Int. J. Pure Appl. Sci. 8(1);149-156 (2022)

ijpas@munzur.edu.tr
ISSN: 2149-0910

Research article/Araştırma makalesi
DOI: 10.29132/ijpas.1054866

Compatibilizer Effect on Optical Properties of Immiscible PMMA/PS Blends

Ersen Yılmaz
Munzur University, Tunceli Vocational School, Departmant of Machinery and Metal Technology, Tunceli, Turkey
ersenyilmaz@munzur.edu.tr
Received date:07.01.2022, Accepted date: 16.02.2022

Abstract

Immiscible polymethyl methacrylate/polystyrene (PMMA/PS) mixtures with various maleic anhydride-styrene-methyl methacrylate (MAStMMA) compatibilizer ratio (0, 2, 4, 6, 8 and 10) % were obtained by solution casting. The spectral results showed that the optical constants such as refractive index (n), extinction coefficient (k) and absorption coefficient increase with increasing terpolymer compatibilizer ratio. On the other hand, the optical energy gap Eg showed an inverse trend to concerning optical constants. The lowest observed energy gap was between 8 and 10 % compatibilizer ratio.

Keywords: compatibilization, maleic anhydride, optical constants, polymer blending

Karışmaz PMMA/PS Harmanlarının Optik Özelliklerine Uyumlaştırıcı Etkisi

Öz

Karışmayan polimetil metakrilat/polistiren (PMMA/PS) harmanları değişik maleik anhidrit-stiren-metil metakrilat (MAStMMA) uyumlaştırıcı oranı (0, 2, 4, 6, 8 ve 10) eklenerek çözeltiden döküm yoluyla elde edilmiştir. Spektral sonuçlar, kırılma indisi (n), sönüm katsayısı (k) ve absorpsiyon katsayısı (μ) gibi optik sabitlerin terpolimer bazlı uyumlaştırıcı ilavesiyle arttığını göstermiştir. Diğer yandan optik enerji boşluğu Eg, anılan optik sabitlere göre zıt bir eğilim göstermiştir. Gözlenen en düşük enerji boşluğu %8 ila %10 uyumlaştırıcı oranı arasında belirlenmiştir.
Anahtar Kelimeler: maleik anhidrit, optik sabitler, polimer harmanlama, uyumlaştırma,

INTRODUCTION

Polymer blending is a simple and efficient technique in the polymer industry for producing new materials with more advanced physical and thermal properties. Compatibilization of various polymers to obtain further materials with different physical properties is of great significance to the plastics industry. The blends thus formed exhibit properties superior to any of the individual polymers. Knowledge of the compatibilization and rheological behavior of polymer mixtures is essential for controlling the properties of the newly formed materials. (Boztug&Yilmaz, 2007; Imren et al., 2008; Imren, 2010; Kumar et al., 2011; Abdullah et al., 2010)

The linear variation of the refractive index values of polymer-polymer mixtures indicates miscibility. Therefore, the effect of the compatibilizer on miscibility improves many properties of polymer mixtures, such as optical and mechanical. (Khan&Baloch, 2014; Imren Koç&Koç, 2016; Imren Koç et al., 2019)

In recent research, polymers' optical and electrical characteristics have attracted much consideration in their use in optical and electronic apparatus. Applications of polymeric mixtures in optical devices are defined by their optical properties such as refractive indices, transmission, dispersion and optical coefficients.(Alwan, 2012; Sultanova et al., 2013) Calculation of the optical constants of polymers is important essential for various applications such as solar cells, diodes made of polymeric material, electrochemical cells and optical systems.(Alias et al., 2013; Jang et al., 2017; Sultanova, 2016) Due to the widespread use of polymers in daily life, there are many studies aimed at improving certain optical and electrical properties (Kim et al., 2013; Nawar et al., 2014). According to their optical properties, PMMA and PS are most often used to manufacture optical lenses and optical devices

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ISSN: 2149-0910

Research article/Araştırma makalesi
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for laser-active media.(Najeeb et al., 2014; Shahin et al., 2019)

The present study involves the compatibilization of polystyrene with amorphous and a rigid polymer, poly (methyl methacrylate) and to produce (PMMA/PS) by adding different compatibilizer ratios and to examine its optical properties for optoelectronic applications. The used terpolymer compatibilizer may be expected to improve the blend's mechanical and optical properties.

MATERIAL AND METHODS

Maleic anhydride Sigma Aldrich brand is purified by recrystallization in anhydrous benzene. Styrene is a Merck brand chemical purified by vacuum distillation. Methyl methacrylate a Merck branded product and used after purification by low-pressure distillation. In our previous study (Yilmaz, 2022) MAStMMA terpolymer was synthesized at our laboratory. Polymethylmethacrylate (PMMA) medium mol weight, a Sigma product. Polystyrene (PS) medium mol weight, a PETKIM, Turkey product. Tetrahydrofuran (THF) a Merck product was at analytical grade.

PMMA/PS films and blends containing compatibilizer were prepared using the solution casting method. The films containing 0,2,4,6,8 and 10 % w/w MAStMMA terpolymer compatibilizer were dissolved in a glass tube with a predetermined (Soygun et al., 2013) co-solvent tetrahydrofuran (THF) and incubated for one night. The obtained viscous and clear solutions were poured into teflon petri dishes. After the solvent evaporation, the films were scraped and kept in oven at 40 ^{o}C for 3 hours. The thickness of the obtained thin films was measured using a micrometer. The absorption and transmittance spectra were recorded in wavelength interval 200-800 nanometer using double beam Optima SP-3000 spectrophotometer.

Theoretical Approach

In an experiment, the absorption coefficient (α) can be calculated from a simple equation :

$$\alpha = [1/d \ln[(1-R)^2 / T] \quad (1)$$

where d is thickness of the specimen, R and T are the reflection and transmission. If transmission and reflection are not available and we have Absorbance (A), this equation transform to:

$$\text{absorption coefficient } (\alpha) = 2{,}303\ A/d \quad (2)$$

where (A) is absorbance of the sample and (d) is thickness of the film.

The Eg value can be found by using the Tauc equation (Aly et al., 2012; Tauc, 1974), which is given below:

$$(\alpha.h\nu) = \beta(h\nu - E_g^{opt.})^r \quad (3)$$

here hν is the photon energy, where:

$$h\nu(eV) = 1241 / [\lambda\ (nm)] \quad (4)$$

Where β is an independent parameter of photon energy, hν = 1241 / λ for the individual transitions, E_g^{opt} is the optical energy gap, and r is the type of the transition. The energy gap value is determined by projecting a tangent to the resulting curve towards the x-axis intersected by it at the point (αhν)1/n= 0, representing the value of the energy gap. The value of n is dependent on the electronic transition type. Where:

r= ½ for direct allowed transition,
r= 2 for indirect allowed transition,
r= 3 for direct forbidden transition and,
r= 3/2 indirect forbidden transition.

The absorption (A) and reflectance (R) parameters can be determined by UV-Vis double beam spectrophotometer. The relation between refractive index (n) and reflectance (R) is;

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (5)$$

The refractive index calculated by the formula;

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad (6)$$

The extinction coefficient was determined with the formula;

$$k = \frac{\alpha\lambda}{4\pi} \quad (7)$$

The optical conductivity determined via the formula

$$\sigma opt = \frac{\alpha nc}{4\pi} \quad (8)$$

RESULTS AND DISCUSSION

Some characteristic properties of the polymers used are given in Table 1. As can be seen from the Table 1, all three polymers used in the experiment are polymers with medium mol weight. In addition, the

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glass transition temperatures (Tg) are close to each other.

From Figure 1. it was revealed that a strong absorption between 340 nm and 385 nm for the mixtures. It is seen that increasing the ratio of the used compatibilizer leads to increasing the absorption peak intensity and very small shifts in the peak position for all amounts of the added compatibilizer. These shifts in wavelength mean there are some weak electronic interactions between the components and the compatibilizer used. This effect becomes more prominent as the amount of compatibilizer increases. In addition, the reason for increase in absorbance is the free electrons in the monomers of the added compatibilizer. (Najeeb et al., 2014)

Figure 2 shows the change in the absorption coefficients (α) which are calculated by equation (2) of the blends with the added compatibilizer. The absorption coefficients of PS/PMMA mixtures containing compatibilizer were read at 385 nm. It was observed that the absorption coefficient increased up to 8% and slightly decreased by 10% with the addition of compatibilizer. It can be said that the contribution of the added compatibilizer to the value of the absorption coefficient is low, but the general trend is towards increasing it.

Figures 3 and 4 are figures related to the direct energy (r=1/2) gap calculated using the Tauc equation (eq. 3). From the curves and Fig. 4 graph, it is seen that the lowest Eg values of the mixtures are 8% and 10% compatibilizer added. And in general, as the compatibilizer ratio increases, the decreasing trend of Eg is also noticeable. This was interpreted as the double bonds and aromatic regions of the added compatibilizer reduce the bond length variation along the backbone of the polymer mixture, thus reducing the band gap (Eg).

From figure 5 we observe an increase in the refractive index while the compatibilizer ratio increases. The highest refractive index values of the polymer blends are seen at 8 and 10 percent compatibilizer. In polymer mixtures the high refractive index values could be seen because of two reasons; thermal annealing and blending of materials.(Kim et al., 2016) In this case, since there is no thermal process, it is possible to say that the mixture formation provides this. Already in previous studies (Dogan&Kismet, 2021; Yilmaz, 2022), MAStMMA compatibilizer has proven to be a good mixing agent for PMMA based blends.

The relation between extinction coefficient and compatibilizer ratio is shown in Fig. 6. The lowest value of extinction coefficient for the polymer blends was measured at zero compatibilizer ratio. It is clear from figure 6 that increasing the ratio of compatibilizer in the mixture of PS and PMMA leads to an increase in extinction coefficient (k) values.

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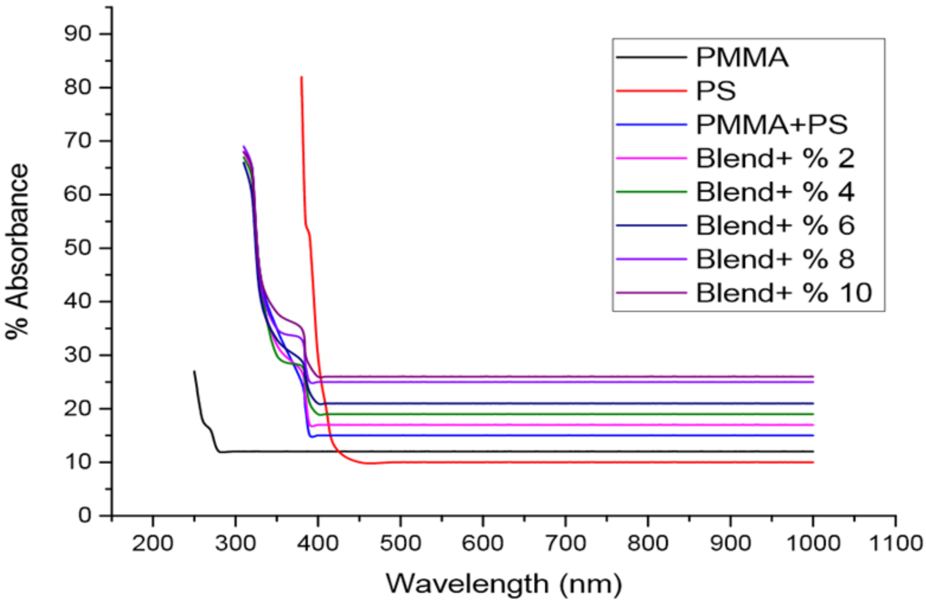

Figure 1. UV-Vis spectrum of pure polymers and compatibilizer added blends

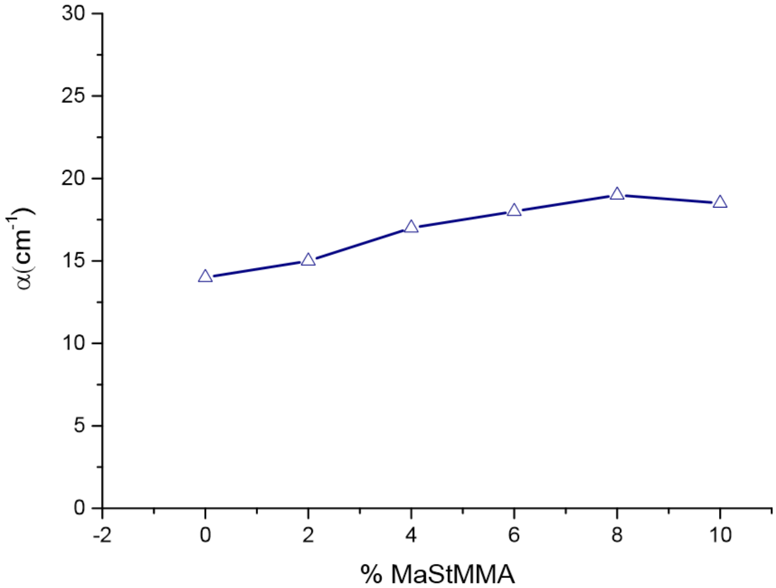

Figure 2. Absorption coefficient of the blends as a function to the compatibilizer % ratio

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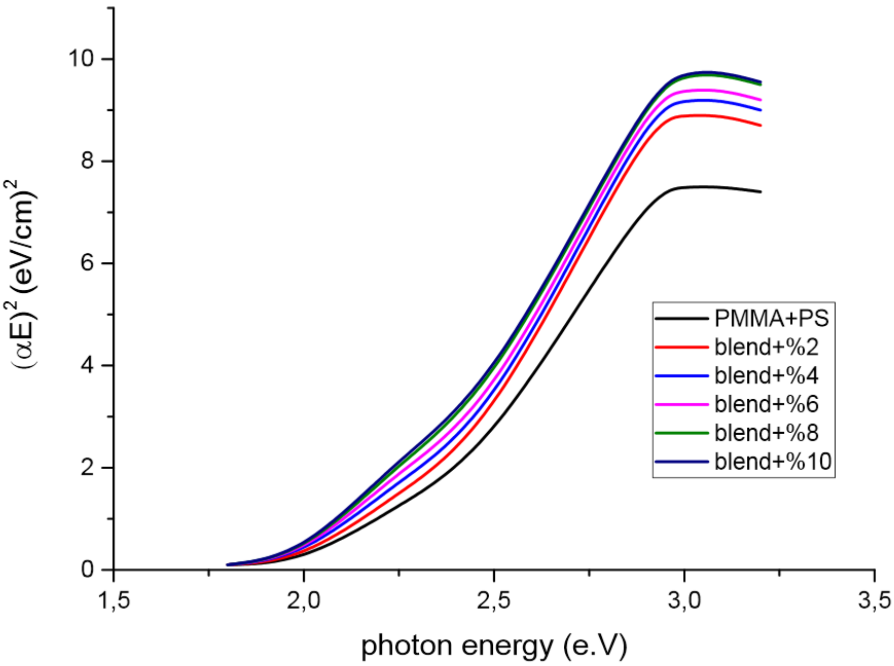

Figure 3. The relation between (αE) square and the photonenergy for the polymer blends

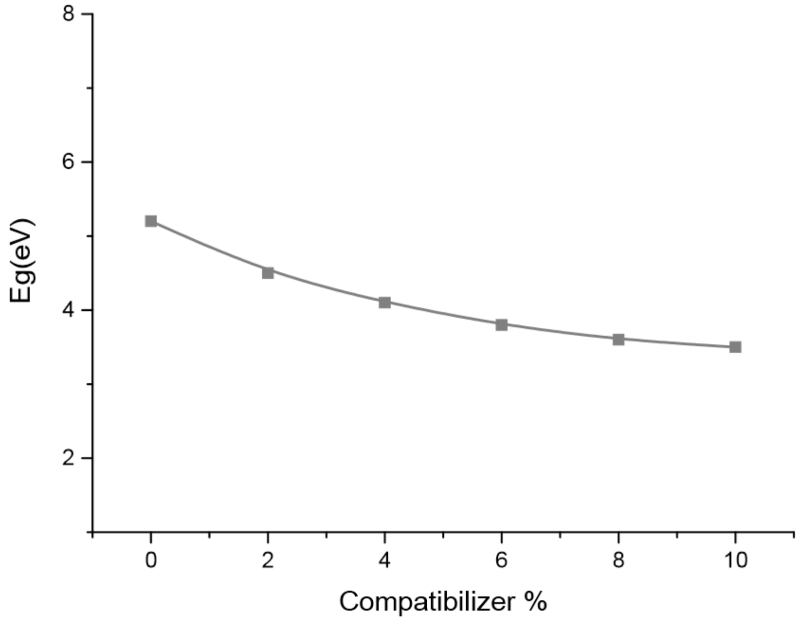

Figure 4. Relation between the Energy gap and compatibilizer percent

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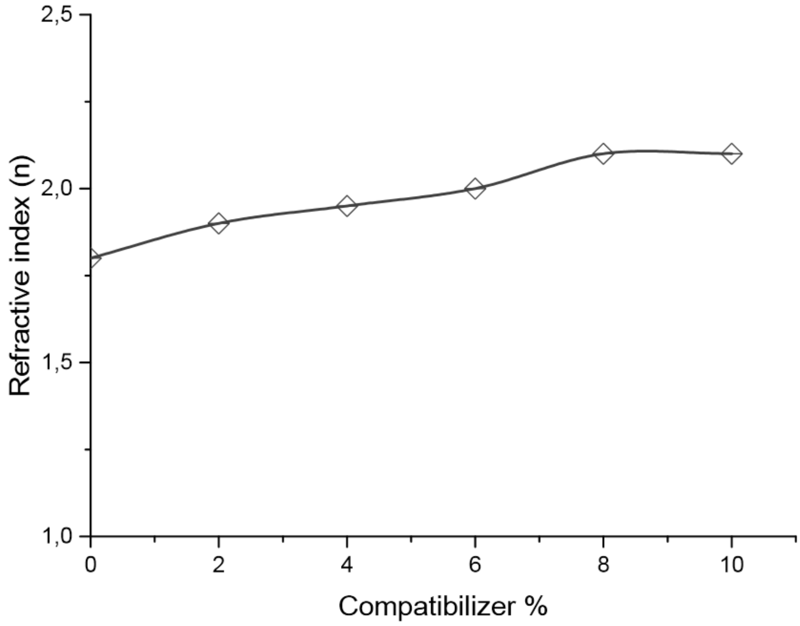

Figure 5. Relation of refractive index MAStMMA compatibilizer ratio

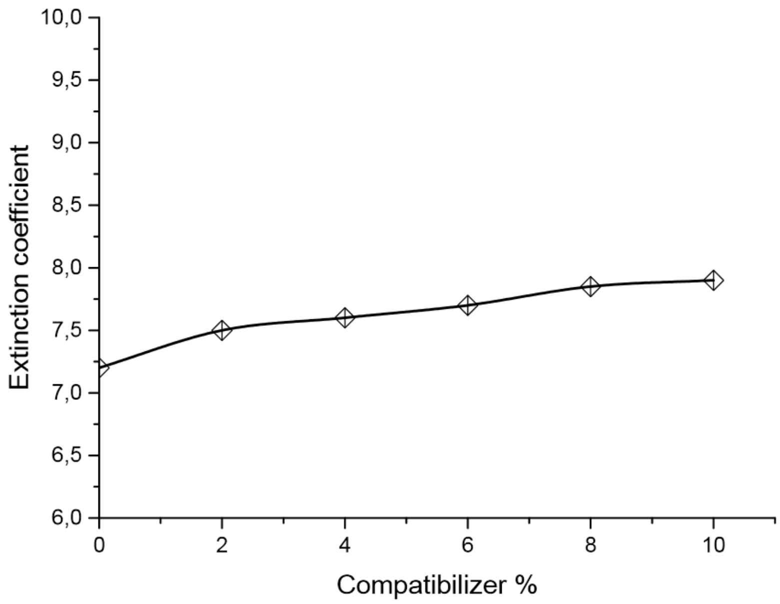

Figure 6. Extinction coefficient of the blends at different compatibilizer ratios

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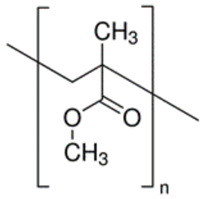
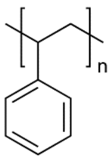
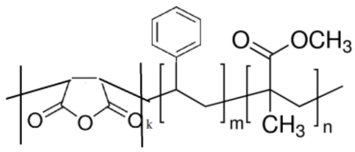
Table 1. *Some characteristic properties of the polymers used*

Material	Formula	average Mw	d(g/mL)	Tg (°C)
PMMA		120.000	1.188	105
PS		192.000	1.040	94
MaStMMA		60.000	---	103

CONCLUSION

Two different polymers with very high usage areas were mixed using a terpolymer compatibilizer that was synthesized in our laboratory. Changing the ratio of the new compatibilizer were led to enhancing some of the optical properties. The absorbance, absorption coefficient, extinction coefficient, and refraction index of the PS/PMMA blends compatibilized with a new MAStMMA terpolymer were found to be increasing with the increasing of compatibilizer concentration. Additionally, the new compatibilizer led to improving the energy gap of the PS and PMMA mixtures via its molecular feature.

CONFLICT OF INTEREST

The Author report no conflict of interest relevant to this article.

RESEARCH AND PUBLICATION ETHICS STATEMENT

The author declares that this study complies with research and publication ethics.

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