Research Article

Optical Study on Poly(methyl methacrylate)/Poly(vinyl acetate) Blends

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Transparent films of poly(methyl methacrylate)/poly(vinyl acetate) blend with different concentrations were prepared by using solution-cast technique. FT-IR transmission spectra were carried for the samples to detect the influence of UV radiation. In addition, optical absorption measurements were carried out for the samples at room temperature across the 190–900 nm wavelength regions before and after exposure to UV and filtered radiation using xenon arc lamp. The study has 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 the samples from specular reflection and absorption spectrum before and after exposure to UV and filtered radiation.

1. Introduction

The popular and economic method of polymer modification is blending two or more components with different properties [1]. Polymer blending is an attractive route for producing new polymeric materials with tailored properties without having to synthesize totally new materials. Other advantages for polymer blending are versatility and simplicity [2]. Poly(methyl methacrylate) is one of the best organic optical materials and has been widely used to make a variety of optical devices, such as optical lenses. It is known that its refractive index changes upon UV irradiation, either in the pure [3, 4] or doped state [5], which provides a means to fabricate structures, such as gratings or waveguides. On the other hand, poly(vinyl acetate) had the ability to improve poly(vinyl chloride) photodegradation, photocross linking and photo-oxidation by making a blend of them [1]. Also,Kaminska et al. [6] studied the thermal and photochemical stability of poly(methyl methacrylate)/poly (vinyl acetate) blends and revealed that poly(vinyl acetate) acts as a stabilizer with respect to thermal and photochemical degradation when the processes take place in air. Indeed, poly(methyl methacrylate) and poly(vinyl acetate) form an important pair of polymers.

In the present study, a trail will be carried out to produce the best product of poly(methyl methacrylate)/poly(vinyl acetate) blend and also to overcome the defects of the individual homopolymers. Furthermore, the change in the optical absorption and the optical parameters will be determined for the samples after exposure to UV (unfiltered light) and filtered radiation. In addition, the refractive index (n) will be calculated for the samples.

2. Materials and Methods

2.1. Materials. Both PMMA (poly methyl methacrylate) and PVAc (poly vinyl acetate) used in this study were obtained from Sigma, Aldrich (Germany) and were reported to have molecular weights of 996000 and 167000 g.mol^{-1}, respectively. Chloroform has purity 99.8% (HPLC) and was used as a common solvent for both PMMA and PVAc.

2.2. Preparation of the Samples. Films (thickness 30–40 μm) of (PMMA/PVAc) blends were prepared by using solution-cast technique. Pure PMMA and PVAc were dissolved separately in chloroform for 48 hours at room temperature. The solutions of the two homopolymers were then mixed
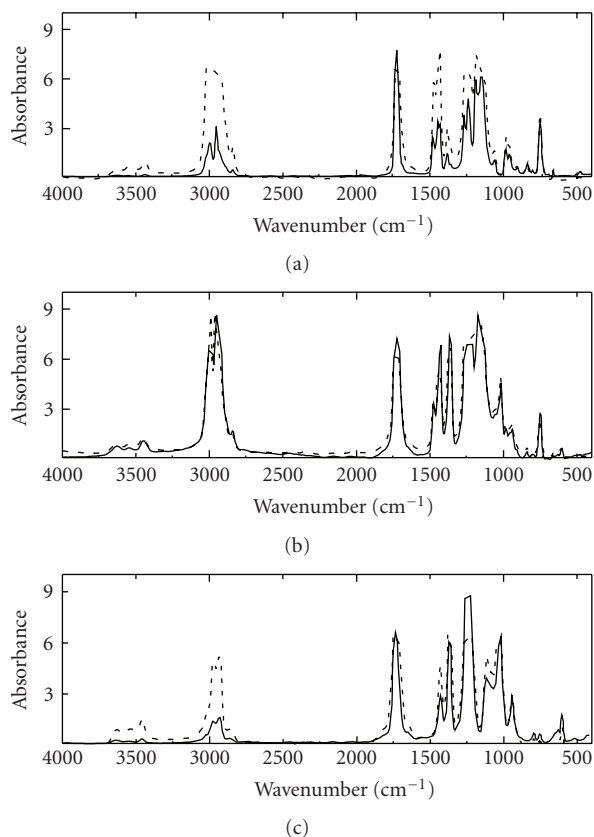
(a)

(b)

(c)

FIGURE 1: FT-IR spectra of (a) pure PMMA, (b) a blend of (50/50 PMMA/PVAc), and (c) pure PVAc before (——) and after exposure to UV radiation (- - -) for 24 hours.

FIGURE 2: Absorption spectra of different concentrations of PMMA/PVAc blend before exposure to radiation.

with different concentrations and subsequently cast onto glass dishes and left in an oven at 40°C for 24 hours to form transparent films. After curing, the samples of the pure PMMA and PVAc and their blends were removed and then cut as desired. The concentrations of the prepared (PMMA/PVAc) blends are (0/100, 25/75, 50/50, 75/25, 100/0) by weight.

2.3. Absorption Spectra. The absorption spectra were recorded using Perkin Elmer Lambda 4B spectrophotometer (190–900) nm.

2.4. UV Radiation. The films were exposed to UV and filtered radiation from a 200 W xenon arc lamp.

2.5. Reflection Measurements. Specular reflection spectra were recorded with UV-Vis-NIR spectrometer (UV-3101 PC) shimadzu (200–600) nm.

2.6. FT-IR Analysis. FT-IR spectra were measured with a Fourier Transform Infrared Spectrometer (FT/IR – 460 plus) in the wave number range (400–4000 cm^{-1}).

3. Results and Discussion

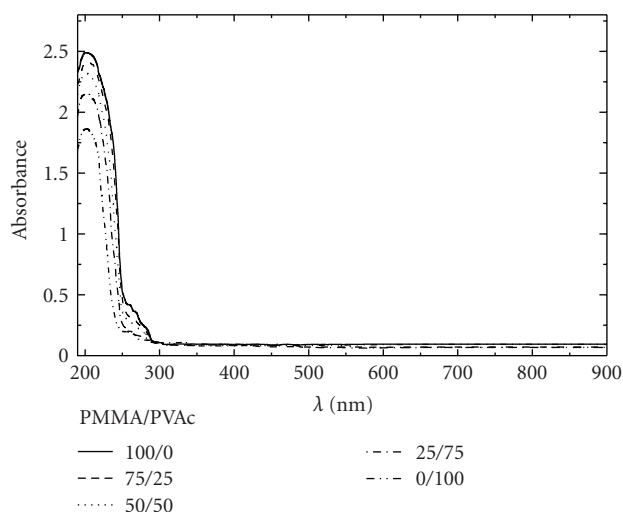*3.1. Characterization of PMMA/PVAc Blend.* FT-IR spectroscopy has long been recognized as a powerful tool for elucidation of structural information. The position, intensity, and shape of vibrational bands are useful in clarifying conformational and environmental changes of polymers at the molecular level [7]. FT-IR transmission spectra as shown in Figure 1 have been studied to PMMA, PVAc, and their (50/50 PMMA/PVAc) blend before and after exposure to UV radiation for 24 hours.

It can be observed that a band at 1435.3 cm^{-1} corresponds to asymmetrical bending vibration (CH_3) of methyl group of PMMA. Besides, the vibrational bands observed at 2855 and 1370.7 cm^{-1} are ascribed to CH_3 symmetric stretching and symmetric bending vibrations of pure PVAc, respectively. In addition, a strong band at 1718.3 and 1726.9 cm^{-1} can be attributed to the carbonyl group of PMMA and PVAc segments, respectively [6]. Also, the frequency shift of the peak due to C–O band of PMMA around 1149.9 cm^{-1} for the sample of the blend implies that there is a specific interaction between PMMA and PVAc [7]. On the other hand, it can be illustrated that the appearance of the C–Cl peak characterizing chloroform [8] at 755 cm^{-1} indicated the presence of solvents molecules.

Moreover, the band around 1063.6 cm^{-1}, due to a stretching vibration of C–O–C group of PMMA, has shifted to a higher value (1066.9 cm^{-1}) after exposure to UV radiation as well as the methoxy carbon (O–CH_3) which appeared at 2841.6 cm^{-1}. Similarly, the wave numbers corresponding to the characteristic transmission peaks of PVAc as acetates group at 1370.7 cm^{-1} have been affected by UV radiation. Also, the decrease in the intensity of carbonyl band for PMMA sample (which is more pronounced than the intensity decrease of the blend) is an evidence of side group elimination from PMMA chains upon UV exposure. The broadening of the whole carbonyl band for the homopolymers indicates that new oxidized groups are formed resulting of photochemical reactions [1, 9]. Besides, the development of the band from 3425 to 3666 cm^{-1} assigned to OH was observed for pure PMMA and PVAc
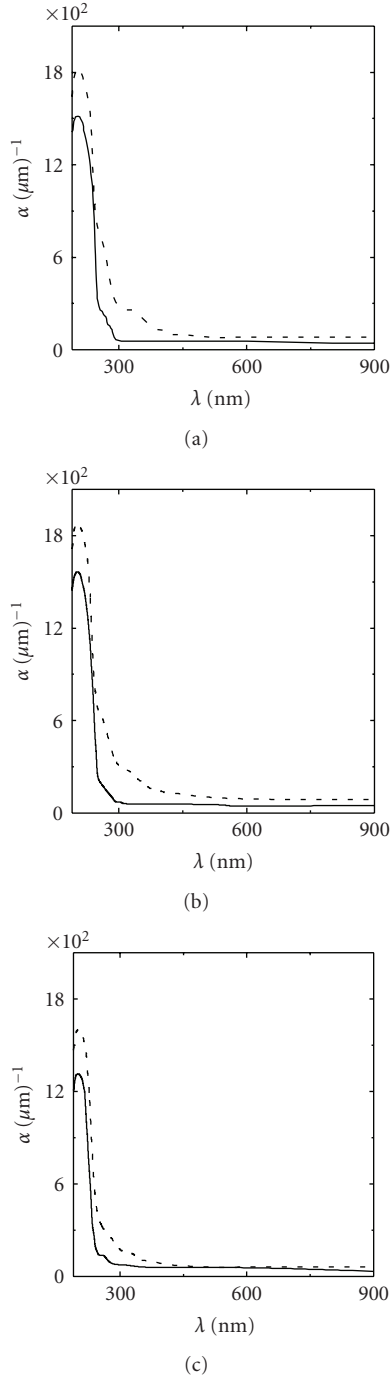
(a)

(b)

(c)

FIGURE 3: Absorption spectrum of (a) pure PMMA, (b) blend of (50/50 PMMA/PVAc), and (c) pure PVAc before (—) and after (- - -) exposure to UV radiation for 24 hours.

more pronounced than their blend after UV irradiation. This change is an obvious evidence of polymer photooxidation [1]. Consequently, (50/50 PMMA/PVAc) blend has improved the degradation of its homopolymer.

Furthermore, the observed decrease of the intensity of IR spectra can be explained on the bases that most synthetic polymers degrade after exposure to solar ultraviolet (UV)

radiation due to the presence of photosensitive impurities and/or abnormal structural moieties which are introduced during polymerization. The presence of groups such as ketones and aldeydes is implicated in polymer degradation [10].

3.2. Optical Absorption Spectroscopy. The study of the optical absorption spectra is one of the most productive methods in developing and understanding the structure and energy gap of amorphous nonmetallic materials. Figure 2 shows the absorption spectra of different concentrations of (PMMA/PVAc) blend before exposure to radiation. It can be observed that the intensity of absorption peak has increased by increasing the concentration of PMMA in the blend. Moreover, the absorption coefficient (α) has been estimated for all samples from (1):

$$\alpha(v) = \frac{2.3 \log(I_i/I_t)}{d} = \frac{2.3A}{d}, \tag{1}$$

where I_i and I_t are the intensity of the incident and transmitted light, respectively, A is the absorbance, and d is the film thickness. Figure 3 shows the absorption coefficient of PMMA, PVAc, and their (50/50 PMMA/PVAc) blend before exposure and after exposure to UV radiation. The observed wideness of the absorption spectrum of PMMA after exposure to UV radiation can be attributed to the existence of more transitions from higher vibration levels of the ground state to higher sublevels of the first excited singlet state [11]. In addition, the same behavior observed for PVAc can be interpreted as the existence of ketones and aldeydes due to the degradation by UV radiation as mentioned before.

3.3. Interband Transitions. When a quantum of radiation is absorbed by a material, the absorption coefficient, as a function of photon energy for simple parabolic band, can be expressed by Davis and Mott formula [12], as in (2)

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

where B is a constant, E_g is the optical band gap of the specimen, 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 4(a) illustrates the dependence of $(\alpha E)^2$ on the photon energy E (eV) for the samples before exposure to light, which brought in to view a linear behavior that can be considered as an evidence of the direct transition (i.e., for $r = 1/2$) [13]. The optical gab was estimated from the intercept on the energy axis of the linear fit of the large energy data of the plot [14]. The absorption spectra [15] clarify an extending tail for lower photon energies below the band edge, which can be described by (3)

$$\alpha = \alpha_o \exp\left(\frac{E}{E_u}\right), \tag{3}$$

where E_u is the energy of Urbach corresponding to the width of the band tails of localized states in the band gap. The values
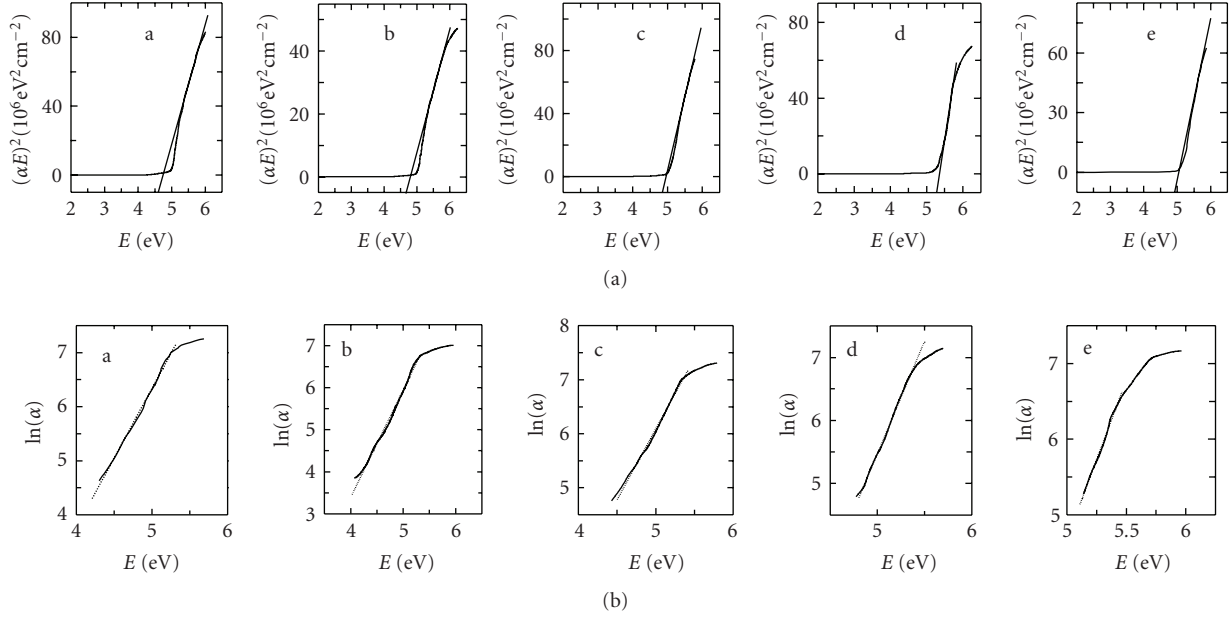
(a)

(b)

FIGURE 4: (a) The dependence of $(\alpha E)^2$ on photon energy E (eV) for (a) pure PMMA, (b) blend of (75/25 PMMA/PVAc), (c) blend of (50/50 PMMA/PVAc), (d) blend of (25/75 PMMA/PVAc), and (e) pure PVAc without exposure to radiation.
(b) The dependence of $(\ln \alpha)$ on photon energy E (eV) for (a) pure PMMA, (b) blend of (75/25 PMMA/PVAc), (c) blend of (50/50 PMMA/PVAc), (d) blend of (25/75 PMMA/PVAc), and (e) pure PVAc without exposure to light.

TABLE 1: The energy gap E_g (eV) for different concentrations of (PMMA/PVAc) blend after exposure to UV and filtered radiation at different exposure times.

PMMA/PVAc	Exposure radiation	Exposure time (hour)					Percentage of decrease of E_g% (eV)
		0	4	12	20	24	
(100/0)	filter	4.60	4.57	4.56	4.52	4.48	*2.61*
	UV	**4.60**	**4.50**	**4.41**	**4.32**	**4.23**	**8.04**
(75/25)	filter	4.67	4.66	4.64	4.60	4.59	*1.71*
	UV	**4.67**	**4.54**	**4.47**	**4.36**	**4.30**	**7.92**
(50/50)	filter	4.85	4.84	4.83	4.80	4.77	*1.65*
	UV	**4.85**	**4.68**	**4.57**	**4.56**	**4.53**	**6.29**
(25/75)	filter	4.92	4.92	4.89	4.88	4.88	*0.81*
	UV	**4.92**	**4.83**	**4.77**	**4.73**	**4.70**	**4.47**
(0/100)	filter	5.28	5.28	5.27	5.24	5.24	*0.76*
	UV	**5.28**	**4.25**	**5.19**	**5.11**	**5.07**	**3.98**

of E_u were calculated as the reciprocal gradient of the linear portion of the plot. Moreover, Figure 4(b) shows the plot of $(\ln \alpha)$ versus photon energy E (eV) samples before exposure to light.

Tables 1 and 2 summarize the values of optical parameters (E_g and E_u), respectively, for different concentrations of (PMMA/PVAc) blend before and after exposure to filtered and UV radiation for 24 hours. 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. Furthermore, Table 1 has illustrated that the decrease of E_g values by increasing the exposure time of UV radiation was more obvious than that after exposure to filtered radiation because UV radiation has an energy higher than the energy of any bond molecules [16]. Moreover, the blend of (50/50 PMMA/PVAc) modified the wideness of PMMA spectra after exposure to UV radiation.

Also, the values of E_u have increased by increasing the exposure time as indicated in [17]. The increase of E_u values by increasing the concentration of PMMA in (PMMA/PVAc) blend can be attributed to the effect of internal potential fluctuation associated with the structural disorder [11]. In addition, the values of constant (B) in (2) were determined from the slope of the linear part of Figure 4(a) for the

TABLE 2: The band tail width E_u (eV) for different concentrations of (PMMA/PVAc) blends after exposure to UV and filtered radiation at different exposure times.

PMMA/PVAc	Exposure radiation	Exposure Time (Hour)				
		0	4	12	20	24
(100/0)	filter	0.40	0.41	0.43	0.45	0.46
	UV	**0.40**	**0.42**	**0.46**	**0.49**	**0.53**
(75/25)	filter	0.39	0.39	0.43	0.43	0.43
	UV	**0.39**	**0.39**	**0.43**	**0.45**	**0.48**
(50/50)	filter	0.38	0.38	0.41	0.42	0.42
	UV	**0.38**	**0.38**	**0.43**	**0.45**	**0.47**
(25/75)	filter	0.28	0.28	0.30	0.30	0.32
	UV	**0.28**	**0.31**	**0.35**	**0.38**	**0.38**
(0/100)	filter	0.24	0.28	0.30	0.32	0.32
	UV	**0.24**	**0.34**	**0.37**	**0.37**	**0.38**

TABLE 3: Values of the constant B (cm^{-1} eV$^{1/2}$) for different concentrations of PMMA/PVAc blend before and after exposure to UV and filtered radiation for 24 hours.

PMMA/PVAc	Before exposure to radiation	After exposure to filtered radiation	After exposure to UV radiation
(100/0)	67.5	58.5	78.8
(75/25)	39.7	78.4	45.5
(50/50)	91.6	78.7	102.6
(25/75)	85.8	69.5	63.2
(0/100)	127.3	123.2	138.5

samples before exposure to light and also after exposure to UV and filtered radiation which are summarized in Table 3. The unit may be given [18] as cm^{-1} eV$^{(1-r)}$.

3.4. Optical Constants. The absorption coefficient (α) of the medium provides valuable optical information for material identification. The attenuation coefficient (k) [19] is directly proportional to the absorption coefficient (α) as seen in(4)

$$\alpha = \frac{4\pi k}{\lambda},\qquad(4)$$

where λ is the free space wavelength of light. For normal incidence, the reflection coefficient (R) [19] is given by (5)

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

The measurements of specular reflection and the absorbance are used to calculate the optical constants (n, k) by the two previous equations. Figure 5 illustrates the refractive index values for the blend of (PMMA/PVAc) with variant concentrations at wavelength of 200 nm. It has been found that the value of (n) increases with increasing the concentration of PMMA in (PMMA/PVAc) blend which is a result of increasing the number of atomic refractions due
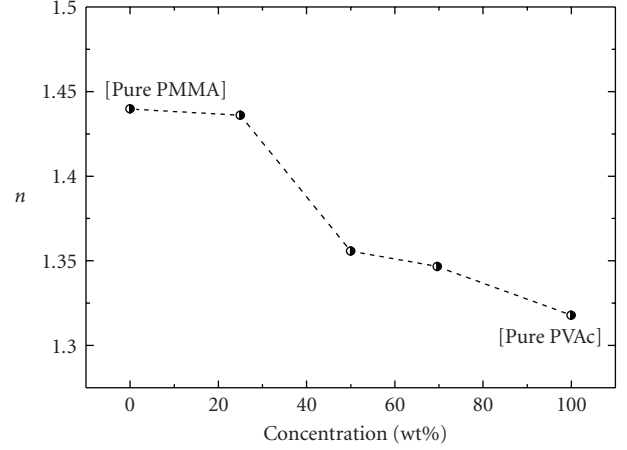

FIGURE 5: The variation of refractive index (n) versus different concentrations of PVAc in (PMMA/PVAc) blends without exposure to radiation at wavelength of 200 nm.

to the increase of the linear polarizability in agreement with Lorentz formula [20], as in (6)

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3}\pi N\alpha_P,\qquad(6)$$

where n, N, and α_P are refractive index, the number density of molecules, and linear polarizability, respectively. On the other hand, Figure 6 shows that there is a minimum peak in the wavelength range of the absorption band followed by an increase of the values of (n), for PMMA, PVAc, and their (50/50 PMMA/PVAc) blend, which clarifies the presence of normal dispersion according to Cauchy's dispersion formula [16], as in (7):

$$\frac{dn}{d\lambda} = -\frac{2B_1}{\lambda^3}.\qquad(7)$$

Also, the curves of refractive index (n) show no minimum caused by absorption in the visible wavelength, which is pointing to the fact that all the samples are colorless [21]. In addition, the increase in the values of the refractive index after exposure to UV radiation for 24 hours could be attributed to localized density increased arising from photoinduced cross linking [22]. Moreover, Figure 6 shows that the increase of refractive index (n) for the samples after exposure to UV radiation was more obvious than that after exposure to filtered radiation due to the effect of UV.

4. Conclusions

Blend films of PMMA and PVAc with different concentrations have been prepared by casting method, and they were exposed to UV and filtered radiation for 24 hours. The films were characterized spectroscopically using FTIR which illustrated that the decrease of the intensity of transmission spectra of (50/50 PMMA/PVAc) blend after exposure to UV radiation for 24 hours was lower than that of PMMA and PVAc. Consequently, (50/50 PMMA/PVAc) blend has improved the degradation of its homopolymer. Furthermore,
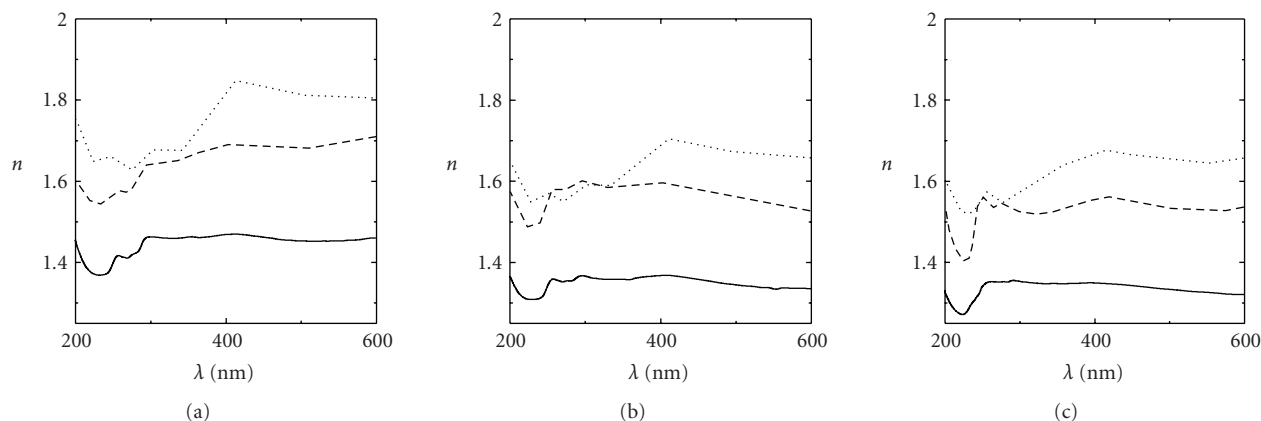
FIGURE 6: Spectral distribution of refractive index (n) for (a) pure PMMA, (b) a blend of (50/50 PMMA/PVAc), and (c) pure PVAc before (—) and after exposure to filtered (- - -) and UV radiation (…) for 24 hours.

the calculated values of the optical parameters illustrated that there was a reduction in E_g values of the films by increasing the concentration of PMMA in the blend and also after exposure to UV radiation. Moreover, the refractive index values have been calculated from a combination of reflectance and absorbance measurements at normal incidence for all films which illustrated that there was an increase of these values by increasing the concentration of PMMA in the blend and also after exposure to UV radiation for 24 hours. In conclusion, from all the previous results, it could be concluded that (50/50 PMMA/PVAc) blend has modified the optical properties of its homopolymers and also it may be suggested to be a good matrix for the dyes used in fluorescent solar collectors.

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