3.The linear portion was best fitted with (r=1/2),which indicates a transition of direct type as in Fig.(4) for homopolymer and binary blends at different concentrations.

it was found that 50% PMMA/ 50% PC (E_g=2.5 eV), which is less than the energy gap of homopolymer (PMMA=5 eV) and (PC=4.25 eV) and is the lowest for the other binary blends.

The decrease in the energy gap of 50%PMMA/50%PC blend can be explained that during polymer mixing, defects formation may occur, such as voids, which give rise to desirable localized states in the band gap of the material [14, 15].

Figs. (5) Show the energy gap values for binary blends at different concentrations. The variation is attributed to the aforementioned reasons [3, 15].

The absorption coefficient is defined as the ability of material to attenuate the light of a given wavelength per unit length [3].

The variation of (α) versus (λ) given in Figs. (6), shows a 50% PMMA/ 50% PC binary blends, the absorption edge shifts towards the longer wavelength side and becomes broader [14]. Also, it can be seen, increasing in α values in these polymer systems, is attributed to decreasing energy gap, which will be discussed. Its behavior was similar to the absorption spectra.

Fig (8) shows the variation of refractive index as a function of wavelength for the homopolymer (PMMA, PC) and Fig (9) shows the refractive index of binary blends at different concentration. The refractive index of 50%PMMA/50%PC, has the highest value in binary blends at different concentrations ,that was attributed to its reflection of the highest value Fig.(2).

Fig (10) shows the variation of extinction coefficient as a function of wavelength for homopolymer and binary blends at different concentration. The binary blend 50%PMMA/50%PC concentration has the highest value of (k), and it was displaced toward the long wavelength. This was due to its lowest energy gap (2.5eV) value.

The plots of the real part (ε_r) and imaginary part (ε_i) of homopolymer, binary blends at different concentration. The figures (12), (13) shows that the real part behaves like the refractive index, while the imaginary part behaves like the extinction coefficient The figures (14), (15). The behavior of ε_r is similar to refractive index because the smaller value of k^2 comparison of n^2, while ε_i imaginary depends on the k value, which are related to the variation of absorption coefficient. It could be concluded that 50%PMMA/50%PC blend had modified the optical properties of its homopolymer.

In Fig. (16A, B), it was no cracks, crazing, and bubbles in its optical micrographs of homopolymers. It can be seen from Fig (16C) 80% PMMA/20%PC, the continuous matrix was PMMA phase, where the PC was dispersed phase as round particle matrix. As PC content of blend was increased to 50%, the

optical micrographs reveal the formation of an interpenetrating network or co-continuous two-phase structure Fig (16D) [15].

Fig (16E) with increase in PC content, the dispersed particles can be assigned to a PMMA phase and PC is the continuous matrix (phase inversion appears) to occur. These results were in good agreement with Tjong, S. C et al [15].

General Conclusions

1- 50%PMMA/50% PC binary blend showed the best optical properties.
2- The energy gap (E_g) which indicates a transition of direct type.

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Table (1) Weight ratios (%) and thickness of polymer blends.

Polymer blend	Thickness (mm)
PMMA	0.1
PC	0.09
PMMA/20%%80	0.15
%PMMA/50%PC50	0.1
PMMA/80%PC20%	0.15

Table (2) Represents the parameters of optical properties of polymer system involved.

Polymer. system	E_g(ev)	λ_{cut}(nm)	n	K×10^{-5}	ε_r	ε_i×10^{-5}	α (cm^{-1})
PMMA%	5	248	1.8	0.196	3.29	0.71	0.98
PC%	4.25	292	1.6	4.2	3.19	1.5	1.8
80%PMMA/20%PC	4.35	285	2.3	0.55	5.2	3.3	3.15
*50%PMMA/50%PC	2.5	496	2.6	4.6	6.78	2.44	11.8
20%PMMA/80%PC	4.28	290	2.5	1.8	6.3	8.8	7.7

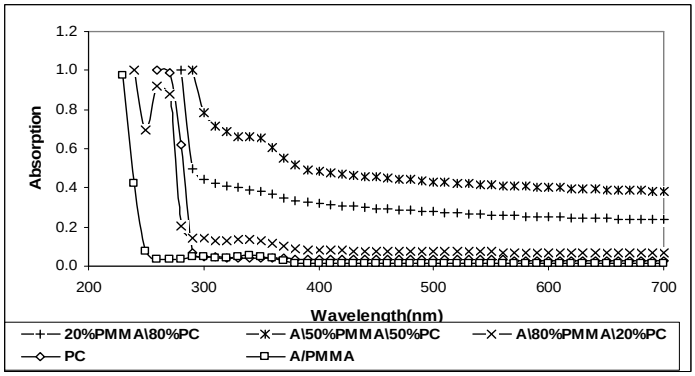


Figure (1) UV/Visible absorption spectroscopy of PMMA/PC blends

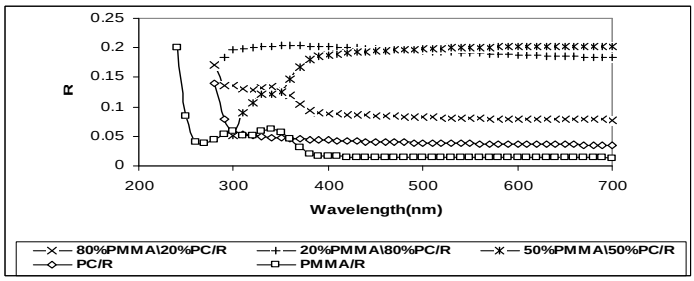


Figure (2) Optical reflection spectra of PMMA/PC blends

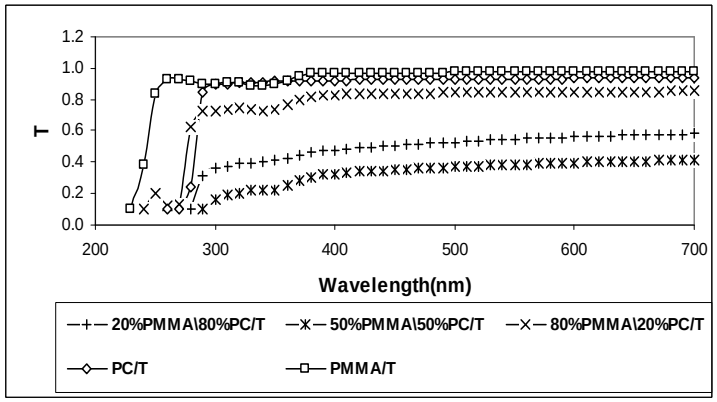


Figure (3) Optical transmittance spectra of PMMA/PC blends

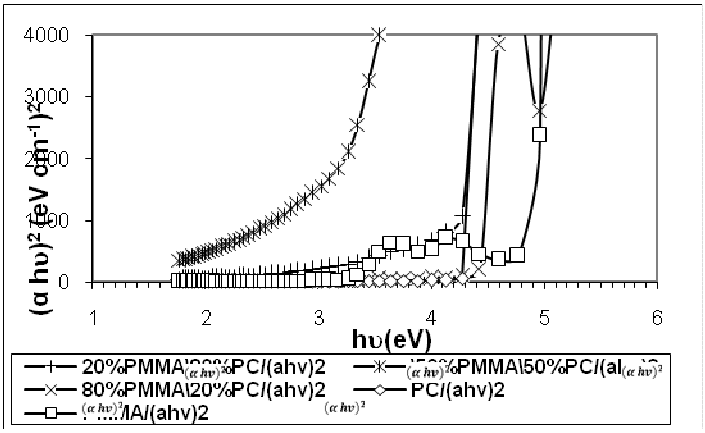


Figure (4) (αhυ) ^{2} versus (hυ) of PMMA/PC blends

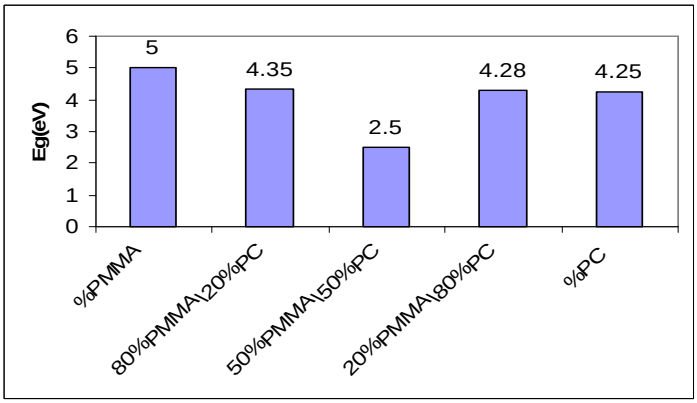


Figure (5) Energy gap values of PMMA/PC blends

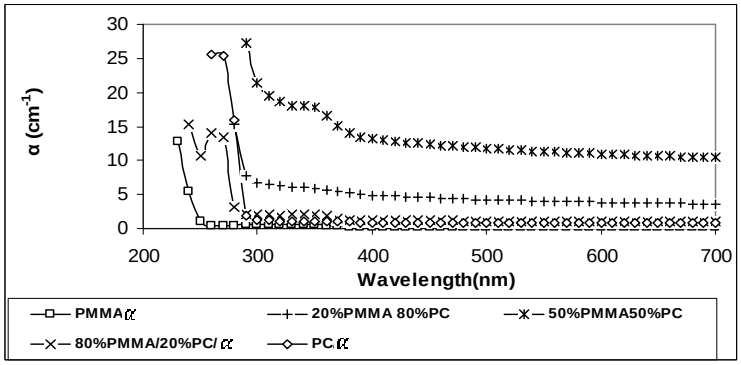


Figure (6) Absorption coefficient versus wavelength of PMMA/ PC blends

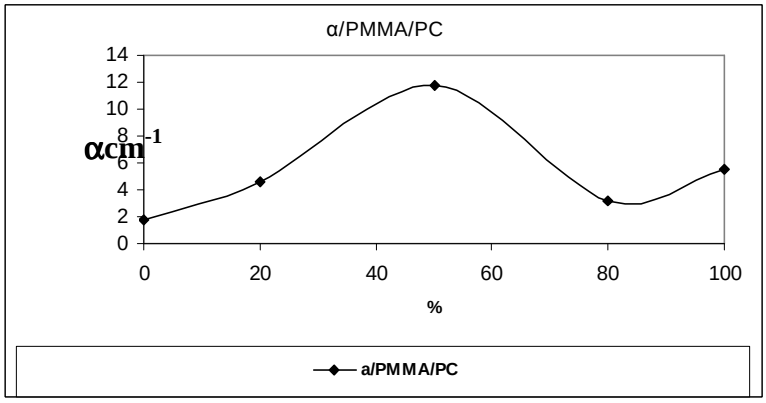


Figure (7) The absorption coefficient versus concentration ratio for binary blends (at $\lambda_{cut\ off}$).

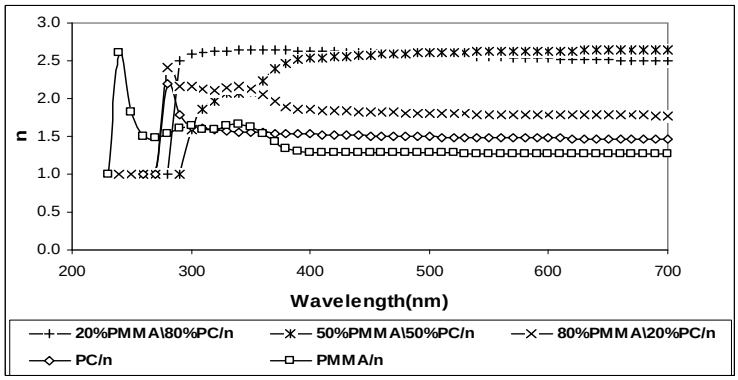


Figure (8) Variation of the refractive index versus wavelength of PMMA blends.

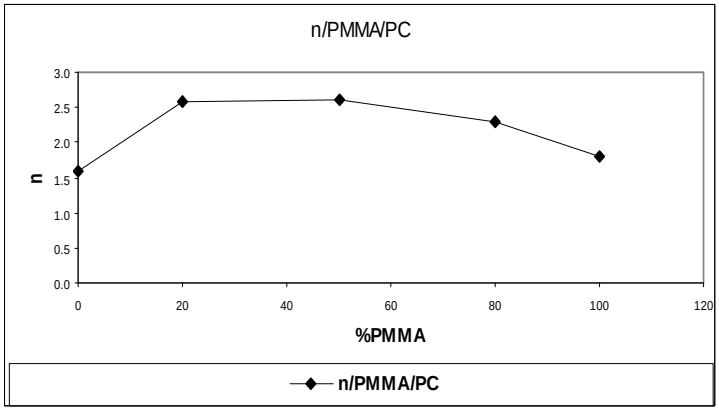


Figure (9) Variation of the refractive index versus the concentration ratio for the binary blends (at $\lambda_{cut\ off}$).

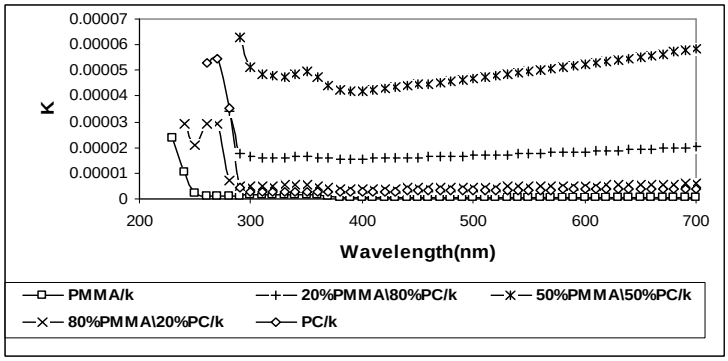


Figure (10) Variation of extinction coefficient as a function to the wavelength of PMMA blends.

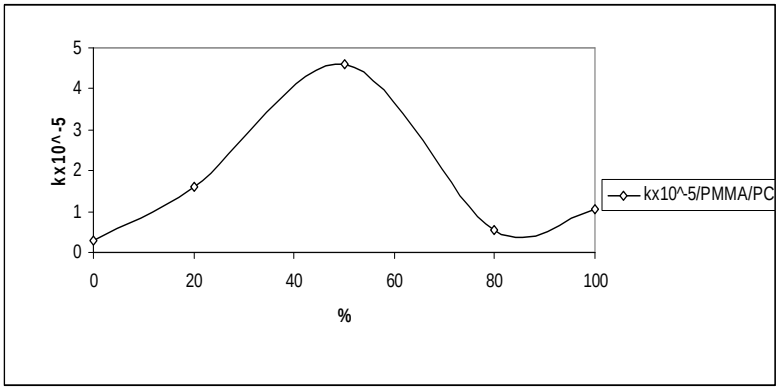


Figure (11) Variation of extinction coefficient versus to the concentration ratio of PMMA/PC

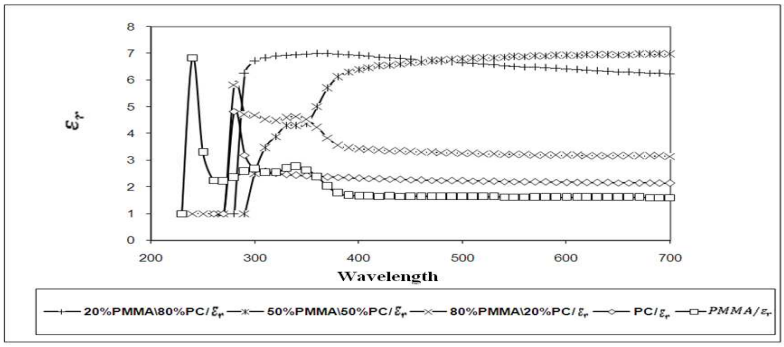


Figure (12) Variation of the real part of the dielectric constant as a function to the wavelength PMMA/PC.

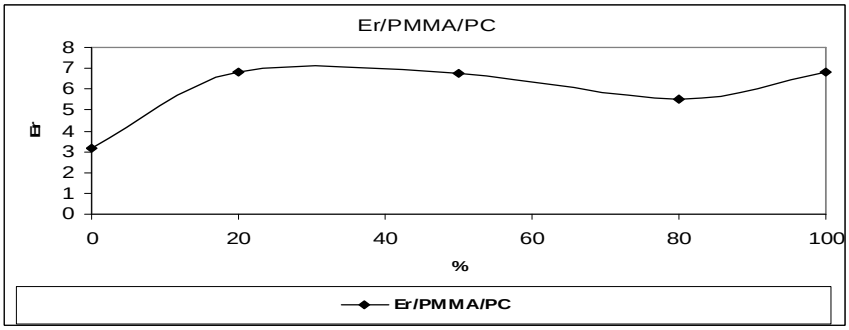


Figure (13) Variation of the real part of the dielectric constant versus to the concentration ratio binary blends.

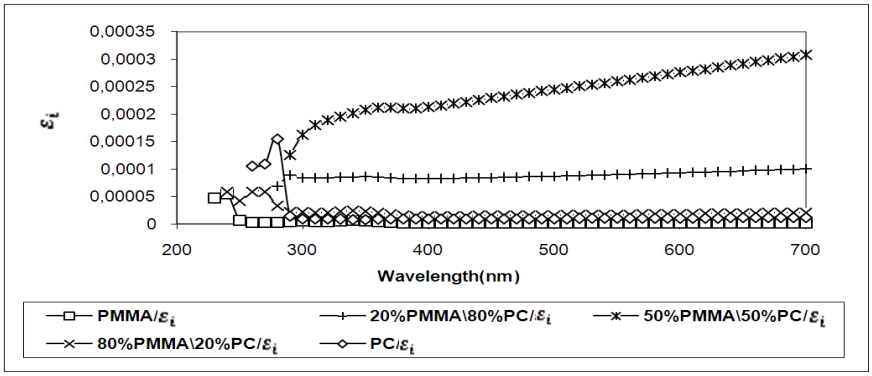


Figure (14) Variation of the imaginary part of the dielectric constant versus the wavelength of PMMA/PC binary blends.

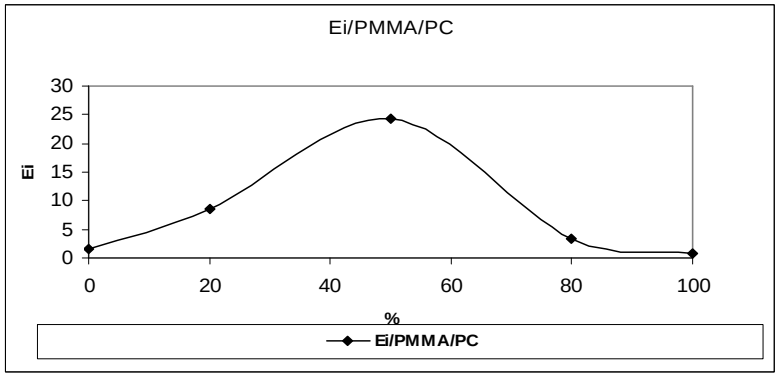
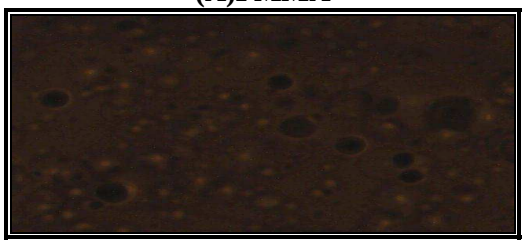
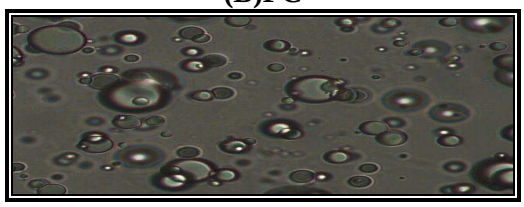


Figure (15) Variation of imaginary part versus concentration ratio of PMMA/PC.

(A)PMMA



(B)PC



(C) 80%PMMA/20%PC

(D) 50%PMMA\50%PC

(E) 20%PMMA/80%PC

Figure (16) Optical micrographs of PMMA/PC; show the immiscibility or phase separations at different concentration(X10).