

IT STUDIES ON THE EFFECT OF UREA ON THE COMPATIBILITY OF PMMA/PVC MIXTURES IN DMF BY A DILUTE- SOLUTION VISCOMETRY METHOD

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Abstract The interaction between poly(methymethacrylate) (PMMA) and poly(vinyl chloride) (PVC) has been studied in dilute urea solutions of dimethylformamide (DMF) at 28 °C using a dilute solution viscometry method. The results show that the polymer mixtures are compatible in DMF solution in the absence of urea. The influence of urea addition on the degree of compatibility of the polymer mixtures has been studied in terms of the compatibility parameters (Δb_m and $\Delta[\eta]_m$). It was found that the compatibility of the polymer mixtures is decreased with increasing urea addition, passing through a minimum at 0.5 M urea.

Keywords Urea addition, Polymer blend compatibility, Intrinsic viscosity and dilute solution viscometry method

INTRODUCTION

Because of its simplicity and importance in the characterization of the intermolecular interaction between two different polymers in solution, the viscosity study on ternary system of two different polymers and a solvent has been a subject of continuing interest^[1–14]. The viscosity measurement of ternary system can be performed by two techniques: firstly the polymer solvent method^[15] is performed by dissolving polymer A (guest polymer) into a solution containing the second polymer B (host polymer) at a constant concentration, this method has received considerable attentions in recent years^[16, 17–20]. The second method is performed by dissolving the polymers A and B simultaneously in a pure solvent. The viscometric interaction parameter, b_m , characterizes both hydrodynamic and thermodynamic interaction between like chains of both polymers, and determines the polymer-polymer compatibility^[21–25]. The intrinsic viscosity of the ternary systems $[\eta]_m$ indicates whether the interactions between unlike i-j polymer segments are attractive or repulsive.

In this paper, the effect of addition of different concentrations of urea on the compatibility of the ternary system DMF (1)/PMMA (2)/PVC (3) has been performed. The compatibility of the mixture is discussed in two different ways through the sign of Δb_m , and through the sign of $\Delta[\eta]_m$, where the intrinsic viscosity is handled as an extra property of the solution.

THEORETICAL

The theoretical consideration starts from the derivation by Krigbaum and Wall^[1] and Cragg-Bigelow^[2]. The specific viscosity $\eta_{sp, m}$ of a mixed polymer solution can be expressed as follows:

$$\eta_{sp, m} = [\eta_2]c_2 + [\eta_3]c_3 + b_{22}c_2^2 + b_{33}c_3^2 + 2b_{23}c_2c_3 \quad (1)$$

where $[\eta_2]$ is the intrinsic viscosity of component 2 alone in the solution with common solvent, c_2 is the

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concentration of component 2 in mixed polymer solution, and b_{23} is the interaction coefficient for the mixture of components 2 and 3. The coefficient b_{22} is related to the constant, K , in the Huggins equation^[26], when component 2 is in the solution alone (This also applies to b_{22}).

$$\frac{(\eta_{sp})_m}{c_m} = [\eta]_m + K[\eta]^2 c_m \quad (2)$$

The relationship between b_{22} and K is written as:

$$b_{22} = K_2[\eta_2]^2 \quad (3)$$

The interaction coefficient between the two polymers (b_{23}) according to Williamson and Wright^[27], can be expressed as

$$b_{23} = (b_{22} + b_{33})/2 \quad (4)$$

Equation (2) can be expressed in a weight-average form since after some mathematical procedure^[28], the general form for b_m is:

$$b_m = b_{22}w_2^2 + b_{33}w_3^2 + 2b_{22}^{1/2}b_{33}^{1/2}w_2w_3 \quad (5)$$

This equation is used to define the theoretical value of the global viscometric interaction parameter between chains of different polymers.

$$b_{23}^{\text{Theor}} = b_{22}^{1/2}b_{33}^{1/2} \quad (6)$$

On the other hand, the experimental value of this parameter, b_m^{exp} , is given by parallelism as:

$$b_m^{\text{exp}} = b_{22}w_2^2 + b_{33}w_3^2 + 2b_{23}^{\text{exp}}w_2w_3 \quad (7)$$

where b_m^{exp} is obtained from the slope of Eq. (2), and b_{22} and b_{33} are easily determined from the binary systems formed by polymers 2 or 3 in the solvent respectively through Eq. (1). Then, the criteria for compatibility in the polymer mixture are based on the comparison between experimental and theoretical b_{23} values^[1]. The values of $b_{23}^{\text{exp}} > b_{23}^{\text{theor}}$ represent compatibility between polymers, or would provide attractive molecular interactions, whereas the values of $b_{23}^{\text{exp}} < b_{23}^{\text{theor}}$ would provide incompatibility or repulsive molecular interactions. In the hypothetical case where $b_{23}^{\text{exp}} = b_{23}^{\text{theor}}$ it would signify that polymer chains do not interact, either favorably or unfavorably. The second compatibility criterion is based on the difference between the experimental and theoretical values of $[\eta]_m$. Therefore, this criterion will be used to explain the compatibility between two polymers, where, they would be compatible if $\Delta[\eta]_m = ([\eta]_m^{\text{exp}} - [\eta]_m^{\text{theor}}) < 0$, or incompatible if $\Delta[\eta]_m = ([\eta]_m^{\text{exp}} - [\eta]_m^{\text{theor}}) > 0$, where $[\eta]_m^{\text{exp}}$ is determined from the intercept of plots of Eq. (2) and $[\eta]_m^{\text{theor}}$ can be calculated by using the mathematical derivation^[28].

$$[\eta]_m = \sum_i [\eta]_i w_i = [\eta]_2 w_2 + [\eta]_3 w_3 \quad (8)$$

EXPERIMENTAL

Chemicals and Reagents

PMMA with an average molecular weight of 120,000 g/mol and PVC with an average molecular weight of 43,000 g/mol were purchased from Aldrich (USA). All other chemicals and reagents used were c.p. grade products.

Viscometric Measurements

All measurements were performed at $28^\circ\text{C} \pm 0.1^\circ\text{C}$ by a Cannon-Fensketype capillary viscometer equipped with a model OSK 2876. The stock solution of each ternary or binary system 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 was loaded to minimize drainage errors into the viscometer and placed in a thermostat. Viscosity measurements were started after an equilibration time of 5–10 min. The elution time of each solution is then determined as an 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.* η_{sp}/c versus c .

RESULTS AND DISCUSSION

Figure 1 shows the variation of reduced viscosity of the binary systems, DMF (1)-PMMA (2) and DMF (1)-PVC (3) against the urea concentration. It can be seen that the reduced viscosity of polymer with constant concentration decrease gradually with increasing concentration of urea at 28°C . This behavior could be attributed to the urea-polymer and the urea-solvent interactions which may in turn attenuate the polymer-polymer and the polymer-solvent interactions. This suggests that the interactive network formed between chain elements of the polymer may be disrupted in the presence of urea. The experimental results for reduced viscosity in the ternary system, DMF (1)/PMMA (2)/PVC (3) of constant polymer concentrations ranging from 0.4–0.8 g/dL and varying the urea concentration from 0.0 to 0.85 mol/L at 28°C are shown in Fig. 2. At finite polymer concentrations the polymer-polymer interaction is of importance, and this effect can be illustrated by the interaction parameter, b , defined by the Huggins' equations (Eq. 2 and Eq. 3).

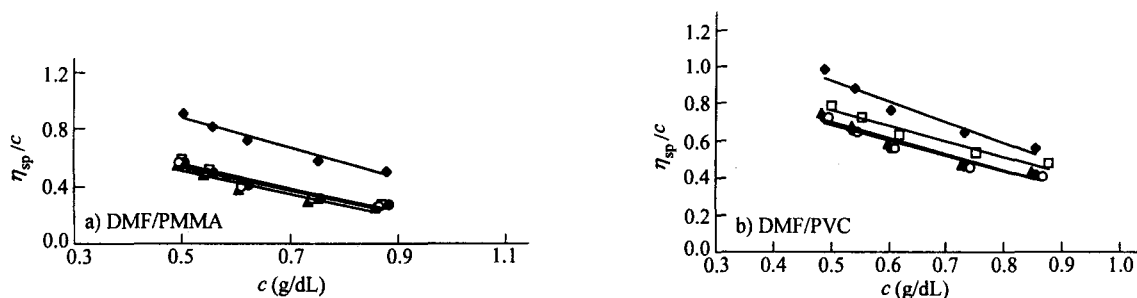


Fig. 1 Plots of reduced viscosity versus concentration for binary polymers (a) PMMA (b) PVC in DMF with different concentrations of urea

◆ 0.0 mol/L urea; □ 0.25 mol/L urea; ● 0.50 mol/L urea; ▲ 0.75 mol/L urea; ○ 0.85 mol/L urea

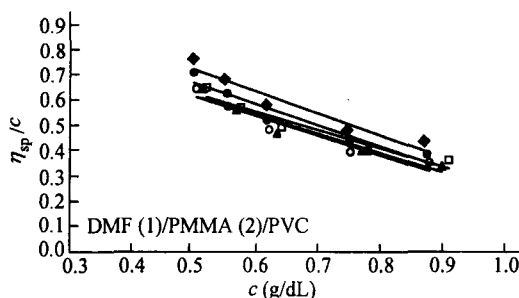


Fig. 2 The variation of reduced viscosity versus concentration for PMMA/PVC at weight fraction 0.50 g in DMF with different concentrations of urea

The reduced viscosities at different polymer concentrations were fitted by using the Huggins' equation. Plots of the reduced viscosity against polymer concentrations for binary systems are shown in Fig. 1. From the intercepts and slopes of the linear plots, the intrinsic viscosities, $[\eta]$ and viscometric interaction parameters, b , were determined respectively. The obtained values of $[\eta]$ and b at different urea concentrations are listed in Table 1.

Table 1. Experimental and theoretical viscometric data for the ternary mixture PMMA/PVC in DMF as solvent with different concentrations of urea at 28°C

Mixture DMF	Conc. Urea (mol/L)	W_2	$[\eta]_m^{\text{exp}}$ (dL/g)	b_m^{exp} (dL/g) ²	$[\eta]_m^{\text{id}}$ (dL/g)	b_m^{id} (dL/g) ²	Δb_m (dL/g) ²	$\Delta[\eta]_m$ (dL/g)
PMMA/PVC	0.00	0.25	1.250	-0.878	1.380	-1.071	0.193	-0.130
		0.50	1.153	-0.866	1.265	-1.008	0.142	-0.112
		0.75	1.051	-0.871	1.150	-0.946	0.075	-0.098
	0.25	0.25	1.130	-0.839	1.123	-0.828	-0.025	0.022
		0.50	0.987	-0.724	1.029	-0.828	0.075	-0.053
		0.75	0.983	-0.790	1.019	-0.832	-0.004	0.008
	0.50	0.25	1.149	-0.867	1.047	-0.807	-0.060	0.101
		0.50	1.084	-0.840	1.004	-0.791	-0.048	0.080
		0.75	1.036	-0.871	0.960	-0.775	-0.096	0.075
	0.75	0.25	1.039	-0.828	1.082	-0.859	0.030	-0.042
		0.50	0.994	-0.759	1.020	-0.836	0.077	-0.026
		0.75	0.916	-0.747	0.959	-0.813	0.066	-0.043
	0.85	0.25	1.082	-0.865	1.058	-0.824	-0.040	0.024
		0.50	0.999	-0.772	1.012	-0.813	0.040	-0.013
		0.75	0.962	-0.818	0.967	-0.801	-0.017	-0.004

Before discussing the compatibility of the two polymers in the ternary system, it is interesting to gain further insight into the effect of urea addition on the viscosity properties. The most prominent feature in Fig. 1 is a decrease in $[\eta]$ accompanied by an increase in b as the concentration of urea increases from 0.0 to 0.85 mol/L. This decrease in $[\eta]$ can be attributed to the destruction of macromolecules as a result of the hydrogen bond formation between the hydrogen atom of urea and the oxygen atom of the carbonyl group of PMMA. The existence of hydrogen bonds may lead to the formation of urea-polymer complexes, resulting in a contraction of the polymer chains. The observed decrease in $[\eta]$ is, after the addition of 0.85 mol/L urea, accompanied by the appearance of turbidity, which could explain the formation of insoluble urea-polymer complexes.

The compatibility of the two polymers was investigated by considering the compatibility criteria based on the difference between the experimental and theoretical values of $[\eta]$ and b . The compatibility criteria, Δb_m and $\Delta[\eta]_m$, tabulated in Table 1, were calculated using equations 1–8 which are given in the theoretical part.

The negative b_m values, collected in Table 1, are consistent with the attractive interactions between the polymer chains in the polymer mixture. There is no value in paying attention to the sign of b_m values or to the sign of $\Delta b_m = (b_m^{\text{exp}} - b_m^{\text{theor}})$, which gives information on the compatibility between the two polymers in the mixture. On the other hand, negative b_m values indicate that the polymer chains prefer to interact with themselves. In considering the signs of Δb_m and $\Delta[\eta]_m$, based on the difference between the experimental and theoretical values of b_m and $[\eta]_m$ listed in Table 1, the compatibility between the two polymers occurs when $\Delta b_m > 0$ and $\Delta[\eta]_m < 0$. On the contrary, the two polymers would be incompatible if $\Delta b_m < 0$ and $\Delta[\eta]_m > 0$. Taking the above comments into account, the influence of urea addition on the compatibility may well be explained in terms of such parameters (Δb_m and $\Delta[\eta]_m$).

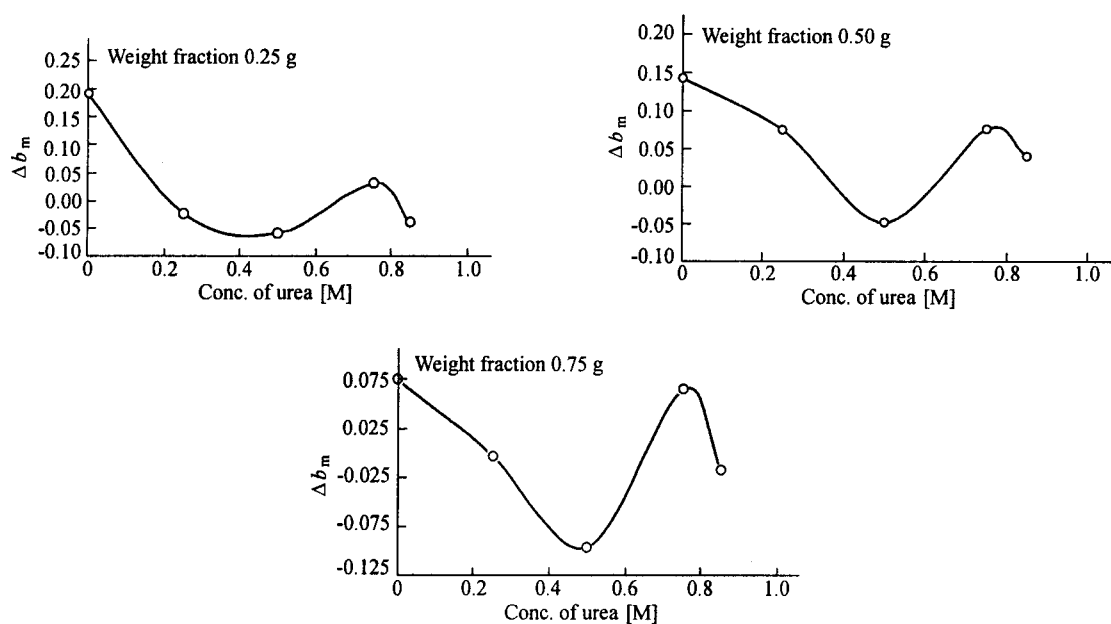


Fig. 3 Plots of compatibility magnitude as a function of concentration of urea for the polymer mixture PMMA/PVC at different weight fractions in DMF

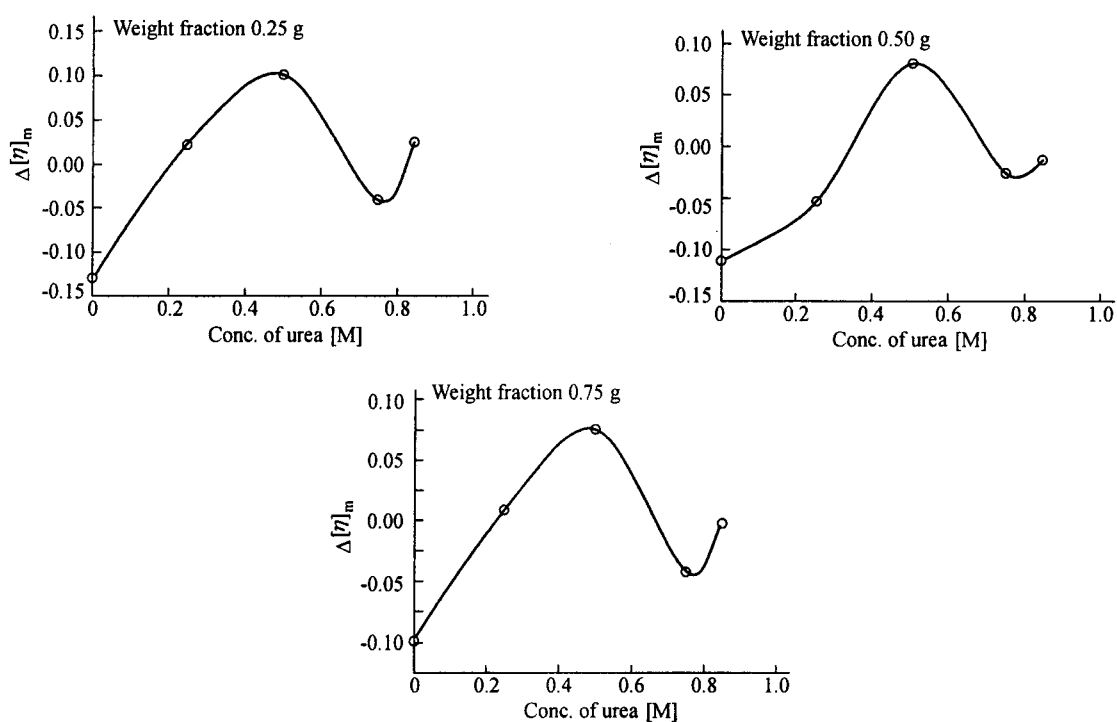


Fig. 4 Plots of compatibility magnitude as a function of concentration of urea for the polymer mixture PMMA/PVC at different weight fractions in DMF

The compatibility data listed in Figs. 3 and 4 show the dramatic evolution of Δb_m and $\Delta[\eta]_m$ for constant PMMA weight fractions with varying amounts of urea due to strong interactions at certain compositions. The

results show that the polymer mixture of PMMA(2)-PVC(3) is compatible in DMF solution in the absence of urea. The addition of urea to DMF solution will increase the $\Delta[\eta]_m$ and decrease the Δb_m values. It can also be seen that the maximum in $\Delta[\eta]_m$ seems to be matched by a minimum in Δb_m value. This suggests that the degree of compatibility of the two polymers was decreased by increasing the urea concentration. The degree of compatibility approaches its minimum at 0.50 mol/L urea. As the urea concentration exceeds 0.50 mol/L, a slight increase in compatibility is observed. Without urea in the system, Δb_m decreases and $\Delta[\eta]_m$ increases by increasing the weight fraction of PMMA in the polymer mixture. On the other hand, the compatibility in the absence of urea is more susceptible to the weight fraction of PMMA than that in the presence of urea. This behavior may be attributed to the gradual protection of the active site of PMMA by urea molecules through the formation of hydrogen bonds.

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