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A study on compatibility of polymer blends of Poly(2,6-dimethyl-1,4-phenyleneoxide)/Poly(ether imide)

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The miscibility criteria of poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) and poly(ether imide) (Ultem) were investigated at 30 ^{0}C in chloroform in dilute solutions by viscometric analysis. The intrinsic viscosity and viscometric parameters of this blend system were determined for several PPO/Ultem mixtures in compositions such as 80/20, 60/40, 40/60, 10/90 in chloroform solutions. The miscibility criteria on the basis of the sign of the parameters Δb_m, $\Delta b'_m$, $\Delta[\eta]_m$ and β proposed by Krigbaum and Wall, Catsiff and Hewett, Garcia et al. and Jiang and Han, respectively, which are the difference between their experimental and ideal values were calculated by applying theoretical equations. The data obtained from the viscometry studies suggested that the prepared blends were partially miscible in all of the studied composition ranges at 30 ^{0}C. The miscibility of the mixtures was also studied by Fourier transform infrared spectroscopy.

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Keywords: Poly (2,6-dimethyl-1,4-phenylene oxide), Poly(ether imide), Miscibility, Viscometry, FTIR

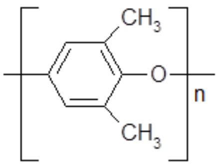
1. Introduction

Polymer blending is one of the most important ways to develop new polymeric materials with a desirable combination of properties. The gain in newer properties depends on the degree of compatibility or miscibility of the polymer at a molecular level. Generally, the polymer-polymer miscibility is due to some specific interactions like dipole-dipole forces, H-bonding and formations of charge complexes between the polymer segments [1-2]. There have been various techniques of studying the miscibility of the polymer blends. Some of these techniques are quite complicated, time consuming and costly. Thus it is desirable to identify simple, low cost and rapid techniques to study the miscibility of polymer blends [3-8]. Many scientists showed that viscometry was a simple and very useful method, because it does not only require inexpensive equipment, but also offers very useful information about the relationship between dilute solution properties and bulk structure of polymer blends [9-10].

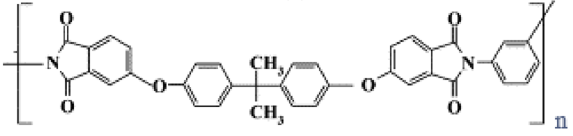
Fourier transform infrared spectroscopy (FTIR) is one of the many techniques that have been applied to investigate specific molecular bonding interactions in polymer blends [11-12]. In the case of immiscible systems, the spectrum of the blend reflects the appropriate addition of the IR spectrum of the two individual components. In the case of miscible polymer blends, the IR spectrum would show formation of new bands as a result of miscibility; and disappearance of some component bands. Shifts in the specific bands would give information on the switches from component specific bonds to the bonds between components [13].

Polyether imides such as Ultem, a well-known class of engineering thermoplastic polymers, offer exceptional thermal, chemical and mechanical stability and are available in large quantities [14]. Their cost is similar to other thermoplastic polymers that offer similar performance and significantly more economical than small batch thermoplastic polymers. Polyether imides have higher diffusivity selectivity due to their fused ring structure and rigid backbone. Their high glass transition temperatures allow higher pressure and temperature applications without plastic deformation [15-16].

Since its invention by Hay in 1954 and its commercial production by General Electric in 1962, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has attracted much attention for its excellent chemical inertness, thermal stability and mechanical properties [17-18]. However, because of its rigid backbone, PPO is also characterized by a high glass-transition temperature (T_g), a very low melt flow index and a very high melt viscosity; consequently, its melt processing is highly energy-consuming. Hence, most commercially available PPOs are in the form of blends with styrenic polymers (e.g., Noryl), [19-21] polyamides [22] and polyesters [23]. Chemical structures of PPO and Ultem were given in Scheme 1. It seems that miscible blends of Ultem and PPO might be appropriate to make some novel polymeric materials resistant to the high temperature and pressure and as well as chemicals.



(a)



(b)

Scheme 1. Chemical structure of PPO (a) and Ultem (b)

In this study, it was the first time, the miscibility criteria of PPO and Ultem were found by viscosity measurements at 30 ^{0}C. And then, specific interactions between the components of the blend have been investigated by FTIR.

2. Experimental

2.1. Materials and Instrumentation

All viscosity measurements were performed at 30 ^{0}C using a home-made modified Ubbelohde-type capillary viscometer in a constant temperature bath controlled with ± 0.02 ^{0}C by a Huber type electronically controlled thermostat. Stock solutions of the binary and ternary systems were freshly prepared by dissolving appropriate amount of polymers in chloroform into a concentration of 0.35 g /100 cm^3. For each measurement, 7 cm^3 stock solution was loaded into the viscosimeter and diluted by adding 2 cm^3 chloroform to yield several lower concentrations. The elution time of each solution was taken as the average of four readings agreed to within ±0.5%.

FTIR spectra were recorded on a Perkin Elmer Spectrum One FTIR Spectrometer at 2 cm^{-1} resolution from Fourier transforms of 60 scans. The samples were prepared as a film on KBr pellets *via* dropping of polymer solutions and evaporating of the solvent.

2.3. Theoretical background on viscosity

For a ternary mixture of polymer (1), polymer (2) and a common solvent, at constant weight ratio of polymer 1 to 2 for a given composition, the well-known Huggins' equation is written as [24]

$$(\eta_{sp})_m / c_m = [\eta]_m^{exp} + b_m^{exp} c_m \tag{1}$$

where c, η_{sp}, η_{sp}/c, $[\eta]$ and b are concentration, specific viscosity, reduced viscosity, intrinsic viscosity and viscometric interaction parameter of the polymer in solution, respectively, while subscript "*m*" and superscript "*exp*" denote "mixture" and experimental, respectively. The miscibility of the polymer (1) and (2) is estimated by the sign of the difference of the experimental values of b_m^{exp} or $[\eta]_m^{exp}$ with their ideal values defined several researchers.

Krigbaum and Wall [25] have defined the ideal value of the interaction parameter b_m^{id} as

$$b_m^{id} = b_{11} w_1^2 + b_{22} w_2^2 + 2 b_{12}^{id} w_1 w_2 \tag{2}$$

where w_1 and w_2 are weight fractions of polymers and b_{12}^{id} is defined as a geometric mean;

$$b_{12}^{id} = b_{11}^{1/2} b_{22}^{1/2} \tag{3}$$

Catsiff and Hewett [26] have defined the ideal value of the interaction parameter $b_{12}^{id'}$ as an arithmetic mean

$$b_{12}^{id'} = (b_{11} + b_{22})/2 \tag{4}$$

Garcia et al. [27] have also proposed another miscibility criterion based on the difference between experimental and ideal values of $[\eta]_m$ assuming that the intrinsic viscosity can be treated as an excess property. The value of $[\eta]_m^{id}$ has defined as

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

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities of corresponding polymers.

Jiang and Han [28] have proposed another miscibility criterion, β for polymer-polymer miscibility defined as;

$$\beta = \frac{2 w_1 w_2 [\eta]_1 [\eta]_2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \Delta k \tag{6}$$

where

$$\Delta k = k_{12} - \sqrt{k_1 k_2} \tag{7}$$

and

$$k_1 = b_1/[\eta]_1^2;\ k_2 = b_2/[\eta]_2^2;\ k_{12} = b_{12}/[\eta]_1[\eta]_2 \tag{8}$$

3. Results and discussion

The intrinsic viscosity and viscometric parameters of this system have been determined at 30 ^{0}C in chloroform. Fig. 1 shows plots of reduced viscosity η_{sp}/c vs concentration, c for the constituent polymers and their blends. The linear relationships are observed for pure polymers and all of the compositions studied.

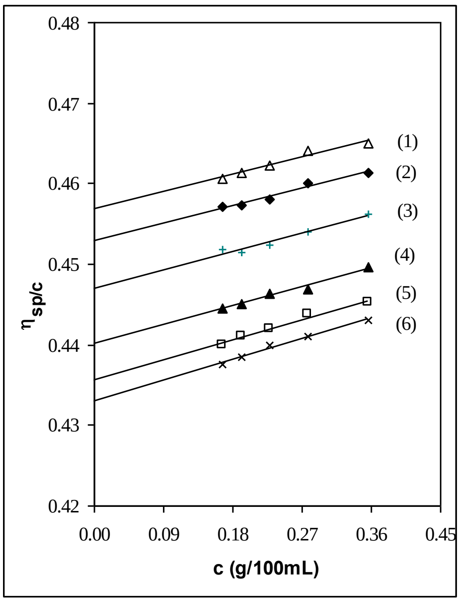


Fig. 1. Variation of reduced viscosity, η_{sp}/c *with total concentrations of the constituent polymers and their mixtures at 30 ^{0}C in chloroform in the following compositions by the weight ratio of PPO/Ultem: 100/0 (1), 80/20 (2), 60/40 (3), 40/60 (4), 10/90 (5) and 0/100 (6).*

The values of b_m^{exp} and $[\eta]_m^{exp}$ are determined from the slope and intercept of the linear lines in Fig. 1 plotted according to Eq.1. The experimental data and linear regression coefficients, r^2 were collected in Table 1. The closeness to the unity of the linear regression coefficients suggests a strong relation between reduced viscosity and concentration of the constituent polymers and their mixture. On the other words, the constituent polymers and their mixtures obey very well to the Eq. 1.

Table 1. Experimental dilute solution viscosity data of the blends and constituent polymers at 30 ^{0}C in chloroform.

PPO/Ultem 30 ^{0}C in chloroform	b_m^{exp} (cm^6/g^2)	$[\eta]_m^{exp}$ (cm^3/g)	r^2
100/0	0.0238	0.4569	0.9537
80/20	0.0241	0.4529	0.9721
60/40	0.0254	0.4470	0.9641
40/60	0.0260	0.4402	0.9749
10/90	0.0275	0.4357	0.9773
0/100	0.0286	0.4330	0.9843

According to the miscibility criterion, Δb_m defined by Krigbaum and Wall as $\Delta b_m = b_m^{exp} - b_m^{id}$ where b_m^{id} is found from Eq. (2) and b_{12}^{id} is found from Eq. (3), the components of a polymer mixture is miscible if Δb_m is positive due to attractive molecular interactions or immiscible if Δb_m is negative due to repulsive interactions. In the case of $\Delta b_m = 0$, neither attractive nor repulsive molecular interactions are present between polymers. The other miscibility criterion, $\Delta b_m'$ proposed by Catsiff and Hewett is obtained as a difference from $\Delta b_m' = b_m^{exp} - b_m^{id'}$ where $b_m^{id'}$ is obtained from Eq. (2) by using $b_{12}^{id'}$ defined in Eq. (4) instead of b_m^{id} defined in the Eq. (3). In this criterion, $\Delta b_m' > 0$ indicates miscibility or *vice versa*. The miscibility criterion on $\Delta[\eta]_m$ is described by Garcia et al. as $\Delta[\eta]_m = [\eta]_m^{exp} - [\eta]_m^{id}$ where $[\eta]_m^{id}$ is defined in the Eq. (5). According to this criterion, the components of the mixture is miscible if $\Delta[\eta]_m$ is negative and they are immiscible if $\Delta[\eta]_m$ is positive. Jiang et al. have described another parameter, β. The sign of β found from Eq. (6) indicates miscibility of the blend, i.e. $\beta > 0$ if miscibility exist whereas $\beta < 0$ if immiscibility exist between polymers in the mixture.

The all miscibility criteria of PPO/Ultem blends obtained using viscosity measurements were given in Table 2. According to the sign of the miscibility criteria of PPO/Ultem mixtures, i.e. Δb_m <0, $\Delta b_m' < 0$ and $\Delta[\eta]_m$ >0, PPO/Ultem blends are immiscible. However, the criterion, β increased from positive to negative values with the increase of Ultem in the blend. This indicates that PPO and Ultem blends show limited miscibility. It was seen that all miscibility criteria are close the zero. Low values of Δb_m, $\Delta b_m'$, $\Delta[\eta]_m$ and positive values of β observed in Table 2 may be due to weaker interaction between PPO and Ultem. As a result, PPO and Ultem are not fully compatible, but physically miscible up to a certain extent.

Table 2. Numerical values of polymer-polymer interaction coefficient for PPO/Ultem blends.

PPO/Ultem at 30 ^{0}C in chloroform	$-\Delta b_m$ (cm^6/g^2)	$-\Delta b_m'$ (cm^6/g^2)	$\Delta[\eta]_m$ (cm^3/g)	$-\beta$
80/20	0.001	0.001	0.001	-0.004
60/40	0.000	0.000	0.000	-0.005
40/60	0.001	0.001	-0.002	0.002
10/90	0.001	0.001	0.000	0.001

The FTIR spectra of PPO, Ultem and PPO/Ultem mixtures in composition: 80/20, 60/40, 40/60 and 10/90 at wave numbers between 1600 cm^{-1} and 1800 cm^{-1} are presented in Fig. 2.

The stretching vibration of carbonyl group of Ultem is seen at 1721.5 cm^{-1}. PPO has not any complicating absorption band in this region. A progressive blue-shifting up to 3 cm^{-1} was observed in the peak position of the carbonyl stretching frequency of Ultem by increasing PPO ratio. This shifting suggests a weak specific interaction proportional to the amount of PPO in the mixture. The criterion β suggests also that the increasing PPO amount increases the miscibility due to attractive forces between the constituent polymers. It can be stated that the criterion β is better than other miscibility criteria in Table 2 to make the miscibility of a mixture visible.

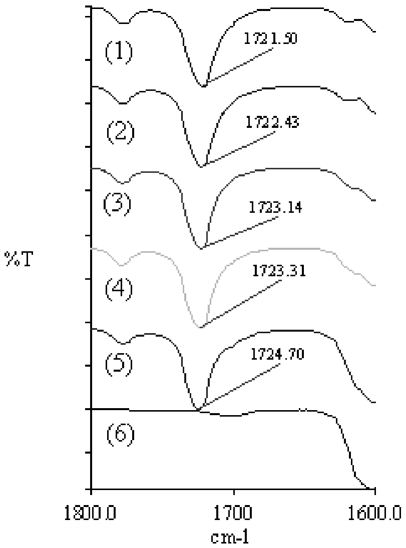


Fig. 2. FTIR spectra of PPO (6), PPO/Ultem (80/20) (5), PPO / Ultem (60/40) (4), PPO / Ultem (40/60) (3), PPO/Ultem (10/90) (2) and Ultem (1).

4. Conclusions

The miscibility of PPO/Ultem blends was investigated by viscosity and FTIR measurements. Using the experimental viscosity data, Δb_m, $\Delta b'_m$, $\Delta[\eta]_m$ and β were calculated. By increasing of PPO content in the mixture, the values of criterion β increased and the peak position of the carbonyl band of Ultem exhibited a blue-shifting. These results suggest that there is a weak attractive interaction between PPO and Ultem with increase of PPO content. Thus, it can be stated that the criterion β is better than other criteria to reveal the interaction between constituent polymers in a mixture, at least in this study.

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