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IMPROVEED COMPATIBILITY BETWEEN POLYSTYRENE and POLY (VINYLIDENE FLUORIDE) BY THE ADDITION OF UREA

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Abstract

The viscosity behaviour of dilute solution of Polystyrene-Poly(vinylidene fluoride) in dimethylformamide (DMF) in presence of urea has been studied at 25°C. The results show that the polymer mixtures are incompatible in DMF solution in the absence of urea. The influence of urea addition on the degree of compatibility of the polymer mixture has been studied in terms of the compatibility parameters (Δb_m , $\Delta b'_m$, $\Delta[\eta]_m$, α and β) respectively.

Keywords: Urea addition, Poly(vinylidene fluoride), Polymer blend compatibility, dilute solution viscometry method.

Introduction

During the last decade, Poly(vinylidene fluoride) (PVDF) has received much attension because of its extraordinary piezolectricity, pyroelctricity, processability, and wide practical uses. Physical modifications of polymers by blending PVDF with polymethacrylate have also attracted a considerable academic and industrial interest [1].However, few researches have been reported on the blends of PVDF and PS, perhaps due to several difficulities such as low increments of index of refraction dn/dc in dimethylformamide (DMF) and dimethylacetamide (DMAC), possible dehydrofluorination, presence of microgel and low solubility at room temperature in most solvents [2]. Polymer-polymer miscibility has been extensively studied by several techniques most of which require highly sophisticated instruments like dynamic mechanical measurements, differential scanning calorimetry, neutron scattering, inverse gas chromatography, electron microscopy, light scattering, FTIR spectroscopy and wide angle X-ray scattering [3]. Most of these techniques are expensive.An alternative simple, inexpensive and reliable method to analyze polymer miscibility in solution is viscometric technique [4-21].

In this paper, the effect of addition of different concentrations of urea on the compatibility of the ternary system DMF(1)/PS(2)/PVDF(3) has been performed. Many criteria have been used by researchers to determine polymer-polymer miscibility by the viscometric method like, , viscometric interaction parameter, b, intrinsic viscosity-composition plots, thermodynamic parameter, α , and modified thermodynamic parameter, β [11,15-16, 22-23], the compatibility of the polymer mixture is discussed through the sign of $\Delta b_m, \Delta b'_m, \Delta[\eta]_m, \alpha$ and β respectively.

Theoretical Background

In 1942 Huggins [24] proposed the following equation for the viscosity of a solution of polymers:

$$\eta = \eta_\circ (1 + [\eta]C + k[\eta]^2 C^2) \quad (1)$$

Where η and $\eta_\circ$ are the viscosity of the polymer solution and the solvent, respectively, C is the mass concentration of the solute, $[\eta]$ is the intrinsic viscosity of the solute and K is the Huggins coefficient. The specific viscosity $\eta_{sp,m}$ of a mixed polymer solution can be expressed as:

$$\eta_{sp,m} / C = [\eta]_m + k[\eta]^2{}_m C \quad (2)$$

Where $[\eta]_m$ is simply the sum of the intrinsic viscosity of the two different molecules [25], i.e:

$$[\eta]_m = [\eta]_2 \mathrm{w}_2 + [\eta]_3 \mathrm{w}_3 \quad (3)$$

Where w_2 and w_3 are the weight fraction of the polymer 2 and polymer 3.Combining equation (2) and (3), we have:

$$\eta_{sp,m} / C = w_2 [\eta]_2 + w_3 [\eta]_3 + k w_2^2 [\eta]_2^2 C + 2k w_2 w_3 [\eta]_2 [\eta]_3 C + k w_3^2 [\eta]_3^2 C \quad (4)$$

Eq.2 can be also written as:

$$\eta_{sp,m} = [\eta]_m C + bc^2 \quad (5)$$

Krigbaum and Wall [26] and Cragg-Bigelow [20] derived the following equation for $\eta_{sp,m}$ in mixed polymer solution

$$\eta_{sp,m} = [\eta]_2 C_2 + [\eta]_3 C_3 + b_{22} C_2^2 + b_{33} C_3^2 + 2 b_{23} C_2 C_3 \quad (6)$$

The parameters b_{22} and b_{33} are easily determined from the binary systems formed by polymer 2 and 3 in the solvent, respectively. Krigbaum and Wall defined an interaction coefficient between the two polymers, b_{23}, as $b_{23} = (b_{22} b_{33})^{1/2}$ only accounting for hydrodynamic interactions. This definition is not valid for systems that have negative values for ; therefore, the modification of Willamson and Wright [27] is used to evaluate b_{23} as $b_{23} = \left(b_{22} + b_{33}\right)/2$, as is usual in the literature [16, 28-29]. Equation (5) can be expressed in a weight average form since after some mathematical procedure [7], the general form for b_m is:

$$b_m = b_{22}w_2^2 + b_{33}w_3^2 + 2b_{22}^{1/2}b_{33}^{1/2}w_2w_3 \tag{7}$$

As discussed above, $b_{23}^{id.} = b_{22}^{1/2}b_{33}^{1/2}$, the experimental value of $b_{23}^{\exp.}$, is given by paraaleism as:

$$b_m^{\exp.} = b_{22}w_2^2 + b_{33}w_3^2 + 2b_{23}^{\exp.}w_2w_3 \tag{8}$$

Where $b_m^{\exp.}$ is obtained from the slope of Eq.(5). Then the criteria for compatibility in the polymer mixture are based on the comparison between experimental and ideal b_{23} values [21]. The values of $b_{23}^{\exp.} > b_{23}^{id.}$ represent compatibility between polymers, or would provide attractive molecular interactions, whereas the values of $b_{23}^{\exp.} < b_{23}^{id.}$ would provide incompatibility or repulsive molecular interactions.

To avoid the erroneous from the values of b_{23} in Eq.(7), depending on the signs of the viscometric interaction parameter, a new viscometric interaction parameter, b'_m , which can be defined as:

$$b_m'^{id.} = b_{22}w_2^2 + b_{33}w_3^2 \tag{9}$$

So compatibility will be possible if $b_{23}^{\exp.} > b_m'^{id.}$ and incompatibility if $b_{23}^{\exp.} < b_m'^{id.}$. The difference between the experimental and the ideal values of $\left[\eta\right]_m$ can be used as compatibility criterion [7]. This criterion states that compatibility exists if $\Delta[\eta]_m = \left([\eta]_m^{\exp} - [\eta]_m^{id}\right) < 0$ and incompatibility if $\Delta[\eta]_m = \left([\eta]_m^{\exp} - [\eta]_m^{id}\right) > 0$, where is determined from the intercept of plots of Eq.5 and from Eq.3 using the viscometric data on binary systems. Cragg and Bigelow [31] proposed the following equation:

$$\eta_{sp,m}/C = [\eta] + k_m[\eta]^2C = \left\{\left[\eta\right] + k_m' + \alpha + k \times \left[\left[\eta\right]_3 - \left[\eta\right]_2\right]/\left[\eta\right]^2\right\}\left[\eta\right]^2 C \tag{10}$$

If there is no formation of double molecules equation (7) becomes:

$$\eta_{sp,m}/C = [\eta] + k_m[\eta]^2C = \left[\eta\right] + \left(k_m' + \alpha\right)\left[\eta\right]^2 C \tag{11}$$

Under ideal conditions, i.e.when there are no thermodynamic interactions between the molecules (α =0), $k_m^{'}$ can be expressed as follows:

$$k_m^{'} = \left\{ k_2 [\eta]_2^2 w_2^2 + k_3 [\eta]_3^2 w_3^2 + 2(k_2 k_3)^{1/2} [\eta]_2 [\eta]_3 \right\} / \left([\eta]_2 w_2 + [\eta]_3 w_3 \right) \quad (12)$$

Sun et al [15] proposed another criteria for polymer-polymer miscibility in terms of a thermodynamic parameter, ($\alpha \geq 0$, miscible and α <0, immiscible), parameter α can be calculated using $\alpha = k_m - k_m^{'}$ where k_m is the experimental values of the polymer mixture which equal $b_{23} / [\eta]_2 [\eta]_3$. Jiang et al. [11] revised the criteria , α , by defining another parameter, β , as:

$$\beta = \frac{2 \Delta k w_2 w_3 [\eta]_2 [\eta]_3}{\left(w_2 [\eta]_2 + w_3 [\eta]_3 \right)^2} \quad (13)$$

Where

$$\Delta k = k_{23} - \sqrt{k_2 k_3} \quad (14)$$

and, $k_2 = \frac{b_{22}}{[\eta]_2^2}$, $k_3 = \frac{b_{33}}{[\eta]_3^2}$, $k_{23} = \frac{b_m}{[\eta]_m^2}$. Thus when $\beta \geq 0$, compatibility exists and when β <0, incompatibility exists.

Results and Discussion

Fig.1 shows Huggins plot ($\eta_{sp,m} / C$ vs.C) for the binary systems at 25°C at different urea concentrations. Using data with Eq. (5), the intrinsic viscosity and viscometric interaction parameter thus obtained for each polymer at different urea concentrations are tabulated in Table 1. It can be seen that the intrinsic viscosity of PVDF at urea solution concentration of 0.50 M is larger than intrinsic viscosity of PS at the same urea concentration. This behavior could be attributed to the urea-polymer and the urea-solvent interactions which is better in case of PVDF than PS. The experimental results for the reduced viscosity in the ternary system, DMF (1)/PS (2)/PVDF (3) of constant polymer concentrations ranging from 0.5-0.9 g/dl, and varying the urea concentration from 0.0 to 0.65 mol/L at weight fraction of 0.75 g in DMF at 25°C are as shown in Fig.2. The values of $b_m^{\mathrm{exp.}}$ and $[\eta]_m^{\mathrm{exp}}$ tabulated in Table 2, indicate an increase in $[\eta]_m^{\mathrm{exp}}$ accompanied by a decrease in $b_m^{\mathrm{exp.}}$ when the concentration of urea is 0.50 M at w_2 = 0.75 g i.e. when the amount of PVDF is predominated in the polymer solution. A reasonable explanation is that the attractive interactions between PS and PVDF in 0.50 M urea concentration at $w_2 = 0.75$g would increase the intermolecular excluded volume and the attraction of PS/PVDF coils in 0.50 M urea concentration and thus increase in the intrinsic viscosity.

The compatibility of the two polymers was investigated by considering the compatibility criteria based on the difference between the experimental and the ideal values of $b_m, b_m'^{id.}, [\eta]_m$, α and β respectively. The compatibility criteria, $b_m, b_m'^{id.}$ and $[\eta]_m$ were calculated using equations 3,7 and 9 respectively for ideal values, the experimental values for the ternary mixture PS/PVDF in DMF with different concentrations of urea at weight fraction of $w_2 = 0.75$g are tabulated in Table 2. The compatibility data listed in Fig.3 show the dramatic evolution of Δb_m and $\Delta b_m'$ for constant PS weight fractions (0.75g) , the values increase when the concentration of urea becomes 0.50 M. The results show that the polymer mixture of PS(2)/PVDF is incompatible in DMF solution in the absence of urea, that means there is strong repulsion interaction of macromolecules, so this negative deviation reflects a decrease of the effective hydrodynamic specific volume, which suggests contraction of the coil due to unfavorable PS/PVDF interactions. It can also be seen that the maximum in $\Delta[\eta]$ seems to be matched by a minimum in Δb_m or $\Delta b_m'$ values. This suggests that the degree of compatibility of the two polymers can be improved by the addition of 0.50 M urea to the polymer mixture. Fig. 3 shows the variation of α and β for constant PS weight fraction with varying amounts of urea and The results show that the polymer mixture of PS(2)-PVDF(3) is incompatible in DMF solution in the absence of urea for all compositions of PS. The addition of 0.50 M of urea solution to the polymer mixture will increase the α values especially when $w_2 = 0.75$ leading to increase the compatibility of the polymer mixture.

Experimental

Chemicals and reagents

PS with average molecular weight of 350,000 g/mol and PVDF with average molecular weight of 180,000 g/mol were purchased from Aldrich (USA). All other chemicals and reagents were c.p.grade products.

Viscometric measurements

All measurements were performed at 25°C ± 0.1°C by Cannon-Fensk type capillary viscometer equipped with a model OSK 2876. The stock solution of each ternary system or binary was prepared by dissolving the polymer samples in filtered DMF-urea solution. The concentration of polymer mixture in the solution was 1.0

g/dL. At least five lower concentrations were made by adding appropriate aliquots of urea to the solution. To measure each solution, 12 ml of the sample were loaded to minimize drainage errors in the viscometer and placed in a thermostat. Viscosity measurements were started after an equilibrium time of 5-10 min. The elution time of each solution is then determined as average of several readings. The dilution procedure was finished after the solution volume reaches 21 ml. Kinetic energy corrections were taken into account for evaluating the intrinsic viscosity $[\eta]$ which was determined by extrapolation to infinite dilution (zero solute concentration) of Huggins plots, i.e. $\eta_{sp,m}/C$ versus C. The uncertainly in the observed measurements was estimated to be less than 5 % for the system.

Table.1 Intrinsic Viscosity $[\eta]$ and viscometric interaction parameter b for the binary polymers in DMF as solvent at different concentration of urea at 25°C

Polymer	Conc. Urea(mol/L)	$[\eta]$	b
Polystyrene	0.00	1.301	-0.8465
	0.15	1.116	-0.7565
	0.25	1.159	-0.7772
	0.50	0.5809	-0.2526
	0.65	0.7527	-0.6444
Poly(Vinylidenefluoride)	0.00	1.874	-1.069
	0.15	1.682	-0.9109
	0.25	1.628	-0.7768
	0.50	1.799	-1.115
	0.65	1.500	-0.8137

Table 2. Experimental viscometric data for the ternary mixture PS/PVDF in DMF as solvent with different concentrations of urea at weight fraction 0.75g at 25°C.

Conc. Urea (mol/L)	$b_m^{\exp}$	$[\eta]_m^{\exp}$	Δb_m	$\Delta b_m^{/}$	$\Delta[\eta]_m$
0.00	-0.8776	1.419	-0.6913	-0.3346	-0.025
0.15	-0.7378	1.197	-0.5666	-0.2553	-0.0605
0.25	-0.8089	1.277	-0.6146	-0.3232	0.001
0.50	-0.3998	1.475	-0.3856	-0.1866	0.5896
0.65	-1.009	1.0261	-0.8681	-0.5965	0.0866

Table 3. Experimental viscometric data for the ternary mixture PS/PVDF in DMF as solvent with different concentrations of urea at 25°C.

Mixture DMF	Conc. Urea (mol/L)	W_2	α	β	k_m^{exp}
PS/PVDF	0.00	0.25 0.50 0.75	-0.1521 -0.2863 -0.1510	-0.3878 -0.5830 -0.5227	-0.3440 0.3692 -0.4358
	0.15	0.25 0.50 0.75	-0.2176 -0.430 -0.3790	-0.3750 -0.5860 -0.5357	-0.3788 -0.4311 -0.5149
	0.25	0.25 0.50 0.75	-0.2096 -0.4192 -0.3431	-0.4339 -0.5626 -0.5033	-0.3376 -0.4192 -0.5015
	0.50	0.25 0.50 0.75	-0.1087 -0.0645 0.2806	-0.2395 -0.4543 -0.4179	-0.4058 -0.5270 -0.7319
	0.65	0.25 0.50 0.75	-0.3233 -0.6606 -0.808	-0.3666 -0.5554 -0.7211	-0.4959 -0.4667 -0.9588

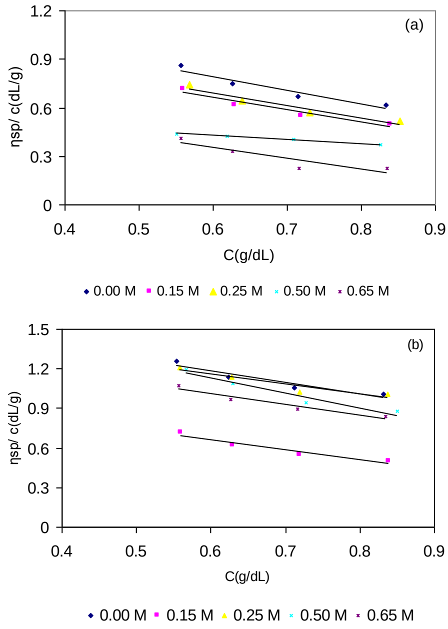

Fig.1 Plots of reduced viscosity versus concentration for binary polymers (a) PS (b) PVDF in DMF with different concentrations of urea at 25°C.

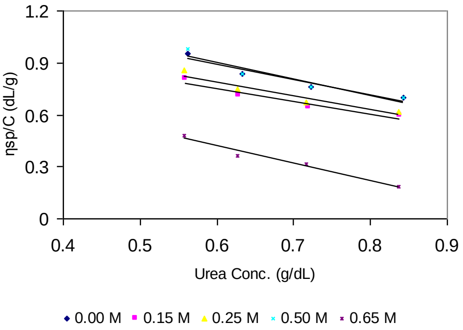

Fig. 2 The variation of reduced viscosity versus concentration for PS/PVDF at weight fraction 0.75 g in DMF with different concentrations of urea.

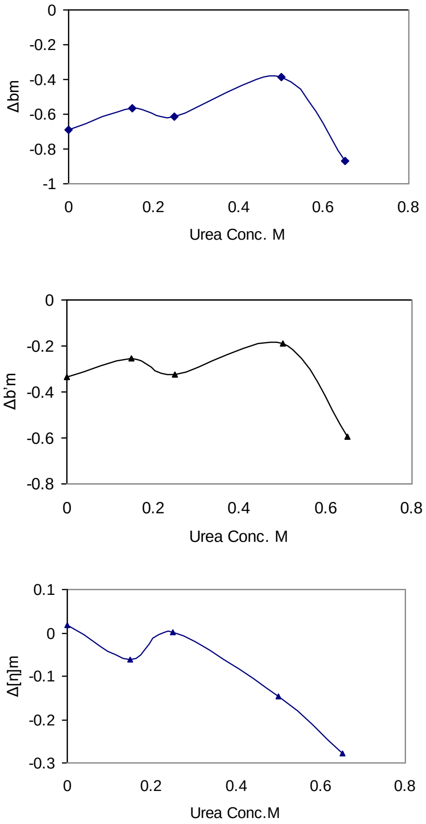

Fig. 3 Plots of compatibility magnitude as a function of concentration of urea for the polymer mixture PS/PVDF at $W_2 = 0.75$g in DMF.

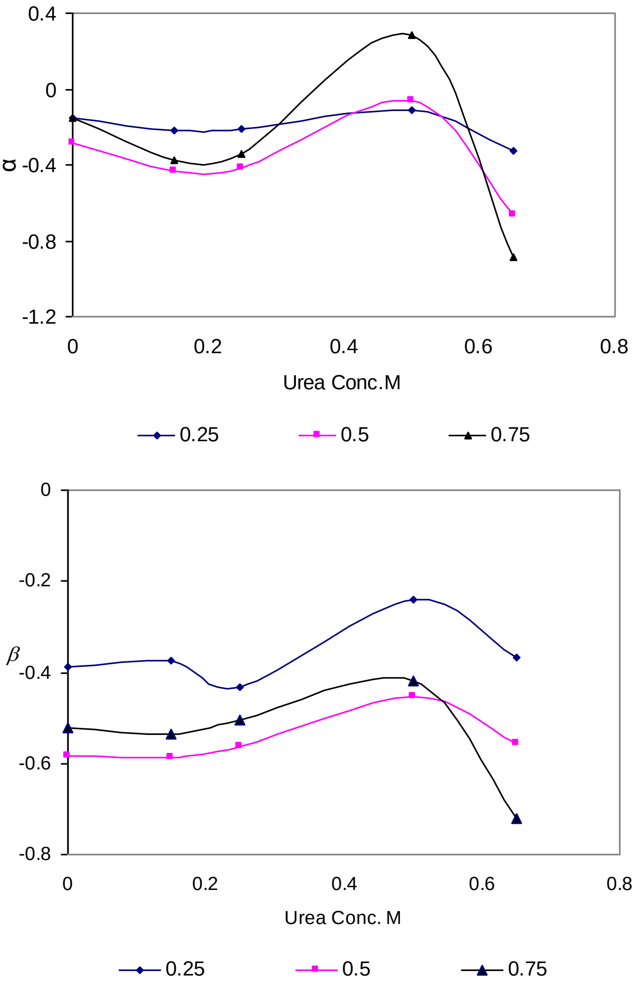

Fig. 4 Plots of compatibility magnitude as a function of concentration of urea for the polymer mixture PS/PVDF at different weight fractions in DMF.

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