Research Article

Studies on miscibility of polyetherimide/polystyrene blends

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ABSTRACT

The miscibility behavior of the blends of Polyetherimide (PEI) and P olystyrene (PS) was studied using different experimental techniques. The intrinsic viscosities were determined for different ratios of PEI/PS blend in dilute chloroform solutions at 25ºC using viscometry. According to different methods proposed by Huggins, Krigbaum and Wall, Catsiff and Hewett using the experimental results of the intrinsic viscosity studies of the PEI/PS blends, some miscibility parameters were obtained. Besides, the miscibility of the PEI/PS blends was studied using Fourier Transform Infrared Spectroscopy (FT-IR) and Differential Scanning Calorimetry measurements.

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INTRODUCTION

Polymer blends can be expressed as structures formed by the combination of two or more polymers (or copolymers). When polymers with certain properties are mixed, the blends obtained have superior properties [1-4]. The preparation of polymer blends is an interesting technique to develop novel material in various fields since it is low-cost, efficient, and easy-to-apply. This technique has advantages such as increasing the performance of materials, decreasing the cost, improving the properties of the polymer units used in the blends such as strength, modulus, flame retardancy, and stress-relaxation resistance.

The properties of polymer blends can be determined using the degree of miscibility of the components [5, 6]. The thermodynamically homogeneous and miscible polymers occur when the free energy of the blend is negative. For high molecular weight polymers to be miscible, enthalpy and entropy must be negative and negligible, respectively. This requirement is provided in situations where the intermolecular interactions between the components are extremely high. The miscibility of polymers is limited when intermolecular interactions between components are moderate or weak. Besides, in this case, miscibility varies depending on

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the temperature and composition. The partial formation of the blends creates a heterogeneous and two-phase structure. Partial miscibility depends on the size of dispersed phase, interaction of the components, and blending conditions. Most of the blends are widely used in commercial applications. Most of them are usually immiscible in nature. These blends are more preferred in raw material processing, engineering, and tailor-made products. Immiscible polymers have also the advantage of allowing control of membrane surface properties compared to miscible polymers [7].

There are many techniques such as DSC [8], FT-IR [9], thermal analysis [10], electron microscopy [11], inverse gas chromatography [12], and viscometry [13-16] to investigate the miscibility of polymers. Among these methods, viscometry is an easy-to-apply, low-cost, highly preferred, and efficient technique.

PS is an inexpensive, widely used, and aromatic polymer obtained as a result of polymerization of styrene monomer produced commercially from petroleum products. PS has a hard and brittle structure. Besides, it has good properties such as very high gamma radiation resistance and good electrical properties, but poor chemical and UV resistance [17].

PEI is an amorphous thermoplastic with high temperature resistance, excellent mechanical and electrical properties. Having high performance, this polymer also has properties such as high tensile strength, difficult flammability, low smoke emission. These properties make it an ideal polymer in automotive, electrical, medical, and many other fields. Studies can be carried out to blend the two polymers mentioned above in order to obtain composites with properties such as gamma radiation, high temperature resistance, and difficult flammability [18-20]. Chemical structures of PEI and PMMA were given in Scheme 1.

In this study, the miscibility of PEI/PS blends was evaluated by several techniques. The miscibility degree of the
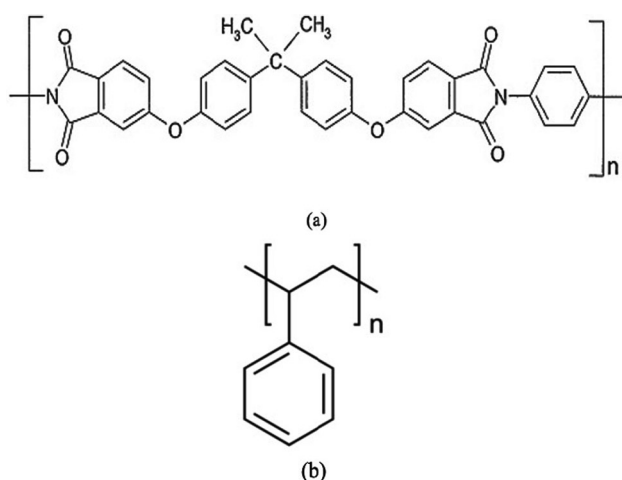
polymer blends prepared in dilute solutions were examined by the viscometry. Huggins equation was used for this, which expresses the relationship between the specific viscosity value and the concentrations of the polymer components. Firstly, the miscibility of PEI and PS was found using viscometry suggested by several research groups. And then, specific interactions between the components of the blend have been examined using FT-IR and DSC.

THEORY OF VISCOSITY

The equation proposed by Huggins [21], depending on the concentration, for polymer blends prepared using dilute solvents is given below.

$$\frac{(\eta_{sp})_b}{c_b} = [\eta]_b + b_b c_b \tag{1}$$

where c_b is the concentration of polymer blend; $(\eta_{sp})_b / c_p$ is the reduced viscosity; $[\eta]_b$ is the intrinsic viscosity of the blend; b is the Huggins coefficient for the interaction parameter of polymer in solution. The degree of miscibility of polymers can be compared with calculation of experimentally and ideally.

The equation proposed by Krigbaum and Wall [22] for the polymer blend prepared in a common solvent for two polymer and used in the ideal calculation of the interaction parameter, b_b^{id}, is given below.

$$b_b^{id} = b_1 w_1^2 + b_2 b_2^2 + 2b_{12}^{id} w_1 w_2 \tag{2}$$

The ideally b_b^{id} value can be calculated with the geometric average according to the following equation.

$$b_b^{id} = (b_1)^{0.5} (b_2)^{0.5} \tag{3}$$

where w_1 and w_2 are the weight fraction of the first and second component in the blend, respectively.

It is shown by the following equation proposed by Catsiff and Hewett [23] that the value of $b_b^{id'}$ can be calculated with the arithmetic average in addition to other methods.

$$b_b^{id'} = \frac{1}{2}(b_1 + b_2) \tag{4}$$

Garcia et al. [24] proposed equation based on differences between experimental and ideal intrinsic viscosity values. Ideally, the equation proposed by Garcia et al. is given below to calculate the intrinsic viscosity of the polymer blend.

$$[\eta]_b^{id} = [\eta]_1 w_1 + [\eta]_2 w_2 \tag{5}$$

Scheme 1. Molecular structures of PEI (a) and PS (b).
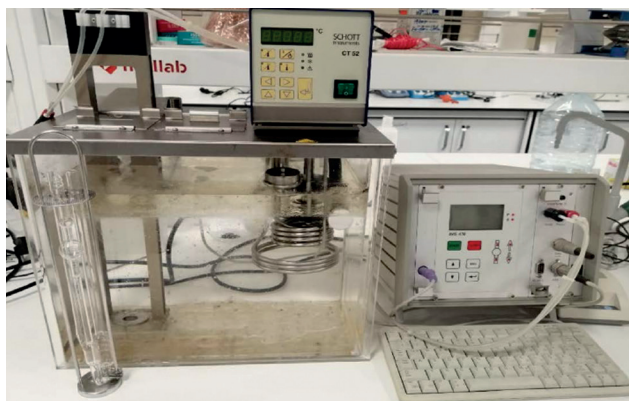
Figure 1. The photo of the Ubbelohde-type capillary viscometer combined with automatic viscometry device.

Figure 2. The linear plot of η_{sp}/c against concentrations of different ratios of PEI/PS blend: 100/0 (6), 80/20 (5), 60/40 (4), 40/60 (3), 20/80 (2), and 0/100 (1) by weight.
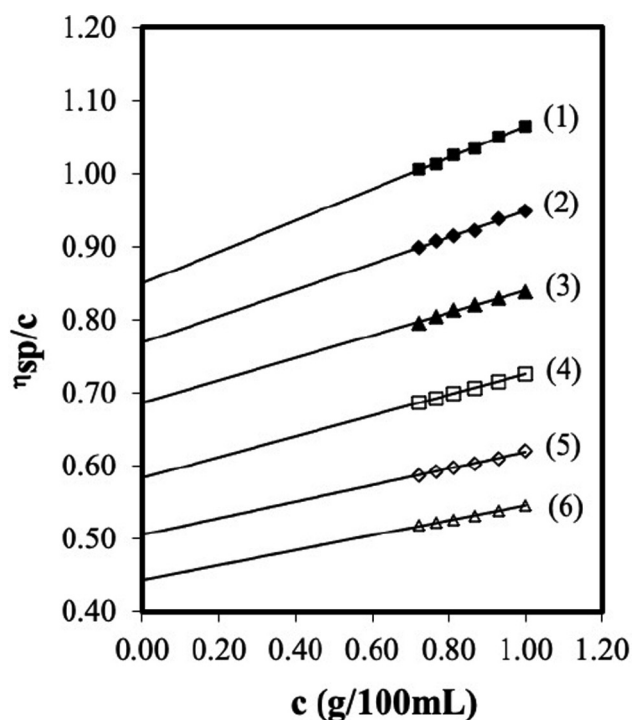
MATERIALS AND METHODS

PEI and PS were supplied by General Electric Plastics and Scientific Polymer Products, Inc., respectively. Chloroform was purchased from Merck AG Inc., *Germany*. Polymers were used as dissolved in dilute chloroform solution. FT-IR spectra were collected using a Thermo FT-IR Nicolet IS 10 model spectrometer. DSC measurements were performed using approximately 10 mg samples with a Perkin Elmer DSC 4000. The DSC curves were recorded at a heating rate of 10°C/min between 60 and 230°C. All viscosity measurements were performed at 25°C using a SI Analytics GmbH model Ubbelohde-type capillary viscometer combined with SCHOTT CT-2 model automatic viscometry device (Fig. 1).

Blending in a solvent is the most common and most simple method for preparing polymer blends. Through blending in a solvent, both of polymers must be dissolved in a dilute solvent. Degradation is avoided in this method in comparison with other methods. The stock solutions of PEI/PS blend were prepared to contain 1.0 g polymer in 100 mL dilute chloroform solvent. Initially, about 13 mL of stock solution was put into the Ubbelohde viscometer. After that, a total of five dilutions were made with 1 mL dilutions. Measurements were taken six times in order to obtain more accurate results at each stage.

RESULTS AND DISCUSSION

Polymer blends were prepared in dilute chloroform solvent by adjusting the ratios of the PEI/PS blends to be 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100 by weight, respectively. Besides, reduced viscosity measurements were performed at 25 °C. Fig. 2 shows the change of reduced viscosity, η_{sp}/c, depending on the change of concentration for polymer blends in different ratios. All of the polymer

Table 1. Experimental data obtained from the linear plot of PEI/PS blends in chloroform at 25°C.

| PEI/PS in chloroform at 25°C	Δb_b^{exp} (cm³/g²)	$-\Delta[\eta]_b^{exp}$ (cm³/g)	r²
100/0	0.1019	0.4444	0.9960
80/20	0.1137	0.5057	0.9963
60/40	0.1419	0.5840	0.9985
40/60	0.1540	0.6863	0.9940
20/80	0.1806	0.7687	0.9946
0/100	0.2156	0.8496	0.9980

blends prepared in different ratios, including the pure PS and PEI in dilute chloroform solvent, are given linearly in plot.

The values of b_b^{exp} and $[\eta]_b^{exp}$ were obtained from the slope and intercept of linear plot (Fig. 2), respectively. The data obtained from the linear plot were given in Table 1.

The miscibility parameters of PEI/PS blends prepared in different ratios can be determined by b_b^{exp} values obtained experimentally from the linear plot drawn in Fig. 2 and b_b^{id} values obtained ideally from the methods explained in the theoretical section. Besides, the miscibility parameter

Table 2. According to the different methods, the parameters of miscibility for PEI/PS blend in chloroform at 25 °C.

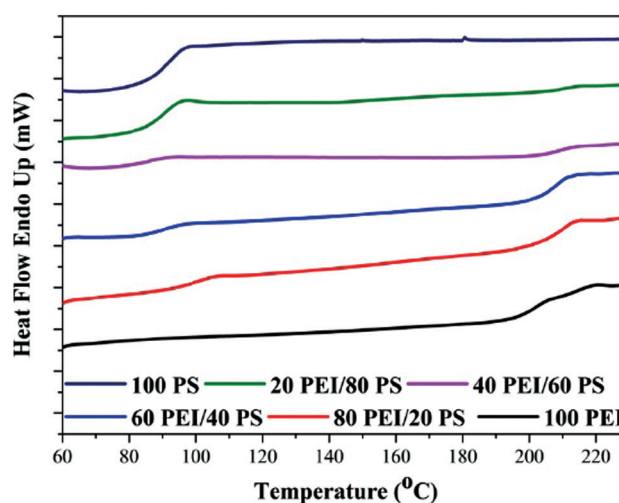| PEI/PS in chloroform at 25°C	Δb_b (cm⁶/g²)	$\Delta b_b'$ (cm⁶/g²)	$-\Delta[\eta]_b$ (cm³/g)	Miscibility
80/20	−0.0076	−0.0109	0.0197	Immiscible
60/40	−0.0005	−0.0055	0.0225	Immiscible
40/60	−0.0110	−0.0161	0.0013	Immiscible
20/80	−0.0089	−0.0123	−0.0002	Immiscible
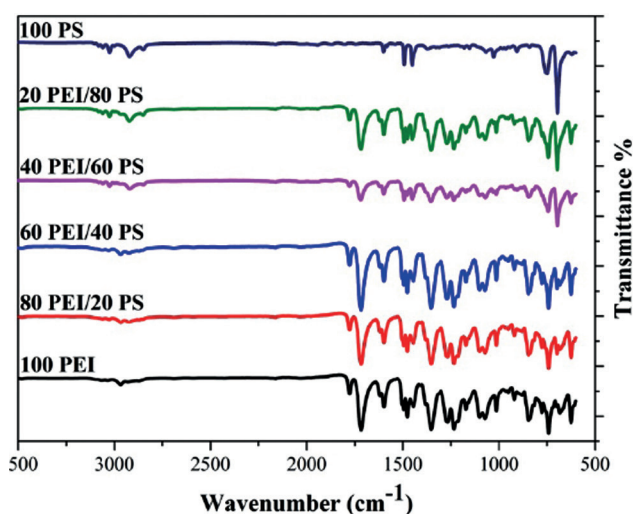
Figure 3. FT-IR spectra of pure PEI, PS and PEI/PS blends in compositions of 80/20, 60/40, 40/60, and 20/80 by weight.

Figure 4. DSC thermograms of PEI, PS, and PEI/PS blend compositions at 80/20, 60/40, 40/60, and 20/80 by weight.

Table 3. Glass transition temperatures of PEI, PS and their blends in the compositions of 80/20, 60/40, 40/60 and 20/80.

PEI/PS	T_g (°C)	
100/0	206.2	–
80/20	204.8	90.6
60/40	205.1	87.4
40/60	206.7	85.6
20/80	207.2	87.9
0/100	–	88.4

can also be determined from the intrinsic viscosity values obtained experimentally from the linear plot drawn in Fig. 2 and ideally obtained when calculated according to Eq. (5).

There are intermolecular interactions between the components of the polymer blends. Considering these interactions, miscibility or immiscibility can be determined according to the numerical difference between experimental and ideal values obtained from different methods.

If the $\Delta b_b > 0$, $\Delta b_b' > 0$, and $\Delta[\eta]_b < 0$, the polymers are miscible. On the contrary, if the $\Delta b_b < 0$, $\Delta b_b' < 0$, and $\Delta[\eta]_b > 0$, the polymers are immiscible. Intermolecular repulsion forces between components are more effective when polymers are immiscible. On the other hand, when polymers are miscible, intermolecular attraction forces between components are more effective.

All of the miscibility parameters of PEI/PS blends obtained from different methods were given in Table 2. According to the values of miscibility criteria of PEI/PS

blends $\Delta b_b < 0$, $\Delta b_b' < 0$, and $\Delta[\eta]_b > 0$ shows that PEI/PS blends are immiscible in all prepared compositions.

The miscibility of polymers was also determined using different techniques. Intermolecular interactions between the components were examined using FT-IR. According to FT-IR analysis, the miscibility of polymers can be determined. The FT-IR spectra of the different ratios of PEI/PS blends are showed in Fig. 3. The carbonyl group stretching vibration is specific for PEI and is seen at 1716 cm⁻¹. C=O stretching band of PEI/PS blends in compositions at 80/20, 60/40, 40/60, and 20/80 are found as 1716, 1716, 1718, and 1717 cm⁻¹, respectively. Similarly, stretching vibrations of the C–O and C=N groups in PEI are seen at 1101 and 1352 cm⁻¹, respectively. The stretching vibrations of PEI/PS blends in compositions at 80/20, 60/40, 40/60, and 20/80 were founds as 1101 cm⁻¹ for C–O group and 1352, 1352, 1353, and 1352 cm⁻¹ for C=N group, respectively. It is known that the miscible systems show small band shifts in the FT-IR spectra. As shown in Fig. 3, the absence of such

band shifts indicates that the blends are not miscible in all the compositions prepared.

If the polymers are miscible or immiscible in nature, they show one or two glass transition temperatures (T_gs) and melting temperatures (T_ms) corresponding to each component [2, 25]. Immiscible polymer blends possess sharp interphase and these indicates the absence of strong interactions between the components. Generally, the weak interactions such as hydrogen bond and Van der Waals interactions can be observed in immiscible polymer blends. On the contrary, most of the useful materials are consist of immiscible blends. The T_gs of components were determined using DSC. The DSC thermograms were shown between 60 and 230°C for all ratios of blends. DSC thermograms of polymers in pure and blends were shown in Fig. 4. The T_gs of pure polymers and their blends were listed in Table 3. It was seen that the blends studied exhibit two glass transition temperature, indicating the immiscibility of the blends.

CONCLUSIONS

The miscibility of PEI/PS blends was examined using viscosity, FT-IR and DSC. The results obtained by viscosity and FT-IR that blends are immiscible in the whole composition range in dilute chloroform solution. According to the results in this study, the miscibility criteria proposed by Krigbaum and Wall, Catsiff and Hewett and Garcia et al. are in agreement in determination of the miscibility of polymers. DSC measurements suggest that the blends are immiscible, because they exhibit two T_g at each studied composition. The DSC technique support the viscosity and FT-IR results.

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AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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