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MISCIBILITY STUDIES OF PVC/PMMA BLENDS IN TETRAHYDROFURAN BY VISCOSITY, DENSITY, REFRACTIVE INDEX AND ULTRASONIC VELOCITY METHOD

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The density and Coefficient of Viscosity for Polyvinyl chloride/poly(methyl methacrylate) (PVC/PMMA) blends in tetrahydrofuran at 303.15 K and 313.15 K were measured. These measured parameters were then used to estimate few other related physical quantities like Huggin's constants and the interaction parameters μ and α proposed by Chee and Sun et al. to identify the molecular interaction arising in the mentioned polymer blend solutions. The peculiar deviation confirms the structural changes in the solution of blends.

Keywords: viscosity, polymer blends, poly(methyl methacrylate), poly (vinyl chloride), molecular interaction.

1. Introduction

Polymers play an important role in all branches of industry today. Many notable advances in technology have followed the exploitation of properties offered by new polymeric materials like blends, composites, etc. Polymer blends are prepared by physical mixing of two or more polymers. The resulting system often exhibits properties that are superior to any one of the component polymers [1-5]. However, the manifestation of superior properties depends upon the miscibility of homo-polymers at the molecular scale. The miscibility results in different morphology of the blends, ranging from a single phase system to two phase or multiphase systems [2]. The basis of polymer-polymer miscibility may arise from several different interactions, such as hydrogen bonding, dipole-dipole forces, and charge transfer complexes for homo-polymer mixtures [1].The importance of polymer blending has increased in recently, because of the preparation of polymeric materials with desired properties, low basic cost and improved processability. Polymer blends are physical mixtures of structurally different polymers or copolymers, which interact through secondary forces with no covalent bonding (Krause, 1978) and are miscible at the molecular level. As stated above, several factors contribute to polymer–polymer miscibility, including the aorementioned hydrogen bonding, dipole– dipole forces and charge transfer complexes for homopolymer mixtures (Varnell & Coleman, 1981; Varenell, Runt, & Coleman, 1983; Woo, Barlow, & Paul, 1986). There are several techniques for studying the miscibility of the polymer blends (Cabanclas, Serrano, & Baselga, 2005; Crispim, Rubira, & Muniz,1999; Jiang & Han, 1998; Patel, 2004; Ping, 1997). Some of these techniques are complicated, costly and time consuming, hence it is desirable to identify simple, low cost and rapid techniques to study the miscibility of polymer blends. Chee (1990) and Sun, Wang, and Fung (1992) have suggested a viscometric method for the study of polymer–polymer miscibility in solution, while Singh and Singh (1983, 1984)) have suggested the use of ultrasonic velocity and viscosity measurements for testing the same properties. Palladhi and Singh (1994a, 1994b) have shown that the variation of ultrasonic velocity and viscosity with blend composition is linear for miscible blends and non-linear for immiscible blends. Recently, (Varada Rajulu, Reddy, and Ranga Reddy (1998) and Varada Rajulu, Siddaramaiah, and Reddy (1998) have used ultrasonic and refractometric techniques to study the miscibility of polymer blends.

2. Experimental

PVC (Chemplast Sanmar limited Chennai) and PMMA (grade LG 2 Sumitomo chemical Singapore), tetrahydrofuran from Fisher Scientific were used after purification by fractional distillation. A dilute polymer solution of 1% w/v was prepared for viscometric studies. Stock solutions of polymers and the blends of PVC/PMMA of different compositions, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30 and 80/20, were prepared in tetrahydrofuran. Viscosity measurements at 303.15K and 313.15K were made using an Ostwald viscometer. The total weight of the two components in the solution was always maintained at 1 g/dL. Different temperatures were maintained in a thermostat bath, with a thermal stability of ±0.05 K.

3. Results and discussion

Viscometry is a simple and effective technique for monitoring the interactions in polymer blend solutions. From viscometric measurements, the relative and reduced viscosities of pure polymers and their blends were obtained. Figures 1 and 2 shows the Huggin's plots for the PVC/PMMA at 303.15 K and 313.15 K for different weight fractions of polymer 1 and polymer 2 (W_1: W_2), respectively. The values of K_H were determined by extrapolation to infinite dilution of the Huggin's plots and the values of 'b' are the slopes of the plots. This has been compared by results obtained from calculation from Huggin's equation. The figure indicates the considerable higher slope variation for PVC/PMMA blend compositions. This may be attributed to the mutual attraction of macromolecules in solution, because of the increase of hydrodynamic and thermodynamic interaction. Hence, the PVC/PMMA blend is found to be miscible. Below this critical concentration, a sharp decrease in the slope is observed in the Huggin's plot, because of the phase separation. To quantify the miscibility of the polymer blends Chee (1990) [4] suggested that the general expression for interaction parameter when polymers are mixed in weight fractions W_1 and W_2 is as follows:

$$\Delta B = \frac{b - \bar{b}}{2w_1 w_2},$$

where $\bar{b} = W_1 b_{11} + W_2 b_{22}$ in which, b_{11} and b_{22} are the slopes of the viscosity curves for the pure components. The coefficient b is related to the Huggin's coefficient K_H as

$$b = K_H [\eta]^2,$$

for ternary system, the coefficient b is also given by

$$b = w_1^2 b_{11} + w_2^2 b_{22} + 2w_1 w_2 b_{12},$$

where b_{12} is the slope for the blend solution. Using these values, Chee (1990) defined a more effective parameter as follows:

$$\mu = \frac{\Delta B}{\{[\eta]_2 - [\eta]_1\}^2},$$

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions. The blend is miscible when $\mu \geqslant 0$ and immiscible $\mu < 0$.

The reduced viscosity data for the PVC/PMMA blends at different compositions at 303.15 K and 313.15 K have been recorded in tables 1 and 2 respectively. Recently, Sun et al. (1992) have suggested a new formula for the determination of polymer miscibility as follows:

$$\alpha = Km - \frac{K_1[\eta]_1^2 w_1^2 + K_2[\eta]_2^2 w_2^2 + 2\sqrt{K_1 K_2}[\eta]_1[\eta]_2 w_1 w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2}$$

where K_1, K_2 and Km are the Huggins's constants for individual component 1, 2 and the blend respectively. The long-range hydrodynamic interactions are considered while deriving this equation. Sun et al. (1992) have suggested that a blend will be miscible when $\alpha \geqslant 0$ and immiscible when $\alpha < 0$.

Table 1. The reduced viscosity data for PVC/PMMA and their blends in tetrahydrofuran at 303.15 K at different concentrations

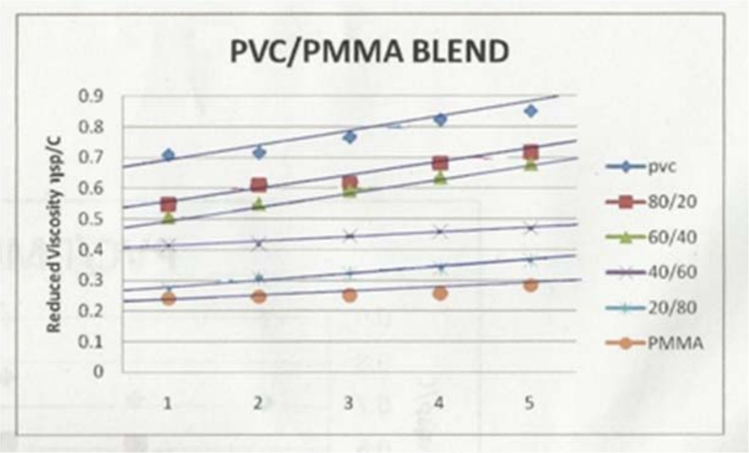
Concentration (g/dl)	Reduced viscosity of different composition (dl/gm)					
	100/0 (PVC)	80/20	60/40	40/60	20/80	0/100 (PMMA)
0.2	0.70892	0.54775	0.50596	0.41444	0.26903	0.24045
0.4	0.71498	0.61076	0.549721	0.41869	0.3072	0.24592
0.6	0.76668	0.61561	0.593481	0.44595	0.31992	0.25133
0.8	0.82374	0.68196	0.637241	0.45928	0.3378	0.25681
1.0	0.85206	0.71755	0.681002	0.4697	0.36366	0.28308

Table 2. The reduced viscosity data for PVC/PMMA and their blends in tetrahydrofuran at 313.15 K at different concentrations

Concentration (g/dl)	Reduced viscosity of different composition (dl/gm)					
	100/0 (PVC)	80/20	60/40	40/60	20/80	0/100 (PMMA)
0.2	0.62975	0.50467	0.46226	0.37212	0.25176	0.22441
0.4	0.66873	0.53613	0.48616	0.39112	0.27847	0.23009
0.6	0.7077	0.56759	0.51165	0.41013	0.30519	0.23577
0.8	0.74668	0.59905	0.53078	0.42913	0.33191	0.24145
1.0	0.78564	0.61095	0.55945	0.44814	0.35863	0.27543

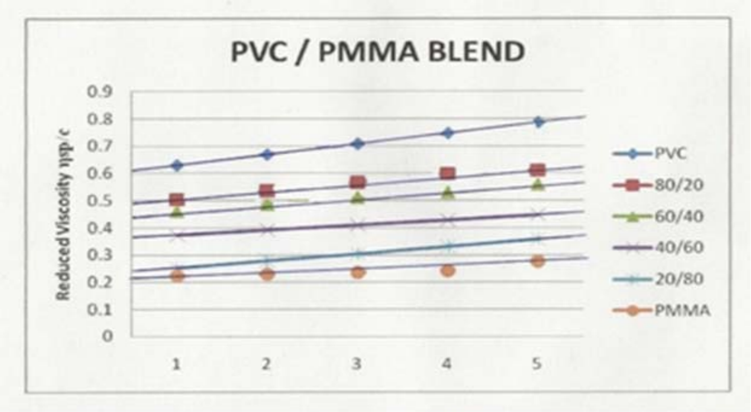
The Huggins's plots for the pure components (PVC and PMMA) and their blends at 303.15 K and 313.15 K are shown in Fig. 1 and Fig. 2 respectively. The figure indicates the considerable higher slope variation for 80/20 and 60/40 PVC/PMMA blend compositions. This may be attributed to the mutual attraction of macromolecules in Solution, because of the increase of hydrodynamic and thermodynamic interaction. Hence PVC/PMMA blend is found to be miscible, Below this critical concentration, a sharp decrease in the slope is observed in the Huggins's plot because of the phase separation.

Blends are miscible in all compositions except the (40/60) at both temperatures mentioned above. Immisciblity of the blend (40/60) has been supported by the fact that both interaction parameters μ and α were found to be negative at both temperatures. μ and α parameters for the (60/40) blend at 313.15 K have been found to be slightly negative,



Concentration (g/dl)

Fig. 1. Plot of ηsp/C *vs.* concentration for PVC/PMMA/THF ternary systems at 303.15 K



Concentration (g/dl)

Fig. 2. Plot of ηsp/C *vs.* concentration for PVC/PMMA/THF ternary systems at 313.15 K

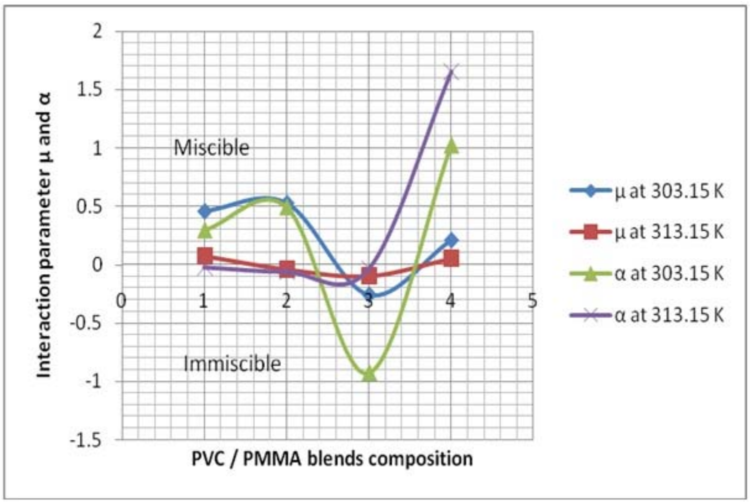


Fig. 3. Effect of temperature on the interaction parameter μ and α of PVC/PMMA blend in at 303.15 K and 313.15 K

Table 3. Interaction parameters and Huggins's constants of PVC/PMMA blends at 303.15 K

PVC/PMMA	$[\eta]$	K_H	μ	α
100/0(PVC)	0.656462	0.4517727	-	-
80/20	0.5146216	0.7798907	0.4575677	0.2949006
60/40	0.4622	1.0242064	0.5261955	0.492312095
40/60	0.39692792	0.472713180	-0.25565	-0.9242617
20/80	0.2527247	1.7430205	0.2102835	1.0213427
0/100(PMMA)	0.2261522	0.9569496	-	-

Table 4. Interaction parameters and Huggins's constants of PVC/PMMA Blends at 313.15 K

PVC/PMMA	$[\eta]$	K_H	μ	α
100/0(PVC)	0.590784	0.5582969	-	-
80/20	0.481523	0.59053915	0.071553727	-0.0189689
60/40	0.4381608	0.6241702	-0.04432155	-0.0581165
40/60	0.353113	0.558296996	-0.10198976	-0.0310992
20/80	0.2250383	2.6379087	0.048943006	1.65734316
0/100(PMMA)	0.2067026	1.3546565	-	-

approximately zero showing the miscibility to some extent. Fig. 3 shows the variation of interaction parameters as a function of blend composition and temperature. The interaction parameter α for blend (40/60) is highly negative at 313.15 K in comparison to that at 303.15 K. Variation of μ parameter, on the other hand, is less pronounced.

4. Conclusion

Viscometric method shows that the polymer blend of PVC/PMMA is found to be miscible. It is also observed that temperature has no significant effect on the miscibility of these blends except in the case of the (40/60) composition, considering the α parameter. As it can be seen, interaction parameter (μ) has been found more satisfactory in dealing with miscibility of blends at both temperatures. The above-mentioned techniques are simple, low cost, rapid and efficient methods for determining the miscibility windows of PVC/PMMA blends in solution.

References

[1] Stephen A.M., Kumar T.P., Renganathan N.G., Pitchumani S., Thirunakaran R., Muniyandi N. Ionic conductivity and FT-IR studies on plasticized PVC/PMMA blend polymer electrolytes. *J.Power Sources*, **89**(1), P. 80-87 (2000).

[2] Subban R.H.Y., Arof A.K. Plasticizer interactions with polymer and salt in PVC–LiCF3SO3–DMF electrolytes. *Eur. Polym. J.*, **40**(8), P. 1841–1847 (2004).

[3] Sun Z., Wang W., Feng Z. Criterion of polymer-polymer miscibility determined by viscometry. *Eur. Polym. J.*, **28**(10), P. 1259–1261 (1992). Tang M., Liau W.R. Solvent effect on the miscibility of poly(4-hydroxystyrene)–poly(ethylene oxide) blends. *Eur. Polym. J.*, **36**(12), P. 2597–2603 (2000).

[4] Chee, Sun et al., Sun Z., Wang W., Feng Z. Criterion of polymer-polymer miscibility determined by viscometry. *Eur. Polym. J.*, **28**(10), P. 1259–1261 (1992).

[5] Wu W., Luo X., Ma D. Miscibility of the segmented polyurethane blends with chlorinated poly(vinyl chloride). *Eur. Polym. J.*, **35**(6), P. 985–990 (1999).

[6] Zhao Y., Prud'homme R.E. A nonradiative energy transfer fluorescence spectroscopy study of poly (vinylchloride)/poly (methyl methacrylate) blends. *Polym Bull*, **26**(1), P. 101 (1991).

[7] Honeycutt J.D. A Theoretical study of tacticity effects on poly(vinylchloride) poly(methyl methacrylate) miscibility. *Macromolecules*, **27**(19), P. 5377–5381 (1994).

[8] Karlou K., Schneider H.A. DSC and PVT study of PVC/PMMA blends. *J. Therm. Anal. Calorim.*, **59**(1–2), P. 59 (2000).

[9] Oh B., Kim Y.R. (1999). Evaluation and characteristics of a blend polymer for a solid polymer electrolyte. *Solid state Ionics*, **124**(1-2). P. 83–89.

[10] Ohno N., Kumanotani J. Synthesis and Physical Properties of Blends of Donor Polymers from 2-(*p*-Dimethylaminobenzyl)-1,3- propanediol and Acceptor Polymers from 2-(3,5-Dinitrobenzyl)-1,3- propanediol: A New Phase Composed of Donor and AcceptorPolymers. *Polym J.*, **11**(12), P. 947–954 (1979).

[11] Singh R.P., Paladhi R. Miscibility and interaction studies on some aqueous polymer blend solutions by ultrasonic and rheological techniques. *J. Appl. Polym. Sci.*, **51**(9), P. 1559–1565 (1994).

[12] Paul D.R., Newman S. *Polymer blends*, vol. 1. Academic Press, New York (1978).

[13] Pingping Z., Haiyang Y., Yiming Z. Viscosity behavior of incompatible poly(vinyl chloride) (PVC)/polystyrene (PS) blends in various solvents. *Eur Polym J*, **35**(5), P. 915–921 (1999).