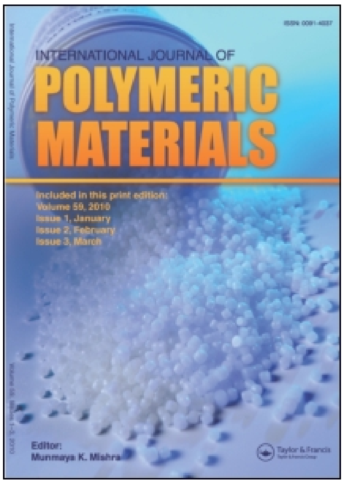

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Study on Different Solution-Cast Films of PMMA and PVAc

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Transparent films of PMMA (poly methyl methacrylate) and PVAc (polyvinyl acetate), previously dissolved in chloroform, toluene and tetrahydrofuran (THF), were prepared by using solution-cast technique. FT-IR transmission spectra were obtained from the samples. Also, different concentrations of PMMA/PVAc blend, dissolved in chloroform, were prepared by the same method. From absorption, transmission and specular reflection spectra, the absorption coefficient (α) and refractive index (n) have been calculated at room temperature and also after heating. The values of the optical band gap (E_g) have been obtained from the direct allowed transitions in k-space. In addition, the values of width of the tails of localized states in the band gap (E_u) were evaluated from Urbach edges.

Keywords: absorption spectra, FTIR, PMMA, PVAc, refractive index

INTRODUCTION

To satisfy the growing needs of new materials with specific properties, chemical modifications of conventional polymers have been proposed [1–3]. On the other hand, the mixture of two or more polymers, forming a polymer blend, continues to be an economical method to obtain new polymeric material. A polymer blend may be obtained by several methods. Among them, melt mixing, co-precipitation and casting are considered the more common [4]. There are many techniques to investigate the blend miscibility such as electron microscopy [5], spectroscopy [6], thermal analysis [7] and the method of preparation [4].

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Much research has been conducted about polymer blends composed of PMMA and PVAc. Crispim et al. [4] investigated the influence of solvent and temperature on the miscibility of PMMA/PVAc blends.

In the present study, a trial was carried out to prepare transparent films of PMMA and PVAc from different solvents by casting method. Furthermore, the change in the optical absorption and the optical parameters has been determined for different concentrations of PMMA/PVAc blends before and after heating. In addition, the refractive index (n) has been calculated for the samples.

EXPERIMENTAL

Materials

Both PMMA (poly methyl methacrylate) and PVAc (poly vinyl acetate) were obtained from (Sigma-Aldrich) and were reported to have molecular weights of 996,000 and 167,000 $g \cdot mol^{-1}$, respectively. Good solvents for both PMMA and PVAc with high purity were used in this study, such as chloroform (HPLC), toluene (Riedel-de Haën) and THF (Sigma-Aldrich).

Preparation of the Samples

Transparent films (thickness 30–40 μm) of PMMA and PVAc were prepared by using the solution-cast technique. PMMA and PVAc had been dissolved in chloroform, toluene and THF and were left at 35–40°C for 24 h in an oven. The homogeneous polymer solutions were then cast onto glass dishes and were left in an oven at 35–40°C for 48 h. After drying, the samples were removed and then cut as desired. Also, different concentrations of PMMA/PVAc blends were dissolved in chloroform and prepared by the same casting method. The prepared PMMA/PVAc blends were (0/100, 25/75, 50/50, 75/25, 100/0) by weight.

Absorption Spectra

The UV-visible absorption spectra were recorded using a Perkin-Elmer Lambda 4B spectrophotometer (190–900) nm.

Reflection Measurements

Specular reflection spectra were recorded with a UV-Vis-NIR spectrometer (UV-3101 PC) Shimadzu (200–600) nm.

IR Analysis

FTIR Spectra were obtained with a Fourier Transform Infrared Spectrometer (FT/IR – 460 plus) in the wave number range of 400–4000 cm^{-1}.

RESULTS AND DISCUSSION

Characterization of PMMA and PVAc

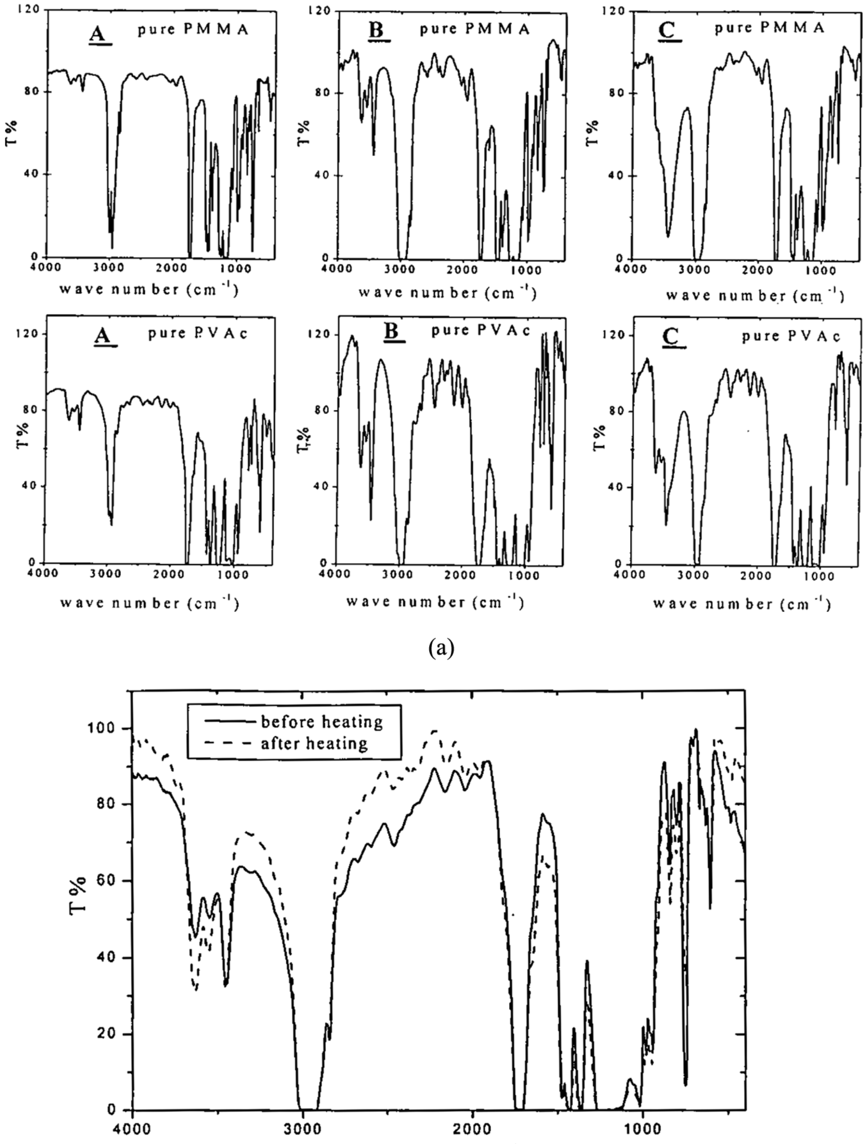
Infrared (IR) spectroscopy has been widely used in polymer studies for the assignment of molecular structure and for monitoring changes in the arrangements of chemical bonds [8]. Figure (1a) shows the IR transmission spectra of transparent films of PMMA and PVAc which had been dissolved in chloroform, toluene and THF and were prepared by casting method. In addition, the wave numbers corresponding to characteristic transmission peaks of the samples have been summarized in Table 1. The appearance of the bands of C−Cl, olefins and cyclic and alkyl ethers, characterizing chloroform, toluene and THF, respectively, indicates the presence of solvent molecules. Moreover, the band of the methoxy moiety (O−CH3), corresponding to PMMA, and also the wave numbers corresponding to characteristic transmission peaks of the PVAc acetate group have been affected by the type of the solvent. Figure (1b) shows the IR spectra of 50/50 PMMA/PVAc blend, from chloroform solution before and after heating at 70°C for 24 h. Table 1 shows that the blend of 50/50 PMMA/PVAc included the functional groups of its homopolymers. The transmission peak of the acetate group in PVAc increased after heating more than methoxy group of the PMMA due to the degradation of PVAc.

Optical Absorption Spectroscopy

The study of the optical absorption spectra is one of the most productive methods in developing an understanding of the structure and energy gap of amorphous nonmetallic materials. The absorption coefficient (α) has been estimated for all samples from the following expression [9]:

$$\alpha = 2.303\ \log\,(I_i/I_t,)/d = 2.303\ A/d \tag{1}$$

where I_i and I_t are the intensity of the incident and transmitted light, A is the absorbance, and d is the film thickness. Figure 2 shows the absorption coefficient of PMMA and PVAc dissolved in different solvents which illustrates that the intensity of absorption peaks is

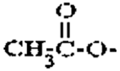
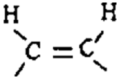


(a)

(b)

FIGURE 1 (a) IR spectra of PMMA AND PVAc dissolved in (A) chloroform, (B) toluene and (C) THF; (b) IR spectra of 50/50 PMMA/PVAc dissolved in chloroform before and after heating at 70°C for 24 h.

TABLE 1 Characteristic Infrared Peaks in Spectra of Pure PMMA and Pure PVAc from Different Solvents and also 50/50 PMMA/PVAc Dissolved in Chloroform before and after Heating

The samples	O–CH$_3$	C–H(CH$_2$–, CH$_3$–)	C=O stretching (ester)	Acetates  $CH_3-\overset{O}{\overset{\|}{C}}-O-$	Olefins 	Cyclic ethers C–O–C sym. Stretch	Alkyl ethers –CH$_2$ – O–CH$_2$–	C–Cl
PMMA in toluene	2843.0	2950.1	1729.9	–	697.1	–	–	–
PMMA in THF	2844.5	2950.0	1728.4	–	–	1242.9	1068.4, 1151.3	–
PMMA in chloroform	2841.6	2950.6	1718.3	–	–	–	–	752.6
PVAc in toluene	–	2929.3	1730.8	1370.7	696.7	–	–	–
PVAc in THF	–	2923.8	1730.3	1371.6	–	–	–	–
PVAc in chloroform	–	2927.4	1726.9	1370.7	–	–	–	757.4
50/50 PMMA/PVAc blend in chloroform	2844.5	2951.0	1747.2	1372.6	–	–	–	754.9
50/50 PMMA/PVAc blend after heating	2845.5	2951.0	1743.8	1373.1	–	–	–	752.6

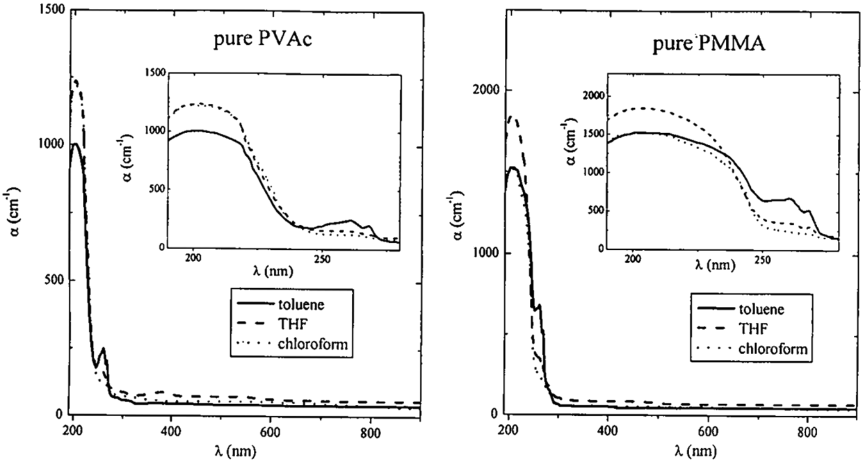


FIGURE 2 Absorption spectra of pure PMMA and pure PVAc from toluene, THF and chloroform.

affected by the type of the solvent. Also, there is an absorption band at about 260 and 268 nm for the films of PMMA and PVAc previously dissolved in toluene, which could be attributed to the carbonyl group in the polymer macromolecule.

Interband Transitions

When a quantum of radiation is absorbed by a material, the absorption coefficient α (whose calculated values lie in the range $1 \leq \alpha \leq 10^{-4}$ cm^{-1}), as a function of photon energy for simple parabolic band can be expressed by the Davis and Mott formula [10]

$$\alpha E = B (E - E_g)^r \tag{2}$$

where B is a constant, E_g is the optical band gap of the specimen, E is the photon energy and r is an index having the values of 2, 3, 1/2 and 3/2, depending on the nature of electronic transition responsible for the absorption. Figure 3 illustrates the dependence $(\alpha E)^2$ on the photon energy E(eV) for the 50/50 PMMA/PVAc blend before and after heating at 70°C for 24 h, showing a linear behavior that can be considered as evidence of a direct transition (i.e., for r = ½) [11]. The optical gap was estimated from the intercept on the energy axis of the linear fit of the large energy data of the plot [12].

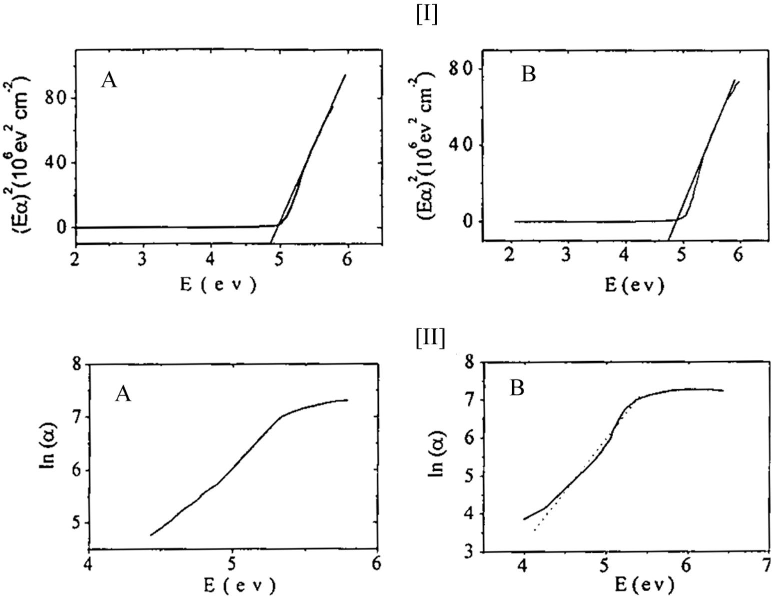


FIGURE 3 (I) The dependence of $(\alpha E)^2$ on photon energy E (eV) and (II) The dependence of (ln α) on photon energy E (eV) for 50/50 PMMA/PVAc blend (A) before and (B) after heating at 70°C for 24 h.

The absorption spectra clarify an extending tail for lower photon energies below the band edge, which can be described by Eq. 3 [13]

$$\alpha = \alpha_0 \exp(E/E_u) \tag{3}$$

where E_u is the energy of Urbach, corresponding to the width of the band tails of localized states in the band gap. Table 2 has summarized the values of optical parameters including E_g and E_u for different

TABLE 2 The Values of Band Tail Width (E_u) and Energy Gap E_g (eV) for the Samples Blend after Heating at 70°C for 24 h

	Before heating		After heating		
Concentration of PMMA/PVAc	E_u	E_g	E_u	E_g	Percentage of decrease of E_g
(0/100)	0.24	5.28	0.29	5.09	*3.59*
(25/75)	0.28	4.92	0.29	4.80	*2.44*
(50/50)	0.38	4.85	0.37	4.74	*2.27*
(75/25)	0.39	4.67	0.40	4.59	*1.71*

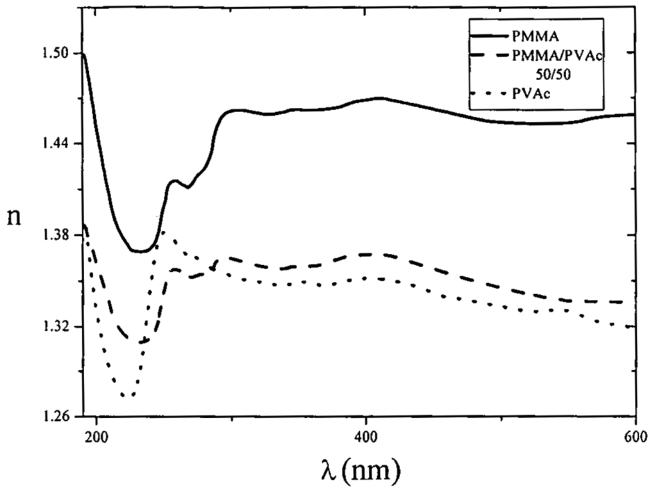


FIGURE 4 Spectral distribution of refractive index (n) for pure PMMA, 50/50 PMMA/PVAc blend and pure PVAc before heating.

concentrations of PMMA/PVAc blend before and after heating at 70°C for 24 h. It can be deduced that by increasing the concentration of PMMA in the blend, the values of E_g decreased and the values of E_u increased. The increase of E_u values by increasing the concentration of PMMA in PMMA/PVAc blends can be attributed to the effect of

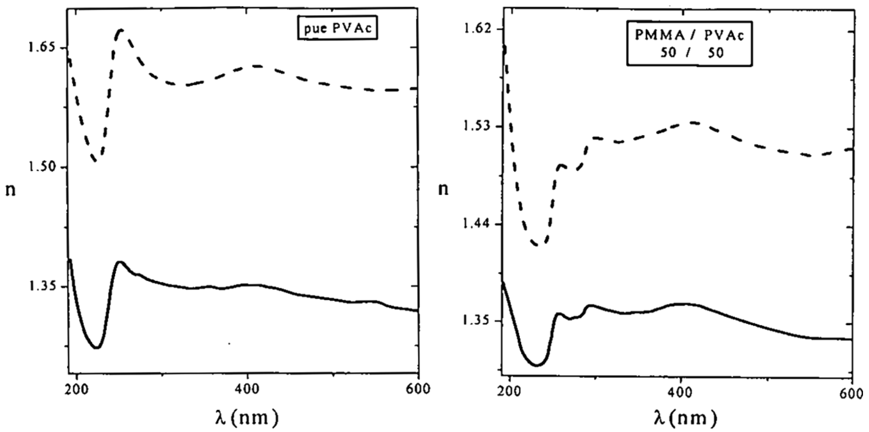


FIGURE 5 Spectral distribution of refractive index (n) for pure PVAc and 50/50 PMMA/PVAc blend before and after heating at 70°C for 24 h.

internal potential fluctuation associated with structural disorder [14]. Moreover, the percentage of decrease of PVAc after heating at 70°C for 24 h has been improved by increasing the concentration of PMMA in the blends.

Optical Constants

The absorption coefficient (α) can also be related to the optical transmission (T) and reflection (R) as follows [15]:

$$\alpha(\omega) = \frac{1}{x}\log\left\{\frac{(1-R)^2}{2T} + \frac{(1-R)^2}{\sqrt{(2T)^2 + R^2}}\right\} \tag{4}$$

And the refractive index can be obtained from [15]:

$$n = \left\{\left[\frac{4R}{(R-1)^2} - k^2\right]^{1/2} - \frac{R+1}{R-1}\right\} \tag{5}$$

where k is the extinction coefficient which is related to the absorption coefficient and the wavelength as [16]:

$$\alpha = 4\pi \mathrm{k}/\lambda \tag{6}$$

where λ is the free space wavelength of light.

The measurements of specular reflection and transmission were used to calculate the optical constants (n, k) by the three previous equations. Figure 4 illustrates the refractive index for the blend of PMMA/PVAc and its homopolymer before heating from which it can be observed that 50/50 PMMA/PVAc blend has improved the refractive index of PVAc. Figure 5 shows the spectral distribution of refractive index (n) for pure PVAc and 50/50 PMMA/PVAc blend before and after heating at 70°C for 24 h. The increasing values of the refractive index after heating could be attributed to the degradation of PVAc and an increased local density.

CONCLUSIONS

Transparent films of PMMA and PVAc previously dissolved in different solvents, were prepared by casting method. Their absorption peaks depended on the type of the solvent. Moreover, FTIR measurements have shown that the molecules of the solvents were retained in the polymer films and that the influence of this residual solvent differs according to the nature of the solvent. In addition, different concentrations of

PMMA/PVAc blend were dissolved in chloroform and films prepared by the same method. An improvement in the percentage of decrease of E_g values for PVAc after heating at 70°C for 24 h was observed as well as an increase in the values of E_u. Increasing the concentration of PMMA lowered the values of E_g in the blends. On the other hand, 50/50 PMMA/PVAc blend has elevated the refractive index of PVAc.

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